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FLUORESCENT PROPERTIES OF METAL NANODOTS

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Introduction : Metal and semiconductor nanoparticles have attracted much interest for the past decades because of their unique properties such as stability, tuneable absorption and emission,[1] and their potential applications, in particular in biological imaging.[2] The size and the shape of these nanoparticles can be varied and so, their optical properties, originating from spatial confinement of electrons, can be modified in the spectral region ranging from visible to Near Infrared (NIR).[3] Lately, attractive metal clusters called metal quantum dots (QDs) have emerged.[4] The emission properties of clusters formed by few gold or silver atoms have recently been studied.[5] As their dimensions are smaller than the Fermi wavelength of electron,[6] these clusters present discrete, size tuneable electronic transitions and display fluorescent properties. Their photoluminescence is size dependent and shifts toward higher energies with decreasing cluster size.

Within this context, we have studied the fluorescence properties of Chini-type platinum carbonyl clusters, $[Pt_3(CO)_6]_4^{2-}$, and their self assembly into fluorescent nanostructures.[7] These clusters, first synthesized by Chini et al.,[8] present a twisted prismatic structure composed of 4 stacking triangular units stabilized by CO ligands and a doubly negative charge (Figure 1).
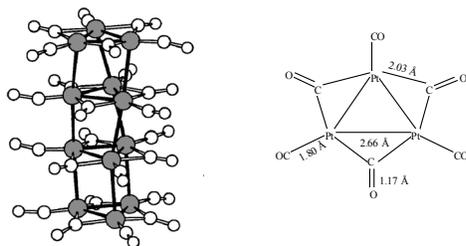
Figure 1: Structure of the Chini-type platinum carbonyl clusters, $[Pt_3(CO)_6]_4^{2-}$. The given interatomic distances and the inter-triangular distances between stacked units (3.08-3.10 Å) are taken from ref. 8a.

Experimental Section :

Platinum carbonyl clusters $[Pt_3(CO)_6]_4^{2-}$ were prepared by γ-radiolysis of strongly alkaline methanol solutions containing 10^{-3} M or 2.5×10^{-3} M platinum complexes, H_2PtCl_6 or $Pt(acac)_2$, and saturated by CO under 1 atm, as previously described.[9] Chemicals were reagent grade and used without further purification: H_2PtCl_6 from Aldrich, $Pt(acac)_2$ from STREM Chemicals, methanol from Aldrich, CO from Air Liquide. A ^{60}Co source was used for the irradiation (dose rate: 2.3 kGy/h, dose 4600 Gy). Alkaline pH was maintained to stabilize the clusters after formation. It is to be noted that the synthesis were done at Pt concentration $\geq 10^{-3}$ M but the fluorescence studies were performed with diluted solutions as the tetrameric clusters remain stable in solution upon dilution.

UV-Visible spectra of these samples were carried out on HP diode array HP8453 spectrophotometer. Fluorescence spectra were recorded using a SPEX fluorolog 111 spectrofluorometer operated at the resolution of 2 nm equipped by a Hamamatsu R3896 photomultiplier. The fluorescence decay curves were recorded using a time-correlated single photon counting setup with standard electronics (Ortec, Phillips & Tennelec, USA). The light source was a Ti:Sappphire laser beam (MIRA 900, 10W Verdi, Coherent, Watford, UK) with a repetition rate reduced to 3.8 MHz using a pulse picker (SiO_2 crystal, APE, Berlin, Germany) and frequency doubled with a BBO crystal to produce the 420 nm excitation wavelength. Average laser power at the sample was 200 μW. Fluorescent images of these clusters were taken with a Nikon TE2000U inverted microscope with a conventional CCD camera (Pixel Fly, PCO).

Results and Discussion :

The steady-sate UV-visible and emission spectra of these $[Pt_3(CO)_6]_4^{2-}$ clusters formed in alkaline methanol from H_2PtCl_6 salt as precursor are shown in Figure 2. The absorption spectrum (green curve, Fig. 2) presents two intense absorption bands at 360 nm (3.44 eV) and 560 nm (2.21 eV) and one weak absorption band at 500 nm (2.47 eV), as previously reported for the tetrameric cluster. Three absorption bands, the first and third transitions being much more intense than the second transition were also determined by molecular orbital (MO) calculations.[10] Upon excitation at 620 nm, the tetrameric clusters exhibit a fluorescence band around 740 nm (red curve, Fig. 2). In contrast, the emission spectrum recorded upon excitation at 380 nm (blue curve, Fig. 2) displays two bands centred around 470 nm and 740 nm respectively, leading to effective stokes shifts of 85 nm and 345 nm from the absorption band maximum. The sharp peak observed at 430 nm is due to Raman scattering and is the only feature present in the emission spectrum of the chloride precursor in alkaline methanol. The excitation spectrum corresponding to the emission at 740 nm resembles the absorption spectrum of the $[Pt_3(CO)_6]_4^{2-}$ clusters and confirms that the 740 nm emission originates from both absorption bands. However, in the excitation spectrum the intensity of the 380

