

Datum: January 15th, 2013

Tijd: 14-17 uur

Zaal: C1

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Voorzie het 1e blad van naam, adres, email, jaar van aankomst en nummer collegekaart.

Schrijf op de andere losse bladen alleen de naam. Bij het tentamen is het gebruik van de syllabus of mobiele telefoon niet toegestaan. Voor elke vraag is de waardering aangegeven.

Gebruikt alstublieft een los blad voor deel A.

On page 1, write your name, address, e-mail, year of enrolment and the number of the college card.

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

Please use a separate page for part A.

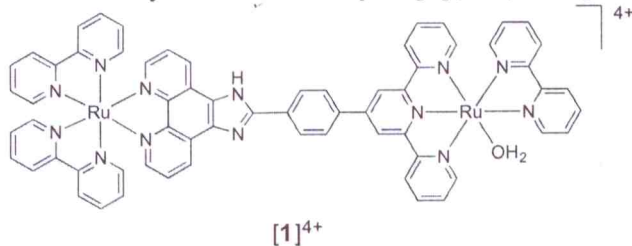
When a justification is asked it counts at least as many points as the answer itself.

Part A (5 points)

1. What means the term "coherent chemistry"? (1/2 point)
2. When do two electronic curves avoid or cross each other? (1/2 point)
3. Twisting of π -bonds: What is the geometry of the double bond in the S_1 excited state? (1/2 point)
4. Explain the structure of the three triplet states and the singlet state of a radical pair using the vector model! (1/2 point)
5. What difference in information on an electronic transition do we obtain from its 'site energy' compared to the 'ensemble averaging'? (1/2 point)
6. Why does nature use antenna complexes? Give reasons! (1 point)
7. How are excitations transferred in phycobilisome antenna from the outer pigments finally in to the reaction center? (1/2 point)?
8. Using Gouterman's four orbitals, explain the spectral positions of the first (Q-band) and the second (Soret band) electronic transition (1 point)

Part B: A Dyad as Photocatalyst for Light-Driven Sulfide Oxidation (3 points)

In a recent article O. Hamelin et al. synthesized the dyad $[1](PF_6)_4$ for photocatalytic applications.



9. Such a dyad is made of two Ru-based mononuclear components, linked by a phenylimidazole linker: one (Ru_{cat}) is a catalyst; the other one (Ru_{phot}) is a photosensitizer. Identify (give the formula of) each of them and justify your choice (0.25 point).

10. In the supplementary information, the photophysical data of the mononuclear photosensitizer Ru_{phot} alone and of the dyad $[\mathbf{1}](\text{PF}_6)_4$ are given, at room temperature in deoxygenated 0.1 M phosphate buffer (see table below). Why is the emission quantum yield of $[\mathbf{1}]^{4+}$ significantly lower than that of Ru_{phot} ? Explain. (0.25 point)

Complex	λ_{em} , nm	τ , ns	ϕ
Ru_{phot}	604	812	0.011
$[\mathbf{1}](\text{PF}_6)_4$	613 ^a	8	0.8×10^{-4}
	710 ^b	1.8	

[a] deactivation of the Ru_{phot} moiety; [b] deactivation of the Ru_{cat} fragment.

The authors use the dyad $[\mathbf{1}]^{4+}$ to perform organic photocatalysis: they monooxidize 4-bromophenyl methyl sulfide into the corresponding sulfoxide in presence of visible light (468 nm), a 0.1 M phosphate buffer at pH 6.8, and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (see Table 1). No sulfoxide product is detected in absence of light.

Table 1. Photocatalytic Oxidation of 4-Bromophenyl Methyl Sulfide Using a Blue LED System As a Source of Light^a

entry	complex	cat./subs./Co(III) ratio	pH	TON (conv %)
1	$[\mathbf{1}](\text{PF}_6)_4$	1:500:1000	6.8 ^c	201 (40)
3	$[\mathbf{1}](\text{PF}_6)_4$	1:500:1000	<i>d</i>	18 (9)
4	$[\mathbf{1}](\text{PF}_6)_4$	1:200:400	6.8 ^c	132 (66)
5	$[\mathbf{1}](\text{PF}_6)_4$	1:200:400	4.4 ^b	83 (42)
6	$[\mathbf{1}](\text{PF}_6)_4$	1:200:400	10.7 ^e	10 (5)
7	Ru_{phot}	1:200:400	6.8 ^c	36 (18)
8	Ru_{cat}	1:200:400	6.8 ^c	45 (23)
9	$\text{Ru}_{\text{phot}} + \text{Ru}_{\text{cat}}$	1:1:200:400 ^g	6.8 ^c	71 (36)

^a Photocatalytic oxidations performed in aqueous conditions with [catalyst] = 0.02 mM for 24 h. ^b A 0.1 M Sodium acetate buffer (pH 4.4). ^c A 0.1 M phosphate buffer (pH 6.8). ^d Reaction performed in unbuffered deoxygenated water. ^e A 0.1 M sodium carbonate buffer (pH 10.7). ^g $[\text{Ru}_{\text{phot}}] = [\text{Ru}_{\text{cat}} - \text{OH}_2] = 0.02$ mM

