ELECTRONIC SUPPORTING INFORMATION (ESI) FOR:

Effective photoreduction of a Pt(IV) complex with quantum dots: a feasible new light-induced method of releasing anticancer Pt(II) drugs

Nina Gomez Blanco, Carmen R. Maldonado and Juan C. Mareque-Rivas*
School of Chemistry, University of Edinburgh,

Joseph Black Building, King's Buildings,

West Mains Road, Edinburgh, EH9 3JJ, UK

Tel:44-(0)131-650-4761

Fax:44-(0)131-650-4743

Materials and Methods.

Materials. All chemicals were obtained from commercial sources and used as received. Cadmium oxide (CdO, 99.5%), tri-*n*-octylphosphine oxide (TOPO, 99%), tri-*n*-butylphosphine (TBP, 97%), hexadecylamine (HDA, 98%), diethylzinc ($ZnEt_2$, 1M in hexane), hexametyldisilathiane [$(TMS)_2S$ 98%] were purchased from Sigma Aldrich. Potassium hexachloroplatinate and 2, 2'-bypiridine (bpy) were obtained from Acros Organic and potassium tetracloroplatinate from Fisher Scientific. Stearic acid (≥98.5%) was purchased from Fluka. Selenium powder (Se, 99.999%) was obtained from Alfa Aesar. Tri-*n*-butylphosphine selenide (TBP-Se, 1M) was prepared in a N_2-filled glove box by shaking 0.08 g of selenium powder in 1 mL of TBP. A ZnS stock solution was prepared in a N_2-filled glove box by reacting $(TMS)_2S$ (0.5 ml, 2.5 mmoles) with $ZnEt_2$ (3.5 ml, 3.5 mM in hexane) in TOP (6 mL).

$[PtCl_4(bpy)]$[1] (bpy = 2,2'-bipyridine) and $[PtCl_2(bpy)]$[2] were synthesised as previously described.

QD Synthesis.

Hydrophobic CdSe and core-shell CdSe-ZnS QDs were synthesised and purified adapting a previously reported procedure with some modifications.[3]

CdO (0.013 g, 0.1 mmol) and stearic acid (0.254 g, 0.89 mmol) were loaded into a three-neck flask and heated to 225°C under N_2 flow and stirring. Once the mixture was completely dissolved, it was allowed to cool to room temperature. Then, TOPO (3 g) and HDA (1 g) were added and the mixture was heated to 225 °C under N_2 flow and vigorous stirring. At this temperature, 1 mL of freshly prepared TPB-Se solution

(1 M) was quickly injected into the flask. Following injection the temperature was adjusted to ~200 °C to promote nanocrystal growth.

For CdSe QDs, on reaching the desired nanoparticle size, as determined by UV/vis and fluorescence spectroscopy, the temperature is lowered to 100 °C to stop further growth. The solution is then heated to 210°C for 2 hr. After cooling to room temperature, the nanocrystals were dispersed in chloroform and precipitated by addition of methanol. After centrifugation the supernatant liquid phase was removed. This procedure was repeated at least three times. The precipitates were combined and dried under a stream of N_2 at room temperature.

For CdSe-ZnS QDs, on reaching the desired nanoparticle size, the temperature is lowered to *ca.* 100 °C to stop further growth. Then, the solution is heated to 210 °C. At this temperature, 0.5 mL of the ZnS stock solution was slowly injected in. The temperature of the mixture was set to 100 °C and stirred for 2 hr. After cooling to room temperature, the nanocrystals were dispersed in chloroform and precipitated by addition of methanol. After centrifugation the supernatant liquid phase was removed. This procedure was repeated at least three times. The precipitates were combined and dried under a stream of N_2 at room temperature.

QDs were characterised by HRTEM, EDS, UV-vis and fluorescence spectroscopy, NMR, FT-IR and ICP-OES.

