Tripodal Osmium Polypyridyl Complexes for Self-Assembly on Platinum Nanoparticles

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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 formation kinetics is limited by the detachment of the electron from the platinum surface into the solution, the particle showing a type of capacitor behavior.

SECTION: Electron Transport, Optical and Electronic Devices, Hard Matter
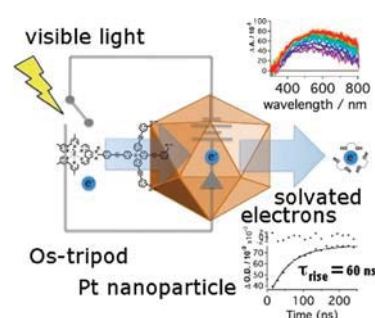
Organometallic complexes self-assembled on metal nanoparticles (MNPs) have received increased attention, especially with respect to their photocatalytic and photoluminescent properties.[1−4] Functionalized tripodal molecules, also named molecular caltrops, are ideal candidates for these systems because their design implies a very well-defined surface attached structure. The tripodal geometry was conceived by Gossauer and coworkers[5−7] and was further developed by, for example, Tour[8] and Gallopini.[9−11] A silicon-based tripod center with three thioacetate groups,[12] the fourth prong bearing the photo- and electroactive osmium center with two 4,4′-dimethyl-2,2′-bipyridyl (dmbpy) and one imidazo-phenanthroline ligand, was used here[13−18] (**Os-trip**, see Chart 1) as well as two reference compounds (e.g., $[Os(bpy)_3]^{2+}$ see Supporting Information [SI]).[19]

The formation of solvated electrons is a remarkable process in which electrons are trapped within a solvent cage. The generation of such trapped charges requires rather drastic chemical conditions or strongly ionizing (UV) radiation (e.g., pulse radiolysis).[20] Here we describe, for the first time to our knowledge, the use of green visible light to generate solvated electrons.

We show that excitation of the **Os-trip** that is attached to Pt MNPs 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.

The **Os-trip** complex in acetonitrile was surface anchored by mixing with a citrate-stabilized Pt-MNP solution and the formed nanocomposite was isolated.[21,22] The attachment was monitored with IR, UV−vis, and emission. (See the SI.) Sulfur-containing groups typically displace the citrate on the platinum surface due to the higher affinity of these groups 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 nanocomposite because the structure of the vibrational band shifts and changes to one broad band, indicating that during the approach and attachment of the tripod to the metal surface, the thioacetate hydrolyses result in a platinum−sulfur bond, displacing the citrate.[8] The UV−vis spectra of the particle-tripod nanocomposite, and its components, are shown in Figure 1A. The observed superposition of the individual components of the spectra is comparable to other examples.[23] The HR-TEM (Figure 1B) shows a good size distribution (2 ± 0.4 nm). The photophysical properties of **Os-trip** are similar to those of the reference complexes (e.g., $[Os(bpy)_3]^{2+}$), although slightly modified by the Si-atom. The attachment of **Os-trip** to the particle, however, quenches the emission of the chromophore. (See the SI.)
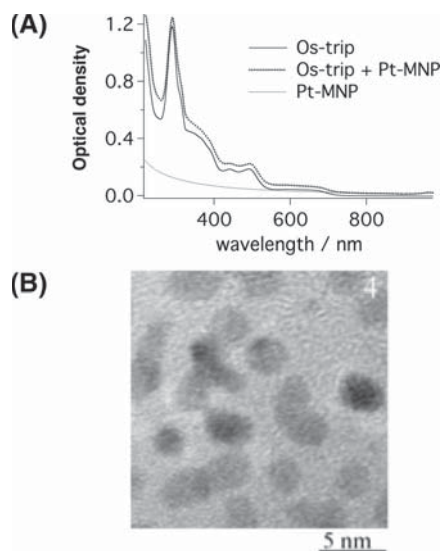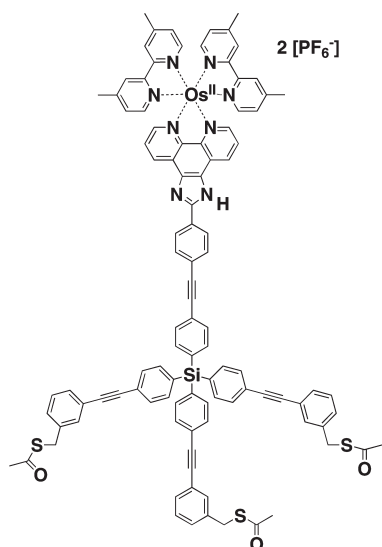
Chart 1. Molecular Structure of Os-trip

