A new member of the oxygen-photosensitizers family: a water-soluble polymer binding a platinum complex

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Chemical Materials and Spectroscopic Methods

Polymethacrylic acid (pMAA) standard samples for size-exclusion chromatography (M_n= 600 - 500000; M_w/M_n = 1.06-1.10) were obtained from Sigma-Aldrich (Sigma Chemical Co., St Louis, MO, USA).

M_n and M_w/M_n were measured by Gel Permeation Chromatography (GPC) using water as eluent at 45°C and at flow rate, 1.0 ml min⁻¹ on Waters Ultrahydrogel-1000 column connected to a Jasco PU-2089 pump and a Jasco 930-RI refractive-index detector. The columns were calibrated using standard pMAA samples.

¹H NMR spectra were acquired on a Bruker Advance DRX-300 spectrometer in DMSO-d6 or D₂O solution, with tetramethylsilane as internal standard. Infrared spectra were recorded with a Spectrum One FT-IR Perkin-Elmer spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer.

Spectrofluorimetric grade solvents were used for the photophysical investigations in solution, at room temperature. A Perkin Elmer Lambda 900 spectrophotometer was used to obtain the absorption spectra. Steady-state emission spectra were recorded on a HORIBA Jobin–Yvon Fluorolog-3 FL3-211 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and single-grating emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube or an InGaAs liquid nitrogen-cooled solid-state detector for singlet oxygen emission measurement. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements were performed using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3. NanoLED at 265 nm, fwhm <1.0 ns with repetition rate at 50 KHz for long
decays and at 1 MHz for short decays, was used to excite the samples. Excitation source was mounted directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm/mm dispersion; 1200 grooves/mm) and the emission was collected with a TBX-04-D (IBH) single-photon-counting detector. A cut/off filter (400 nm) was used to prevent harmonics of the excitation light reaching the detector. The photons collected at the detector were correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH Data Station Hub photon counting module, and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The quality of the fit was assessed by minimizing the reduced $\chi^2$ function and visual inspection of the weighted residuals. Deaerated samples were prepared by the freeze-pump-thaw technique. Emission quantum yields ($\Phi$) in solution were determined by using the optically dilute method \cite{1} on aerated solutions with low absorbance ($< 0.1$) at excitation wavelength, according to the formula (where the superscript text R refers to the reference standard):

$$
\Phi = \Phi^R \frac{A_{em}}{A^R_{em}} \frac{Abs^R}{Abs} \left( \frac{n}{n^R} \right)^2
$$

where $A_{em}$ is the integrated corrected emission area obtained exciting the sample at the wavelength $\lambda_{ex}$, $Abs$ is the absorbance measured at the $\lambda_{ex}$, $n$ is the refractive index of the solvent; in the case of the fluorescence quantum yield (FQY) $A_{em}$ was considered the area of the fluorescence emission, while, in the case of the phosphorescence quantum yield (PQY), $A_{em}$ correspond to the area of the phosphorescence emission. Ru(bipy)$_3$Cl$_2$ (bipy = 2,2′-bipyridine) in water was used as reference standard ($\Phi = 0.028$) \cite{2}. The experimental uncertainty on the emission quantum yields is 10%. The examined compounds are stable in solution, as demonstrated by the reproducibility of their absorption spectra over a week period.


Characterization of the complex

(PyCH₂NH₂)Pt(Cl)₂ Yield: 87%, 394mg. IR (KBr) ν = 3217-3186, 2971-2927, 1615 cm⁻¹. ¹H NMR (DMSO-d₆, 300 MHz) δ = 8.92 (d, 1H, J = 5.5 Hz), 8.12 (1H, t, J = 7.7 Hz), 7.61 (d, 1H, J = 8.11 Hz), 7.48 (1H, t, J = 6.6 Hz), 6.18 (2H, s), 4.08 (2H, t, J = 5.68 Hz). ppm. Anal. calcd. for C₆H₈N₂Cl₂Pt (374.14): C, 19.26; H, 2.16; N, 7.49 %; found: C, 19.85; H, 2.58; N, 7.12 %.

Fig. S1. Absorption spectrum of 2-picolyamine at room temperature in water solution at the concentration of 5.23E-6 mol/L
Fig. S2. Time-resolved fluorescence decay recorded at 340 nm upon irradiation at 265 nm in air-saturated CH$_3$CN solution of the \((\text{PyCH}_2\text{NH}_2)\text{Pt(Cl)}_2\) complex \((\tau = 2.4 \pm 0.06 \text{ ns}; \text{Chi}^2 = 1.004)\).

![Fluorescence Decay](image)

Fig. S3. Time-resolved phosphorescence decay recorded at 510 nm upon irradiation at 265 nm in degassed CH$_3$CN solution of the \((\text{PyCH}_2\text{NH}_2)\text{Pt(Cl)}_2\) complex \((\tau_1 = 2.05 \pm 0.04 \mu\text{s}; \tau_2 = 3.0 \pm 0.04 \text{ ns}, \alpha_1 = 97.1\%, \alpha_2 = 2.9\%; \text{Chi}^2 = 1.06)\).

![Phosphorescence Decay](image)

Fig. S4. Singlet oxygen phosphorescence upon irradiation at 265 nm of the complex in air-saturated CCl$_4$ solution.

![Singlet Oxygen Phosphorescence](image)
**TCSPC data of the grafted polymer**

![Graph](image)

Fig. S5. Time-resolved phosphorescence decay recorded at 515 nm upon irradiation at 265 nm in air-saturated water solution of the complex grafted polymer ($\tau_1 = 0.68 \pm 0.04$ μs; $\tau_2 = 3.0 \pm 0.04$ ns; $\alpha_1 = 60\%$, $\alpha_2 = 40\%$; Chisqr = 1.07).
Fig.- S6. Time-resolved phosphorescence decay recorded at 510 nm upon irradiation at 265 nm in degassed water solution of the complex grafted polymer ($\tau_1 = 2.05 \pm 0.02 \mu s; \tau_2 = 3.0 \pm 0.06 \text{ ns}; \alpha_1 = 96.7\%, \alpha_2 = 3.3\%; \text{ Chisqr} = 1.08$).

Fig.- S7. Absorption spectra of the polymer and of the grafted polymer at room temperature in water solution.