11. What is the role of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$? (0.25 point)
12. The authors assume an oxidative quenching mechanism; what is the first step of the mechanism after the initial photon absorption? (0.25 point)
13. According to the literature the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ oxidation potential of Ru_{phot} in aqueous solution is +1.26 V vs. NHE. According to Hamelin *et al* $[\mathbf{1}]^{4+}$ shows one reversible, two-electron oxidation process at +0.79 V vs. NHE attributed to the oxidation of Ru_{cat} . In which direction is the electron flow going in the excited state of $[\mathbf{1}]^{4+}$ during the photocatalytic process? From Ru_{cat} to Ru_{phot} or from Ru_{phot} to Ru_{cat} ? Justify. (0.25 point)
14. Where must the oxygen atom of the sulfoxide come from? Write the global chemical equation of the photocatalytic process (0.5).
15. Do you know another energetically relevant photocatalytic oxidation half-reaction performed in water and involving mononuclear or dinuclear Ru catalysts? Write the corresponding chemical equation. Why is this reaction important on the practical point of view? (0.25 point)
16. In Table 1 the author compare the performances of the dyad $[\mathbf{1}]^{4+}$ to that of a 1:1 mixture of the two mononuclear building blocks, simply mixed together (entry 9). Why is the TON of

the 1:1 mixture smaller than that of the dyad? Is the strategy of the authors successful? Justify. (0.5 point)

17. In the supplementary information the photocatalytic setup is described as follows: "Illumination was performed with a home-made apparatus constituted by a 30 blue Light Emitting Diodes array (purchased from Kinbright (T-1 3/4 5mm) and emitting at 468 nm) immersed in the deoxygenated reaction mixture." Why does the solution need to be deoxygenated? Explain. (0.5 point)

Part C: Spin crossover nanomaterials doped with a fluorophore (2.5 points)

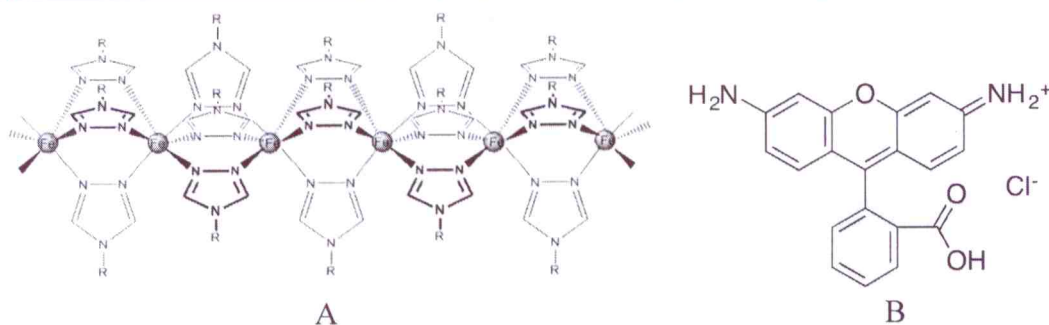


Figure 1. Formula of $[\text{Fe}(\text{Rtrz})_3](\text{OTs})_2$ (A) and of rhodamine 110 (B).

Compounds of the type $[\text{Fe}(\text{Rtrz})_3](\text{OTs})_2$ (Figure 1A) are one-dimensional coordination polymers based on bridging triazole ligands and iron(II) metal centers in an octahedral environment. Each iron center can exist in two different electronic configurations, the HS and the LS state. These compounds have raised much interest because they can switch between these two states around room temperature with large hysteresis cycles.

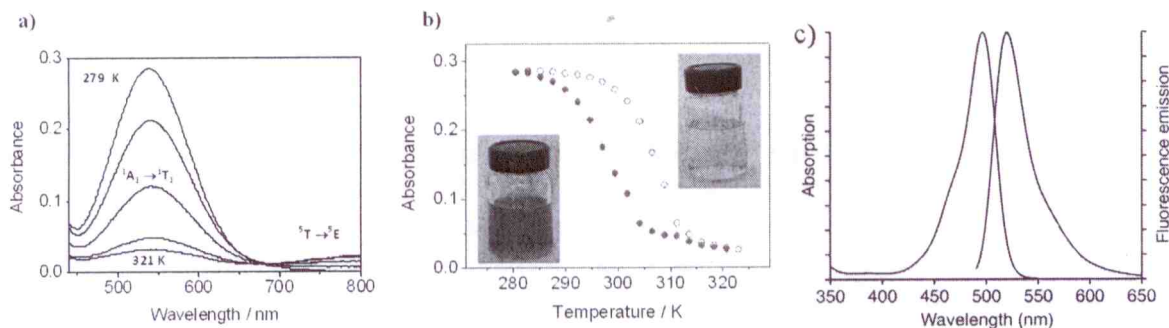


Figure 2. a) Absorption spectra of an octane suspension of $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{OTs})_2$ nanoparticles at a few selected temperatures in the cooling mode, and in b) the thermal variation of the absorbance of the suspension at 540 nm in the heating (open symbols) and cooling (closed symbols) modes. The inserts show the photographs of the sample at 295 K (violet) and 320 K (transparent).

18. With macroscopic SCO samples it is easy to measure the switching behavior, for example by UV-vis spectroscopy (Figure 2). With nanoscale samples however, such as thin layers deposited on a transparent surface, it is much more difficult. Assuming that the high-temperature state is colorless and that the low-temperature state has an extinction coefficient of $100 \text{ cm}^{-1} \cdot \text{M}^{-1}$ (Laporte-forbidden, $^1\text{A}_1 \rightarrow ^1\text{T}_1$ transition), calculate the difference in absorbance ΔA of a 85 nm SCO thin layer of $[\text{Fe}(\text{Rtrz})_3](\text{OTs})_2$ deposited on a transparent slide when it goes from the HS to the LS state. In this calculation you can assume that the density of the pure material is $1.5 \text{ g} \cdot \text{cm}^{-3}$, and that its molar mass is $644.5 \text{ g} \cdot \text{mol}^{-1}$. Is such a difference experimentally measurable? (0.5 point)

