

Photochemistry exam
Datum: February 2nd, 2018
Tijd: 14-17 pm
Zaal: C1
Docent: Bonnet, Buda

On each page write your name and the number of the college card.

It is not allowed to use the syllabus or a cell phone during the examination. For each question the rating is given.

Please write the Bonnet and Buda part on separate sheets of papers, as they will be corrected by different teachers.

When a justification is asked it counts at least as many points as the answer itself. The number of points per question is indicative and may be re-evaluated.

Important advices:

- *do not lose time on questions you can't do. First answer the questions you can answer, then spend time on the more difficult ones.*
- *If you don't know the value of a physical constant (Avogadro, Planck, etc.) ask for it!!!*
- *If an answer cannot be read because it is badly written you will get 0 point for it.*

Part A: Upconversion (Bonnet, 6 points)

Part A1-Upconverting nanoparticles (2.5 points)

Upconversion materials can drive photochemical processes using the NIR part of the spectrum, either to use a larger part of the solar spectrum, or because NIR light penetrates deeper in biological tissues. In that context researchers from the University of Amsterdam studied lanthanoid-doped upconverting nanoparticles (UCNPs) and used them for exciting a Pt-based photosensitizer covalently attached to the surface of the nanoparticle (Figure 1B). The upconverting nanoparticle itself is made of a NaYF₄ solid matrix where 20% of the Y³⁺ ions have been replaced by Yb³⁺ ions, and 0.2% by Er³⁺ ions. Y is photophysically silent. Yb³⁺ is called a "photosensitizer" because it can be excited with 980 nm light into an *f-f* excited state noted ²F_{5/2} (Figure 1A). *Note: the notation of the lanthanoid excited states follows the usual convention ^{2S+1}L_J; for example, the term ⁴S_{3/2} has 2S+1=4 ie S=3/2, L=0, J=3/2; a term ²F_{5/2} has 2S+1=2 ie S=1/2, L=3, J=5/2.* On the other hand, Er³⁺ does not absorb at all at 980 nm, but it has many *f-f* excited states (Figure 1A) that can be sensitized by the excited state of Yb³⁺. Upon 980 nm irradiation of the UCNPs, the excited state of Yb³⁺ can transfer energy to the Er³⁺ ions situated nearby in the crystal. Upon repeating this phenomenon several times, the Er³⁺ ion can climb up the "ladder" of its excited states (Figure 1A, pink arrows), to reach higher-lying excited states that can emit green (548, 557 nm) or red (672 nm) photons (green and red arrows in Figure 1A), thus realizing upconversion. Wiggling black arrow represent non-radiative decay due to coupling with vibrations of the crystal lattice.

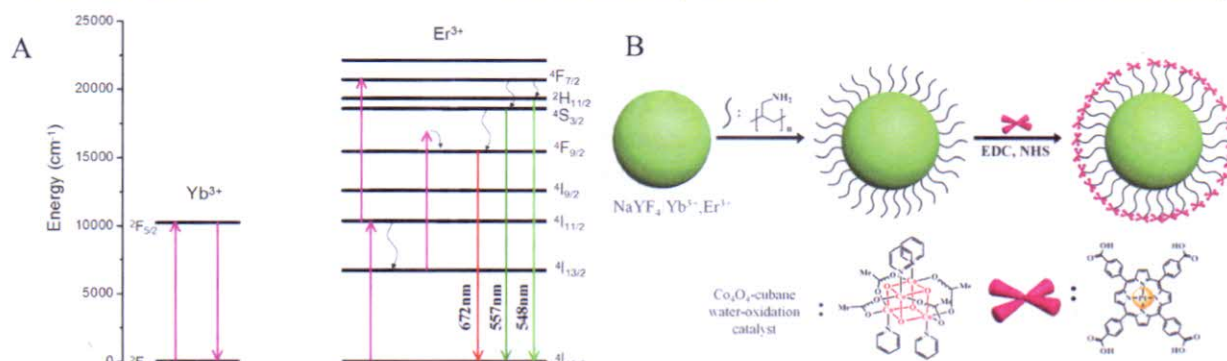


Figure 1. A: excited states of Yb^{3+} and Er^{3+} . Pink arrows represent direct excitation (980 nm) or energy transfer processes; red and green arrow represent Er^{3+} -based emission. B: functionalization of UCNP with a platinum(II) porphyrin photosensitizer (Pt(II)-TCPP); formulae of the Co_4O_4 cubane water oxidation catalyst and of Pt(II)-TCPP photosensitizer used in this study.