nm band is smaller than that of the 620 nm band contrary to the absorption spectrum, that clearly indicates the existence of other relaxation paths from the highest excited states (in particular emission around 470 nm). Taking the quinine sulfate as a reference, the total emission quantum yield of these clusters is evaluated to be 3×10^{-3} and 2.9×10^{-2} upon excitation at 380 nm and 620 nm, respectively. Time-resolved fluorescence measurements were performed using laser pulses at 420 nm for excitation. The decay profiles registered at 460 ± 6 nm reveal two components. The fast component with the highest contribution matches the instrumental response function and is attributed to scattered and Raman light as observed in Figure 2. The slowest part decays with an average lifetime of 5.1 ns. The absence of photobleaching during illumination for hours at high laser power (200 µW) indicates the high photostability of these clusters which is a necessary condition for fluorescent applications.

The steady-state UV-visible and emission spectra of the $[Pt_3(CO)_6]_4^{2-}$ clusters formed in alkaline methanol from $Pt(acac)_2$ as precursor exhibit similar features as those just described for $[Pt_3(CO)_6]_4^{2-}$ synthesized from H_2PtCl_6. The fluorescence decay is also identical. These results indicate that the photophysical properties of the clusters in alkaline methanol solution do not depend on the precursor salt.

The dual fluorescence of these clusters, with two well-resolved intense emission bands for a single excitation, is uncommon. The double emission could originate from the stacking properties of the triangular platinum units, one transition being in the triangular unit plane and the other one in the stacking direction.
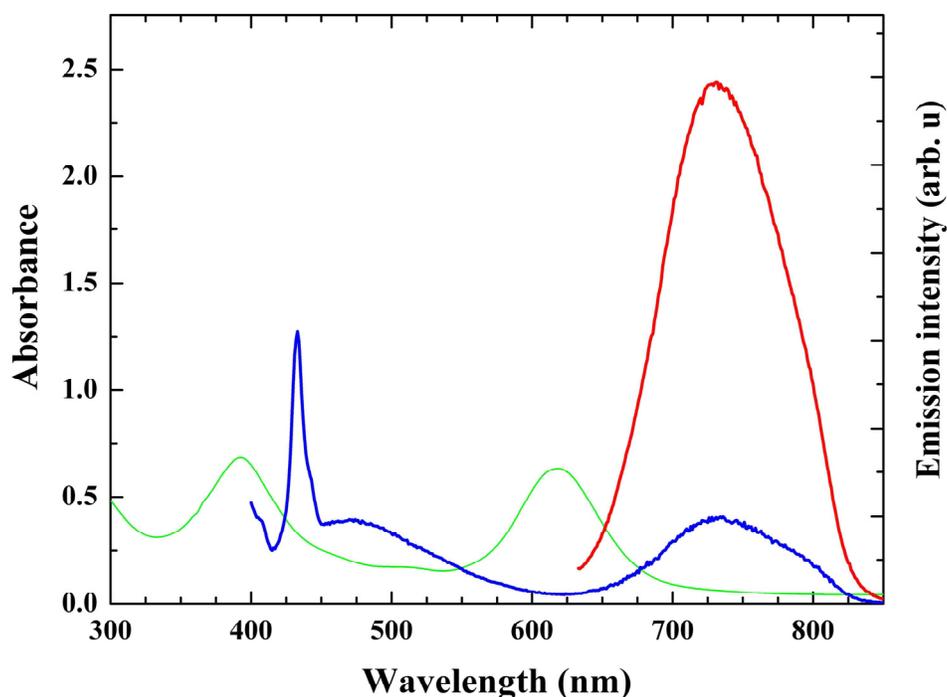
Figure (2) : UV-Visible absorption and emission spectra of alkaline methanol solutions of platinum carbonyl clusters $[Pt_3(CO)_6]_4^{2-}$ synthesized from 10^{-3} M H_2PtCl_6 by radiolytic reduction (dose rate= 2.3 kGy/h, dose = 4600 Gy). Absorption spectrum, path length 2 mm (—); Emission spectra recorded after dilution in 1 cm cell for two excitation wavelengths: λ_{exc} = 380 nm (—), λ_{exc} = 620 nm (—).

