Supporting Information

Photoactive dendrimer for water photoreduction: a scaffold to combine sensitizers and catalysts

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Experimental section

Photophysical experiments. Photophysical experiments have been performed in water air-equilibrated solution. UV-Vis absorption spectra were recorded by a Perkin Elmer λ40 spectrophotometer. Fluorescence spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube for the UV-VIS range. Fluorescence quantum yields were measured following the method of Demas and Crosby[1].
The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient, emission intensity in the UV-Vis spectral region.

Trasmission Electron Microscopy. Transmission Electron Microscopy (TEM) characterization has been carried out with a FEI Tecnai F20 TEM equipped with a Schottky emitter and an Energy Dispersive X-Ray (EDX) spectrometer, and operated at 200 keV in both conventional TEM and Scanning Transmission (STEM) mode. Samples were prepared by drop casting an aqueous solution of **RuPAMAMPtNps** on conventional TEM Holey Carbon film copper grid, then heated at 150°C for 10 min to evaporate the solvent.

Photolysis Apparatus. The hydrogen evolution experiments were carried out upon continuous visible light irradiation with a 175 W xenon *CERMAX* arc-lamp (cut-off filter at 400 nm) of a reactor (a 10 mm pathlength pyrex glass cuvette with head space obtained from a round-bottom flask) containing the solution. The measuring cell is sealed during the photoreaction: the head to which cell is attached has indeed four ports, closed with Swagelok connections, two of them are part of a closed loop involving GC gas inlet and sample vent in order to analyze head space content without an appreciable gas consumption, and the other two are for the degassing procedure (input and output).

Gas Chromatography. The gas phase of the reaction vessel was analyzed on an *Agilent Technologies* 490 microGC equipped with a 5 Å molecular sieve column (10 m), a thermal conductivity detector, and using Ar as carrier gas. 5 mL from the headspace of the reactor are

sampled by the internal GC pump and 200 nL are injected in the column maintained at 60°C for separation and detection of gases. The unused gas sample is then reintroduced in the reactor in order to minimize its consumption along the whole photolysis. The amount of hydrogen was quantified through the external calibration method. This procedure was performed, prior to analysis, through a galvanostatic (typically 1 mA) electrolysis of a 0.1 M H_2SO_4 solution in an analogous cell (same volume) equipped with two Pt wires sealed in the glass at the bottom of the cell. A 100% faradaic efficiency was assumed leading to a linear correlation between the amount of H_2 evolved at the cathode and the electrolysis time.

Hydrogen Evolution Experiments. In a typical experiment, samples of 5 mL were prepared in 20 mL scintillation vials by mixing the RuPAMAMPtNps solution with ascorbic acid. The pH was then regulated at the desired value upon addition of few droplets of a 5 M NaOH solution. The solution was then put in the reactor, degassed by bubbling Ar for 30 min, and thermostated at 15°C. The cell was then irradiated under continuous vigorous stirring of the solution. The gas phase of the reaction was analyzed through GC and the amount of hydrogen quantified.

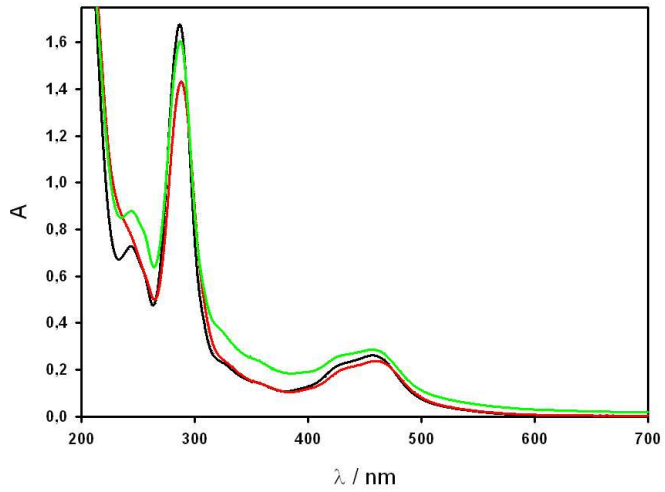

Figure S1. Absorption spectra of **RuPAMAM** 1.47×10^{-6} M in H_2O (black line), after addition of 20 eq of K_2PtCl_4 (red line) and after reduction with $NaBH_4$ (green line).

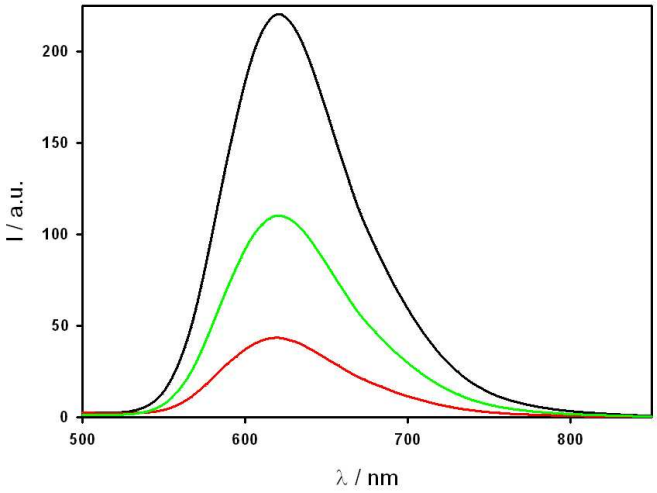

Figure S2. Emission spectra of **RuPAMAM** 1.47×10^{-6} M in H_2O (black line), after addition of 20 eq of K_2PtCl_4 (red line) and after reduction with $NaBH_4$ (green line).

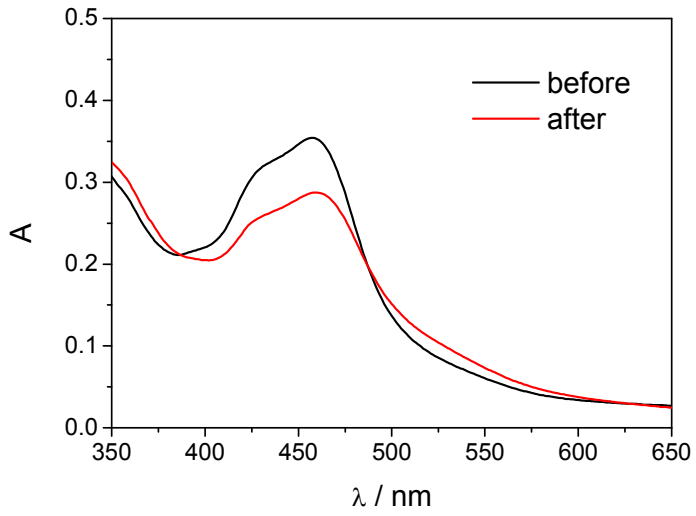

Figure S3. Comparison of absorption spectra before and after (5 h) irradiation of a pH 5 water solution containing 1.6 μM **RuPAMAMPtNps** and 0.1 M ascorbic acid.

[1] J. N. Demas and G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.