The researchers covalently functionalized the surface of 26 nm diameter UCNP nanoparticle with Pt(II)-TCPP, a platinum(II) porphyrin represented in Figure 1B. These functionalized nanoparticles, noted UCNP/Pt(II)-TCPP, were dispersed in a neutral phosphate buffer and compared to Pt-free UCNP. The absorption spectrum of Pt(II)-TCPP is compared to the emission spectrum of UCNP in Figure 2A, and the emission spectrum of the UCNP (before attachment) and of UCNP/Pt(II)-TCPP (after attachment) are shown in Figure 2B. The time-resolved emission spectra (Time Correlated Single Photon Counting) of UCNP and UCNP/Pt(II)-TCPP, excited by a pulse at 980 nm, as well as the lifetimes τ of the upconverted green and red emissions, are shown in Figure 3.

Answer the following questions:

- 1) Are the three main emission from the Er^{3+} ion fluorescence or phosphorescence? Justify (0.5 point).
- 2) Are they spin and/or Laporte allowed or forbidden? Justify (0.5 point).
- 3) Which excited states of the Er^{3+} ions are quenched by the surface Pt(II)-TCPP molecules? Justify with data from the text. (0.25 point)
- 4) Is energy transfer between the Er^{3+} ions in the crystal occurring via Förster or Dexter mechanism? Justify. (0.25 point)
- 5) What are the two main photophysical criteria for the upconverted light to be able to be transferred non-radiatively to the Pt(II)-TCPP complex? Are these criteria followed for all emission bands of the UCNP? Explain (0.5 point).
- 6) For the upconverted emissions that is/are quenched by the platinum sensitizer, is it static or dynamic quenching? Justify with data from the text (0.25 point).
- 7) The lifetime for UCNP and UCNP/Pt(II)-TCPP are 150 μs and 80 μs , thus leading to $(\tau^0 - \tau)/\tau^0 = 0.47$, while in the steady state emission measurement mode $I^0 - I/I^0 = 0.96$ (τ^0 and I^0 represent the lifetime and emission intensity of the 540 nm band in UCNP; τ and I represent the lifetime and emission intensity of the 540 nm band in UCNP/Pt(II)-TCPP). Is there also radiative quenching or only non-radiative quenching? Justify (0.25 point).

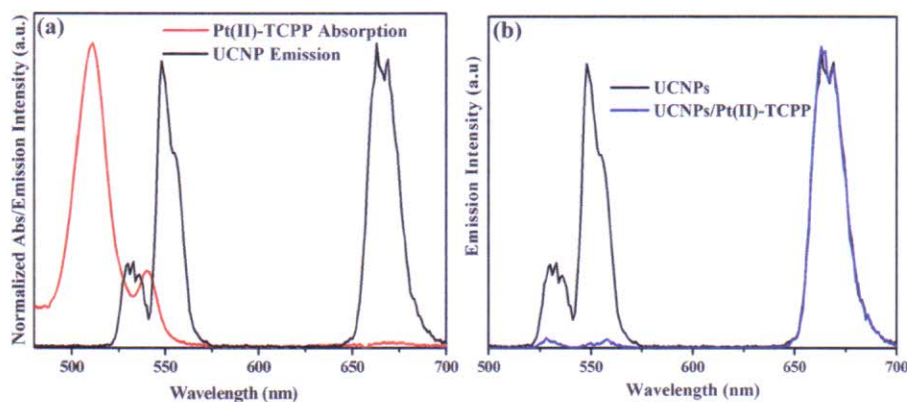


Figure 2. (a) Emission spectrum of Ln-UCNPs (black) and absorption spectrum of the Pt(II)-TCPP in pH = 7.0, 0.1 M phosphate buffer. (b) Emission spectra of UCNPs and UCNPs/Pt(II)-TCPP nanoparticles under excitation at 980 nm.