Figure 3 presents the microscopy images of the $[Pt_3(CO)_6]_4^{2-}$ clusters synthesized from both H_2PtCl_6 and $Pt(acac)_2$ deposited on a glass microscope coverslip. The images were taken after complete evaporation of the solvent. The transmission images (Fig. 3A) show that the clusters made from H_2PtCl_6 assemble into spherical aggregates while the clusters made from $Pt(acac)_2$ gather into linear assemblies forming long wires of a few microns length. These results highlight the influence of the ligands and counterions on the self-assembly processes occurring during solvent evaporation, the linear assembly into wires being facilitated by the acetylacetonate ligands. Self-assembly of $[Pt_3(CO)_6]_n^{2-}$ clusters into semicontinuous or continuous conductor wires upon cristallization[11] or upon deposition onto flat supports[12] has already been reported. In addition, the formation of infinite platinum chains based on stacked $Pt_3(CO)_6$ units was predicted Hoffmann et al.[10b] As the clusters in solution exhibit two well resolved emission bands, the deposited clusters were imaged after excitation by collecting the emission in two different spectral regions (Fig. 3B and 3C). The luminescence observations show that the aggregated clusters keep the emission properties of the isolated clusters in solution and can be imaged in two different wavelength ranges. It is worth noticing that the fluorescent images obtained for the 1D assemblies by collecting the emission light around 480 nm reveal that the whole linear superstructures are fluorescent (Fig. 3B bottom)

whereas the images recorded for emission light above 530 nm show only luminescent dots (Fig. 3C bottom) on these linear structures. These results suggest the presence of low-energy traps from which the red emission originates.

To conclude, the luminescence properties of platinum carbonyl clusters $[Pt_3(CO)_6]_4^{2-}$ were demonstrated. These clusters present two emission bands for single visible excitation, which is relatively new in the field of fluorescent metal quantum dots and render them particularly attractive as fluorophores for imaging and detection. These clusters self-assemble into either spherical aggregates or long nanowires, which both exhibit fluorescence properties. The study of the size dependent emission of these clusters as well as their self-assembly into superstructures is under work. Theoretical calculations are also in progress in order to investigate the origin of the observed dual emission and to try to understand the role of the counter ions and the ligands in the self assembly process.
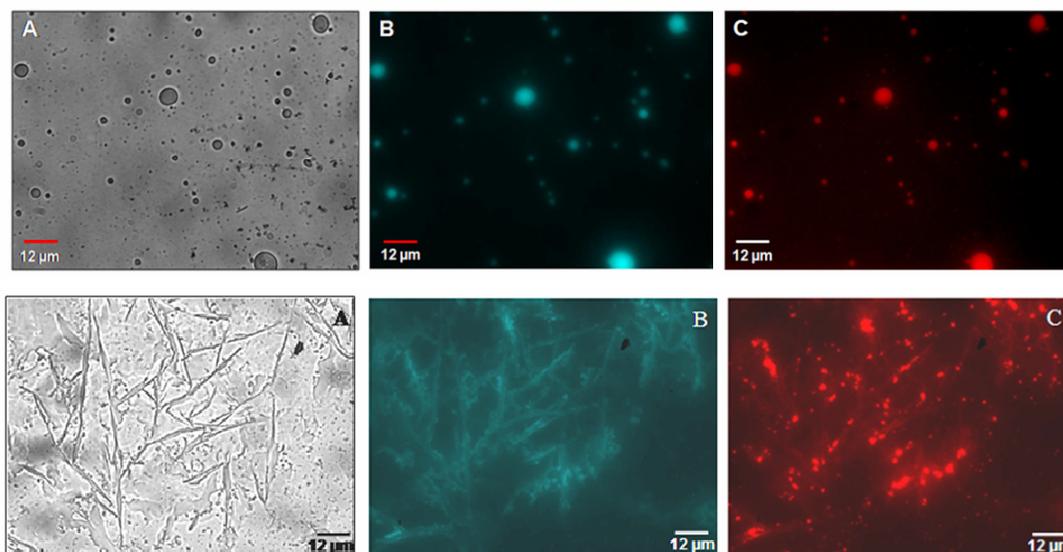
Figure 3: Microscopy images of the $[Pt_3(CO)_6]_4^{2-}$ clusters made from H_2PtCl_6 (top) and $Pt(acac)_2$ (bottom) deposited on glass; (A) transmission mode image, (B-C) false-colour luminescence images: (B) excitation around 440 nm and emission around 480 nm, (C) excitation around 440 nm (top) or 500 nm (bottom) and emission above 600 nm (top) or above 530 nm (bottom).

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