The CdSe QDs used in this study had an average diameter of 5.6 nm (based on HRTEM and position of the first excitonic peak[4]), whereas the CdSe-ZnS QDs had an average diameter of 5.8 nm. The number of Cd, Se, Zn and S atoms per QD was calculated using the bulk densities and formula weights of CdSe and ZnS, and the volumes of 5.6 nm, 4.4 nm (CdSe core diameter) and 5.8 nm (total diameter) spherical nanoparticles, and was confirmed experimentally by ICP-OES: CdSe QDs, ca. 1600 Cd and Se atoms; CdSe-ZnS QDs, ca. 750 Cd and Se atoms, and ca. 1450 Zn and S atoms.

Irradiations. Mixtures of QD (50-100 nM) and $[PtCl_4(bpy)]$ (75 μM-0.75 mM) in $CHCl_3$:DMSO (7:3) were freshly prepared and irradiated with laser light at 530 nm for 1 hour. In each case a control solution of $[PtCl_4(bpy)]$ without QD was also irradiated in the same way. These studies were conducted with a laser (COHERENT INNOVA 70C Spectrum) equipped with a fibre optic (FT-600-UMT, ∅ = 600 mm;

Elliot Scientific Ltd.) to enable delivery of light to a sample in the NMR probe. The fibre optic was placed ~2 mm above the solution in the NMR tube at which distance the power (*ca.* 10 mW cm^{-2}) was measured with a Fieldmate Powermeter (Coherent, OP2-VIS head).

UV-vis studies. UV-vis electronic absorption spectra were obtained for solutions of [$PtCl_4$(bpy)] (75 µM-0.75 mM) and solutions composed of QD (50-100 nM) + [$PtCl_4$(bpy)] (75 µM-0.75 mM) in $CHCl_3$:DMSO (7:3) before and after irradiation with laser light at different time intervals. The size and concentration of the QDs solutions were estimated by the method of Peng *et al.*[4], and confirmed by TEM and ICP-OES. The instrument used was a Perkin Elmer Lambda 900 UV-vis Spectrometrer and the cuvettes had a path-length of 1 cm.

NMR studies. ^{1}H NMR spectra were acquired for [$PtCl_4$(bpy)] and for mixtures of [$PtCl_4$(bpy)] and QD in $CDCl_3$:DMSO-d_6 (7:3), before and after irradiation with laser light at different time intervals. Measurements were carried out at 298 K with a Bruker DMX500 spectrometer operating at 500.13 MHz (^{1}H). Processing was carried out using Xwinnmr (version 2.0, Bruker UK Ltd.)

Fluorescence studies. Measurements were made with an Edinburgh instrument FS900 fluorimeter. Excitation was at 395 nm with bandwidths of 2 nm for excitation (unpolarised) and emission (unpolarised). Temperature was maintained at 25°C.

Electrochemistry. Electrochemical studies were carried out using an Autolab PGSTAT 20 potentiostat. Cyclic voltammograms at varying scan rates of 25-500 mV s^{-1} were obtained by using a three electrode configuration consisting of a graphite disk working electrode, a Pt rod counter electrode, and a Ag/AgCl (saturated KCl) reference electrode. The measurements were made under N_2 atmosphere in a mixture ~ 70% CH_2Cl_2, 30% DMSO with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte at room temperature. The reported potential (–0.15 V *vs* NHE) is the potential extrapolated to 0 mV s^{-1} scan rate.

Transmission electron microscopy. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) studies were conducted on a JEOL JEM-2011 electron microscope operating at 200 kV. The samples were prepared by depositing a drop of a solution of nanocrystals in pyridine onto a copper specimen grid coated with a holey carbon film and allowing it to dry.

