

Datum: January 19th, 2011

Tijd: 14-17 uur

Zaal: L144

Docent: Dr. Jörg Matysik & Dr. Sylvestre Bonnet

*Voorzie het 1e blad van naam, adres, e-mail, 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 cell phones niet toegestaan. Vragen 1 t/m 7: waardering is aangegeven.
In delen 2 en 3 het hoeft niet de "Bonus" vragen te beantwoorden om een 10 te hebben, maar goede antwoorden brengt wel meer punten.*

*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. Questions 1 to 7: the rating is given.
In parts 2 and 3 you don't need to answer the "Bonus" questions to get a 10, but if you answer them you will get more points.*

*In the whole document any star * represent the excited state of the corresponding molecule.*

Part A (4 points)

1. What is the meaning of the "non-crossing rule"? (1/2 point)
2. Under which conditions orbital interaction is favorable (1/2 point)
3. What is the meaning of "coherent chemistry"? (1/2 point)
4. Why energy transfer can be interpreted as concerted electron transfer? (1/2 point)
5. Which experiment can distinguish Förster and Dexter mechanisms? (1/2 point)
6. Describe the "chromatic adaptation" of phycobilisomes. (1/2 point)
7. Show the four spin states of a radical pair in the vector model. Describe the EPR transitions for a radical pair in its Boltzmann state. (1 point)

Part B: Rhenium-based photoreduction of CO₂ (4 points + bonus)

Below the abstracts of an article from Kurz *et al*, *Eur. J. Inorg. Chem.* **2006**, *15*, 2966:

"Two series of complexes [MX(diimine)(CO)₃] (M = Tc, Re) have been prepared, fully characterised and investigated for their ability to act as photocatalysts for the reduction of CO₂ to CO. One series consists of complexes with different aromatic diimine ligands while keeping X = Br⁻ constant. The second series describes complexes with diimine = 2,2-bipyridine and variations in the anionic ligand X⁻. Although numerous complexes of this type have been prepared and investigated before, a systematic study of their photocatalytic activity has not yet been carried out. Electrochemical and spectroscopic characterisation of these complexes has been performed with the objective of better understanding their respective activity in the photocatalytic CO₂ reduction. Despite various modifications, catalytic activity is retained for all compounds exhibiting fluorescence, including [⁹⁹TcCl(bipy)(CO)₃], whereas nonfluorescing compounds did not convert CO₂ to CO. The correlation of catalytic activity and spectroscopic or electrochemical properties such as absorption or emission wavelengths, redox potentials or Stern-Volmer constants for the reductive quenching of the excited complexes is difficult. Nevertheless, the study emphasises the possibility to obtain [ReX(CO)₃(diimine)] complexes with a wide range of physicochemical

properties by ligand variations and the great potential of compounds of this class of complexes as inorganic photosensitisers."

In the Annexes are given:

- Scheme 2, which depicts the different diimine ligand used and the corresponding numbering of the Re complex
- Table 2 giving spectroscopic data & redox potentials vs. Ag/AgCl

Supplementary data:

- Compound **2** ($[\text{ReBr}(\text{bpy})(\text{CO})_3]$): The cyclic voltammetry shows a one-electron, ligand based reduction; the emitting state is a triplet state with MLCT character.
- Irradiation conditions: "The light source was a Leica Pradovit S AF slide projector equipped with a 250-W Osram Xenophot HLX lamp. The light was filtered by a 400 nm cut-off filter (Schott GG 400) before reaching the sample at 40 cm distance from the projector."
- Standard enthalpy of formation of CO_2 gas: -393.509 kJ/mol
- Standard enthalpy of formation of CO gas: -110.525 kJ/mol
- Redox potential of the CO_2 / CO couple: $\Delta E_{1/2}^0 = -0.53 \text{ V}$ vs. NHE
- Redox potential of the H^+ / H_2 couple: $\Delta E_{1/2}^0 = 0.0 \text{ V}$ vs. NHE
- Redox potential of the $\text{H}_2\text{O} / \text{O}_2$ couple: $\Delta E_{1/2}^0 = +1.23 \text{ V}$ vs. NHE
- Redox potential of the $\text{TEOA}^+ / \text{TEOA}$ couple: $\Delta E_{1/2}^0 = +0.80 \text{ V}$ vs. Ag/AgCl (TEOA = triethanolamine)
- Redox potential of the Ag/AgCl couple: $\Delta E_{1/2}^0 = +0.22 \text{ V}$ vs. NHE