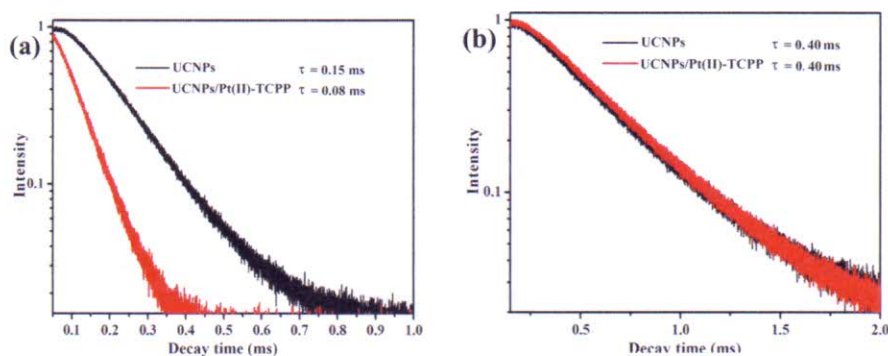


Figure 3. TCSPC of upconversion emissions monitored at (a) 540 nm and (b) 650 nm for UCNPs (2×10^{-3} M) and covalently conjugated UCNPs/Pt(II)TCPP (2×10^{-3} M).

Part A2 – Use of UCNPs to drive photocatalysis (1.5 point)

On their way to mimicking natural photosynthesis the researchers mixed the UCNPs/Pt(II)-TCPP nanoparticles with a Co_4O_4 -cubane water oxidation catalyst. Photocatalytic water oxidation experiments were then carried out in solutions containing 1.83×10^{-3} M UCNPs/Pt(II)-TCPP nanophotosensitizer as evaluated by Pt(II)-TCPP absorption, 0.15 M $\text{Na}_2\text{S}_2\text{O}_8$ as sacrificial electron acceptor, and 1.50×10^{-4} M Co_4O_4 -cubane catalysts in phosphate buffer solution (0.1 M, pH = 7.0) at room temperature. Photocatalytic oxygen generation was monitored through the detection of dissolved O_2 using a Clark-type electrode. A 980 nm continuous diode laser was used as the irradiation source. The result of light-driven oxygen formation is shown in Figure 4a. The maximum turnover frequency TOF_{max} of the catalyst was observed to be 6.6×10^{-4} mol O_2 (mol of Co_4O_4 -cubane) $^{-1} \cdot \text{s}^{-1}$ in the nanophotosensitizer (excitation power 750 mW). The overall quantum yield of NIR photons induced O_2 generations is $\sim 9 \times 10^{-3}\%$ in UCNPs/PtTCPP nanophotosensitizer under excitation with three different powers of 980 nm.

Usually, peroxodisulfate is considered as a 1-electron acceptor with a redox potential $E(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-}) = +0.6$ V vs. NHE, while the sulfate radical $\text{SO}_4^{\cdot-}$ generated by 1-electron transfer processes is itself a highly oxidizing agent with a redox potential $E(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) > 3.0$ V vs. NHE, so that peroxodisulfate is usually considered as a sacrificial two-electron acceptor triggered by 1 photon. The standard redox potential of the $\text{O}_2/2\text{H}_2\text{O}$ couple is +0.82 V vs. NHE at pH=7.0. In these conditions the cobalt water oxidation catalyst starts to catalyze water oxidation at a potential of +1.3 V vs. NHE. The Pt(II)-TCPP porphyrin sensitizer emits at 681 nm, and the redox potentials of $E(\text{Pt}^{\text{III}}/\text{Pt}^{\text{II}})$ and $E(\text{Pt}^{\text{II}}/\text{Pt}^{\text{I}})$ are +1.42 V and -1.00 V vs. NHE, respectively.