References:

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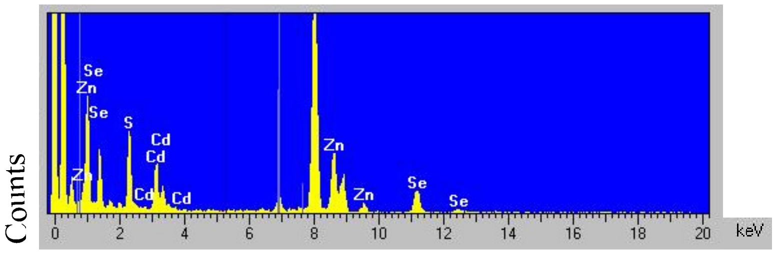

Fig. S1. EDX spectra of the CdSe-ZnS QDs shown in Fig 1B.

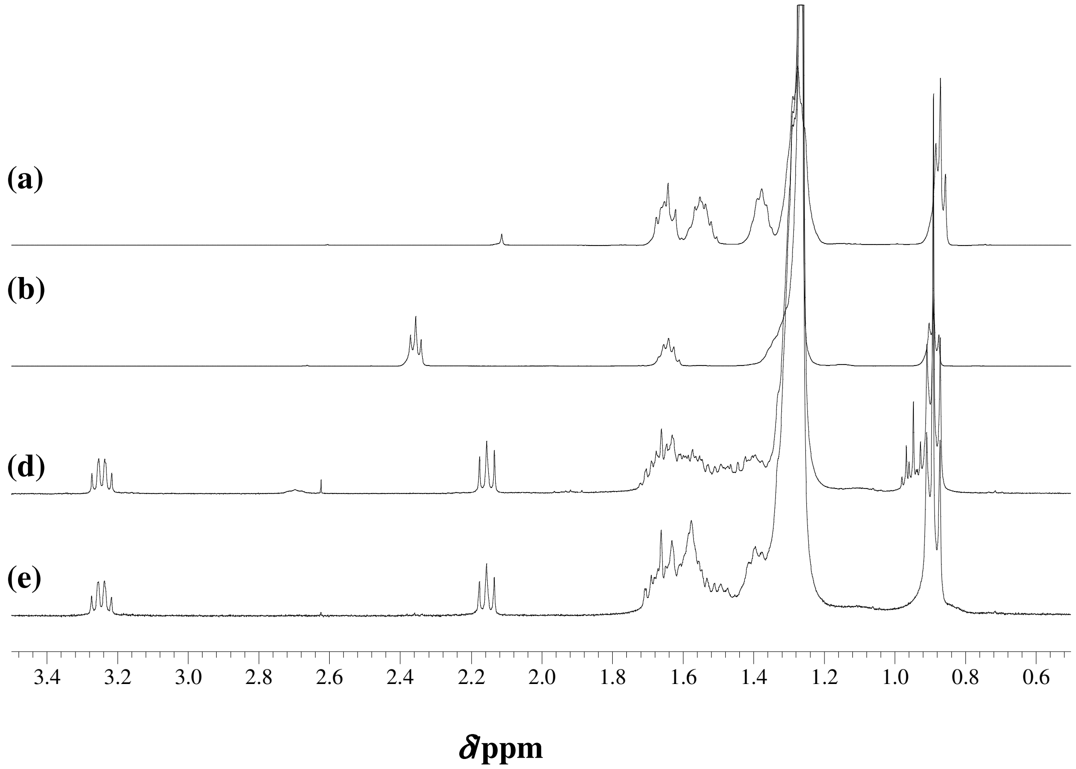

Fig. S2. ^{1}H NMR spectra (500 MHz) of TOPO (a), stearic acid (b), CdSe QDs (c) and CdSe-ZnS QDs (d) in $CDCl_3$.