Figure 1. (A) UV—vis of components and composite. (B) HR-TEM of the nanoparticles.
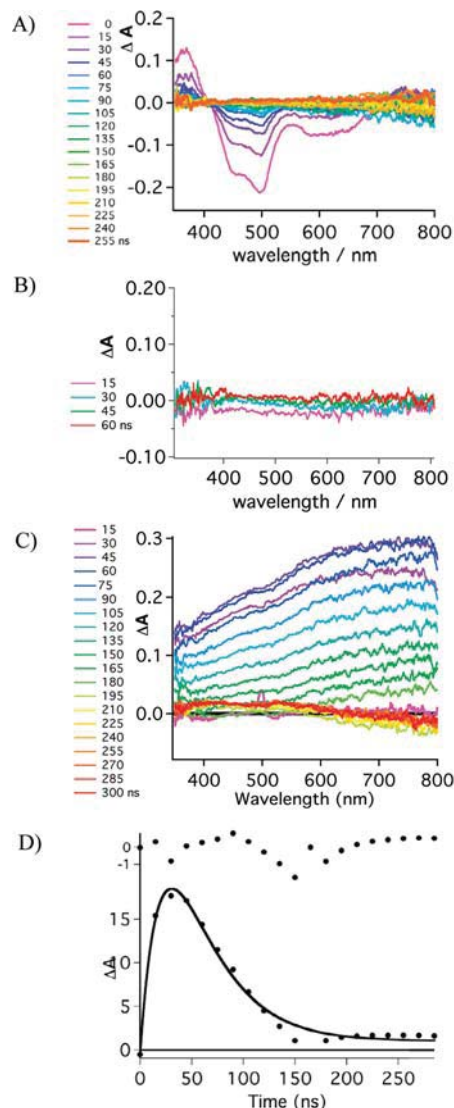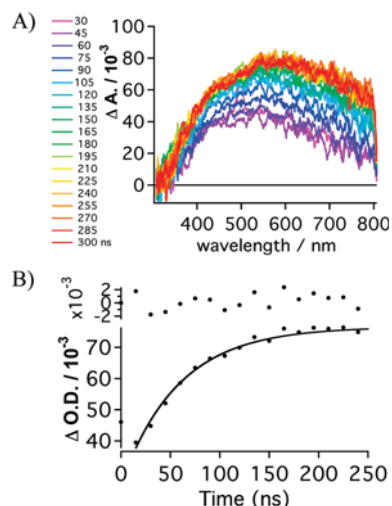

Figure 2. Transient absorption spectra (with zero line) of **Os-trip** and Pt-MNP (A,B) and the nanocomposite (C) in deaerated dioxane with the formation and decay kinetics (at 400—500 nm) of the solvated electron (D); the excitation was at 500 nm, 20 frames recorded with 150 accumulations per frame. Incremental time delay is 15 ns for all. (The legends show the times of the traces with rainbow color scheme, from violet to red.)

Transient absorption spectroscopy on the nanosecond time scale shows clear differences in the excited state processes of the individual components and the nanocomposite (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 ^{1}MLCT bleaching between 400 and 550 nm as well as the ^{3}MLCT 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).[24] The assembly of **Os-trip** on the platinum shows a very different behavior. The features of the osmium complex are masked, and a broad band over the whole spectral region grows within 40—60 ns depending on the solvent used (Figures 2D and 3). In dioxane, this band then decays in 50 ns, having, however, also a longer component ($\tau_{\text{decay}} \approx 15 \mu$s). These lifetimes are in good agreement with kinetic studies on

solvated electrons in water and ammonia.[25] 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.[26−28] 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.[29] If the solvent is other than water (or a protic solvent), then the maximum of this very broad band is shifted further to lower energies.[30−33] We were able to see convincing features of the solvated electron in ethylene glycol, with a maximum for the absorption band at 600 nm[34−36] (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

Figure 3. (A) Transient absorption spectrum of the **Os-trip**−Pt-MNP assembly after excitation at 500 nm in ethylene-glycol. The broad band is centered at 600 nm and has a rise time of 60 ns (B, at 600 nm). 15 ns increment per frame with 500 accumulations per frame. (The legends show the times of the traces with rainbow color scheme, from violet to red.)
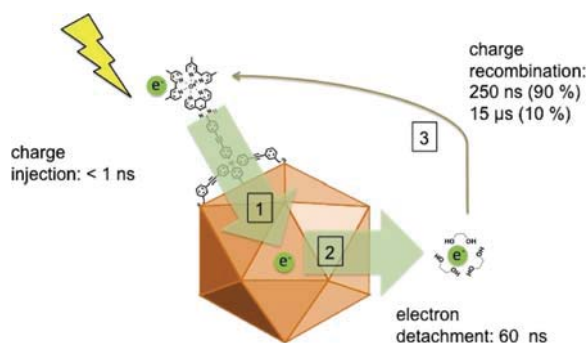
Figure 4. Schematic representation of the chemical steps and kinetics occurring in the nanocomposite in ethylene glycol.

solvated electron has to be the release of the electron from the platinum surface into the solution. The quantum yield (number of electrons produced/number of photons absorbed) was estimated to be ∼4% in ethylene glycol. (See the Supporting Information.) Kinetic observations and correlated chemical steps are combined in Figure 4. Attempts to trap the solvated electron from the solution with a viologen were made. (See the Supporting Information.) Further experiments are currently in progress and will be published separately.

Self-assembly of thioacetate-functionalized tripodal molecules containing an osmium polypyridyl complex onto platinum nanoparticles 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 a lifetime that lies in the 50 ns range with a long component of 15 μs, indicating a faster disappearance of most of the solvated electrons from the solution and a residual concentration that remains solvated on the longer time scale. Prospective new photocatalytic systems using these concepts are envisioned.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Compounds used and their photophysical properties, synthesis of Pt-MNP and the nanocomposite, IR and emission of attachment, nanosecond and femtosecond transients of reference compounds, and setups used.

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