Answer the following questions:

- 8) What is the oxidation number, and number of d electrons, of Re and Tc in $[\text{MX}(\text{diimine})(\text{CO})_3]$ complexes?
- 9) Write and equilibrate the two redox reactions involving CO_2 / CO and H^+ / H_2 .
- 10) Calculate the Stokes shift (in nm) for compound **2**. What is the physical origin of the Stokes shift?
- 11) From the spectroscopic properties of compound **2** give an approximate value of E_{0-0} (in eV), the approximate energy difference between the $^3\text{MLCT}$ emitting state and the ground state of compound **2**.
- 12) On a redox potential scale place the CO_2 / CO couple, the H^+ / H_2 couple, the $[\text{ReBr}(\text{bpy})(\text{CO})_3] / [\text{ReBr}(\text{bpy})(\text{CO})_3]^-$ couple, and the $[\text{ReBr}(\text{bpy})(\text{CO})_3]^* / [\text{ReBr}(\text{bpy})(\text{CO})_3]^-$ couple.
NB: To avoid mistakes in converting the Ag/AgCl and NHE potential scales it is recommended – although not obligatory – to put both scales on the same scheme (two vertical axes, one vs. Ag/AgCl, the other vs. NHE). One correct scale is enough to get full points.
- 13) Throughout the paper TEOA is called a "sacrificial electron donor". a) Is TEOA able to reduce CO_2 ? Justify. Can it reduce $[\text{ReBr}(\text{bpy})(\text{CO})_3]$? Justify? b) Compare the oxidizing properties of $[\text{ReBr}(\text{bpy})(\text{CO})_3]^*$ and $[\text{ReBr}(\text{bpy})(\text{CO})_3]$.
- 14) According to Table 2, not all of the complexes exhibit room-temperature fluorescence in DMF when irradiated with light. The emission maxima are between 520 and 585 nm for **2**,

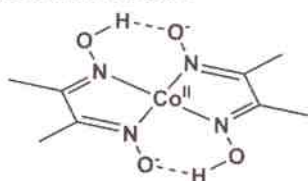
8, 9, 10 and 12, but 11, 13, 14 and 15 do not fluoresce. a) Which processes might be responsible for the lack of fluorescence in absence of quencher? b) Interpret the following sentence taken from the abstract: "Despite various modifications, catalytic activity is retained for all compounds exhibiting fluorescence [...] whereas nonfluorescing compounds did not convert CO₂ to CO."

15) **Bonus:** a) Considering the quenching experiments and the link between fluorescence and catalytic activity, what is the initial step of the photocatalytic cycle? b) Which species reduces CO₂? In this species precise the oxidation state of the metal. c) Is this mechanism called reductive or oxidative quenching, and why?

16) **Bonus:** In the conclusion the authors state the following: "While many of the rhenium complexes are able to catalyze the two-electron photoreduction of CO₂, none show any reactivity for the reduction of the much more important substrate H₂O." a) Which reaction is called "water photoreduction"? b) In link with question 6 for which reasons do you think water photoreduction is not possible with this system? 12

Part C: Rhenium-based proton photoreduction (2 points + bonus)

In Probst et al, *Inorg. Chem.* **2009**, *48*, 1836 the same research group as in Part B proposed a modification of the photocatalytic system, which allowed photocatalytic production of H₂ to occur. To the same [ReBr(bpy)(CO)₃] complex and TEOA in DMF, addition of acetic acid and [Co(dmgh)₂] (dmgh = dimethylglyoxime) allowed H₂-evolution to occur under white light irradiation. The cobalt complex is represented below:



The abstracts of the article is reproduced here:

"We present an artificial photocatalytic model for photosystem I (PSI) using [ReBr(CO)₃bipy] (**16**) as a photosensitizer, [Co(dmgh)₂] (**17**) as a hydrogen evolution reaction catalyst, and triethanolamine as an irreversible reductive quencher. Complex **16** is more robust in the long run, and turnover numbers were more than doubled in the present study as compared to the commonly used photosensitizer [Ru(bipy)₃]²⁺. The quantum yield for hydrogen production with **16** was found to be 26(2) % (H produced per absorbed photon). Forward electron transfer between **16**^{*} and **17** was found to occur at a rate close to diffusion control ($k = 2.5(1) \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$). The rate of hydrogen production exhibited a linear dependence on the photon flux and a quadratic dependence on the total concentration of Co ($k_{\text{obs}} = 3.7(1) \text{ M}^{-1} \cdot \text{s}^{-1}$). Therefore, a second-order process in Co^{III}-H is proposed. The process showed a complex dependence on [AcOH]. An excess of dimethylglyoxime was systematically added to the system to ensure the complete formation of **17** and reduce the portion of free [Co]_{solv}²⁺, an efficient quencher of the excited state of **16**."

Answer the following questions:

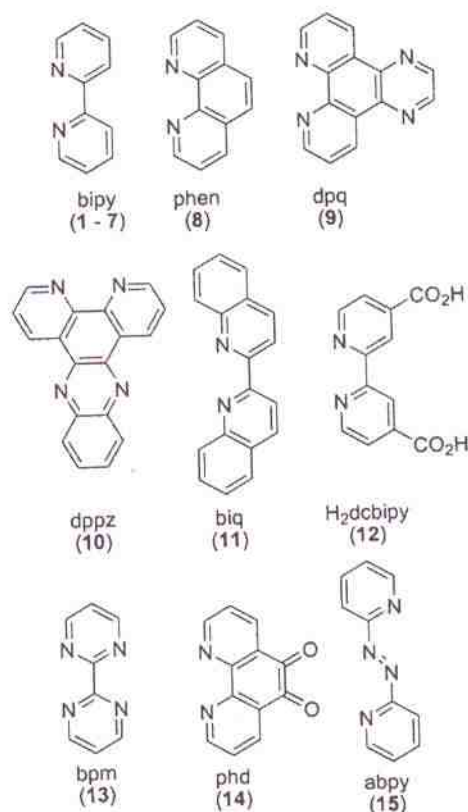
17) a) Is this reaction identical to "water photoreduction"? b) How industrially relevant do you think this system might be?

18) To measure the flux of absorbed photons, the authors put a photon detector on the beam path after the reaction flask, first in absence of photosensitizer, then after having added the

photosensitizer **16** to the solution mixture, and they calculate the difference in photon flux. In the experimental conditions (1 M TEOA, 0.1 M AcOH, 0.5 mM of compound **16**, 1 mM of compound **17**, DMF, under Ar, in a 5600 μl suprasil cell), using a 415 nm laser, the measured flux of absorbed photons is $10^{-8} \text{ mol}\cdot\text{s}^{-1}$. Which volume of dihydrogen (in cm^3) does the system produce within 2 hours under a pressure of 1.5 bar at 25 $^\circ\text{C}$?