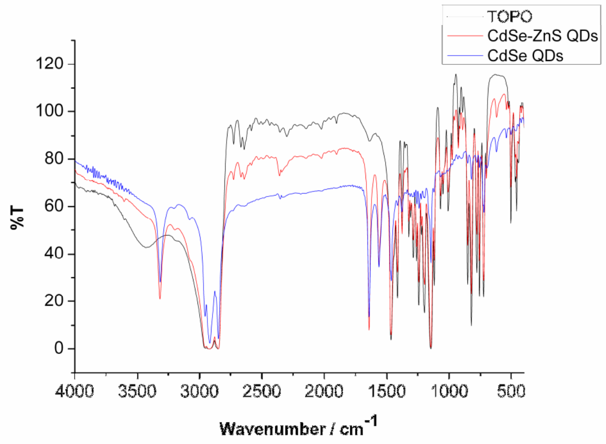

Fig. S3. FT-IR spectra (solid state) of TOPO, CdSe QDs, and CdSe-ZnS QDs in KBr

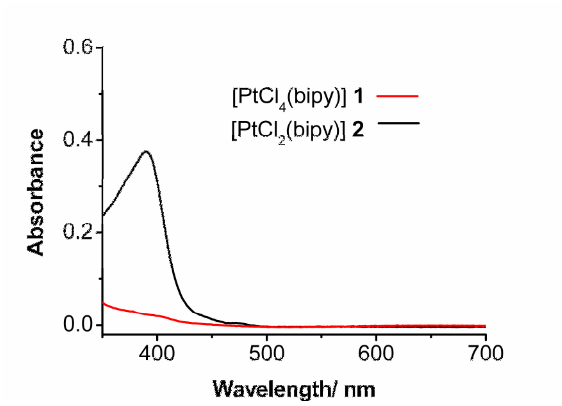

Fig. S4. UV-vis spectra of **1** and **2** in $CHCl_3$:DMSO (7:3).

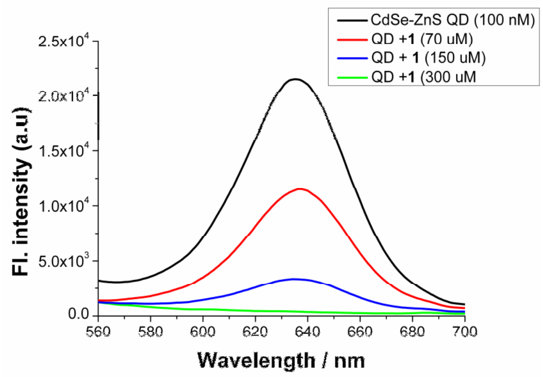

Fig. S5. Photoluminescence of core-shell CdSe-ZnS QD (~ 100 nM) without and in the presence of **1** (0-300 μM) in $CHCl_3$:DMSO (7:3).

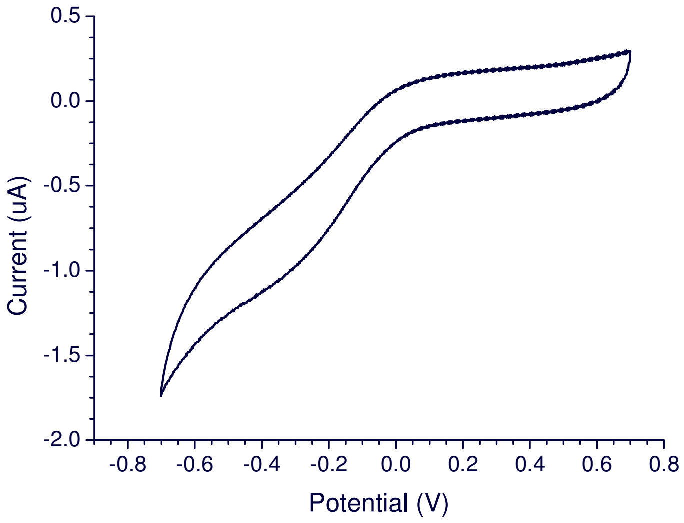

Fig. S6. Cyclic voltammogram of **1** recorded in a mixture CH_2Cl_2 (~70%) and DMSO (~30%) with 0.1 M [^{n}BuN][BF_4] as supporting electrolyte and a scan rate of 50 mV/s (*E vs* Ag/AgCl).