- 19) **17** is not a stable complex but it is formed in situ by adding an excess of the ligand dmGH to $\text{Co}(\text{OAc})_2$ (see Figure 5B). When 6 equivalent of dmGH are used compared to $\text{Co}(\text{II})$ and at high photon flux, the efficiency of the system is linear in $[\text{Co}]_{\text{tot}}^2$ (see Figure 4). The author state the following: " $[\text{Co}]_{\text{free}}^{2+}$ should not interfere with excitation, quenching, and electron transfer. It is, however, known from other systems that paramagnetic cations rapidly quench triplet excited states." To which phenomenon do they refer? Explain.
- 20) **Bonus:** In high photon flux condition, the author state that "the rate of H_2 production was found to have a square dependence on $[\text{Co}]_{\text{tot}}$ [...]. This square dependence implies hydrogen formation via a path second-order in $\text{Co}^{\text{III}}\text{-H}$." As simple protonation of $\text{Co}^{\text{III}}\text{-H}$ to release H_2 would be first order in Co_{tot} (which is not observed), can you propose a mechanistic cycle for the whole photocatalytic process, knowing that a) reductive quenching takes place, and that b) the mechanism involves a $\text{Co}^{\text{III}}\text{-H}$ hydride species? In each of the intermediate precise the formal oxidation state of the rhenium and cobalt centers and the global charges of each species.
- 21) **Bonus:** Which difference do you see between Part 2 and Part 3, *i.e.*, between the two photocatalytic system? For which reason can the second system reduce protons, and not the first one?

Annexes



Scheme 2. Diimine ligands used for the synthesis of [ReBr(diimine)(CO)₃] complexes with the numbering of the corresponding complexes in brackets: 2,2'-bipyridine (bipy) (1-7); 1,10-phenanthroline (phen) (8); dipyrido[3,2-*f*:2',3'-*h*]quinoxaline (dpq) (9); dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) (10); 2,2'-biquinoline (biq) (11); 2,2'-bipyridine-4,4'-dicarboxylic acid (H₂dcbipy) (12); 2,2'-bipyrimidine (bpm) (13); 1,10-phenanthroline-5,6-dione (phd) (14); 2,2'-azobispyridine (abpy) (15).

Table 2. Spectroscopic and electrochemical properties of [ReBr(diimine)(CO)₃] complexes.

Diimine ligand	λ_{\max} [nm] ^[a]	λ_{em} [nm] ^[a]	$\tilde{\nu}_{\text{CO}}$ [cm ⁻¹] ^[b]	$E_{1/2,\text{red}}$ [mV] ^[c]
bipy (2)	370	575	2019, 1905	-1190
phen (8)	370	570	2018, 1933	-1090
dpq (9)	≈ 375 ^[d]	585	2025, 1948	-975
dppz (10)	≈ 425 ^[d]	520	2018, 1918	-705
biq (11)	435	^[e]	2014, 1895	-735
Hdcbipy (12)	360	540	2024, 1896	-1250 ^[f]
bpm (13)	385	^[e]	2030, 1931	-860
phd (14)	375 ^[d]	^[e]	2033, 1943	-15, -755
abpy (15)	550, 360 ^[d]	^[e]	2020, 1924	+50

[a] In DMF solution. [b] KBr pellets. [c] In DMF solution containing 0.1 M NBu₄PF₆. [d] Absorption shoulder. [e] No fluorescence observed at room temperature in DMF solution. [f] Irreversible reduction.

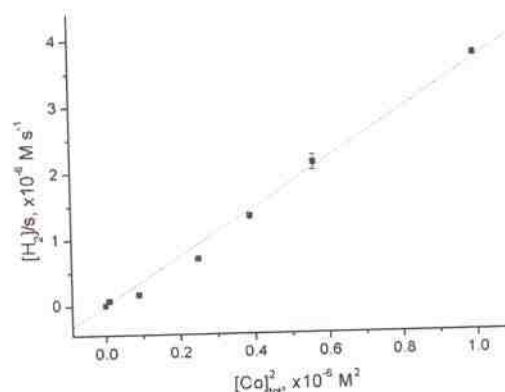


Figure 4. H₂ production rates as a function of [Co]_{tot}². An excess of 6 equiv of dmgH₂ was used per cobalt, 0.5 mM 1, 1 M TEOA, 0.1 M AcOH, DMF, and argon.