Fachhochschule
Münster University of
Applied Sciences

**Lab Work Advanced Inorganic Chemistry**

**FB Chemieingenieurwesen**

Labor für Anorg. Chemie
Angew. Materialwiss.

# Experimental description

# Grätzel Cell

# 11/2012

# Synthesis of cis-$Ru^{II}(dcbpy)_2(NCS)_2$

Chemicals: $RuCl_3 \cdot x\ H_2O$
5,5´-Dicarboxyl-2,2`-bipyridine
DMF (MSDS!!)
Acetone
NaOH c = 0,1 mol/L
NaSCN

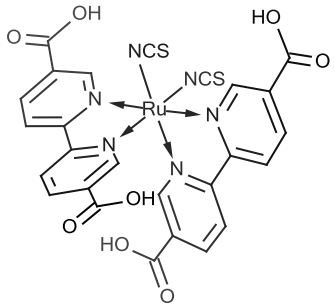
Apparatus: 250 mL Two-neck-round-bottom flask
Condenser
Washing flask
Oil bath and stirring plate
Suction filtering device

Equation:

$2\ RuCl_3 \cdot 3\ H_2O + 5$ dcbpy → cis-$Ru^{II}(dcbpy)_2Cl_2 \cdot 2\ H_2O + Ru^{III}(dcbpy)_3$

cis-$Ru^{II}(dcbpy)_2Cl_2 \cdot 2\ H_2O$ → cis-$Ru(dcbpy)_2(NCS)_2 \cdot 2\ H_2O$

**cis-$Ru(dcbpy)_2(NCS)_2 \cdot 2\ H_2O$:**




# 1. Synthesis of $Ru^{II}(dcbpy)_2Cl_2$

## Day 1:

540 mg $RuCl_3 \cdot x\ H_2O$ and 1017 mg 5,5'-Dicarboxyl-2,2`-bipyridin were dissolved in 180 ml DMF and stirred under reflux for 6-8 hours ($Bp._{DMF}$:153°C) .
Meanwhile the starting material 5,5`-Dicarboxyl-2,2`-bipyridine needs to be prepared for the next group. Experimental details are described later.
Furthermore several ITO´s must be coated with $TiO_2$ and one Grätzel cell should be prepared using blueberry juice.

## Day 2:

After removing the by-product $Ru(dcbpy)_3$ with Büchner funnel and Filter 602h the DMF (120-130 ml) is evaporated, water bath temperature 43°C.
150 ml Acetone is added and the product $RuL_2Cl_2$ precipitates. The complex is then subsequently filtered, washed (Acetone) and dried.

## 2. Synthesis of $Ru^{II}(dcbpy)_2(NCS)_2$

The $RuL_2Cl_2$ is dissolved in 120 mL DMF, filled up with 60 mL 0,1 mol/L NaOH and a solution of 1050 mg NaSCN in 6 mL $H_2O$ and hereupon stirred for 5 hours under reflux in Argon atmosphere.

**Day 3:**

Approx. 80 mL DMF are removed at the rotary evaporator, the product is precipitated with Acetone , filtered and washed (Acetone). Take the output weight.
Analytical measurements:

- Infrared spectra, step1 and 2
- Absorption measurement, step 2

## Grätzel cell preparation

Experimental:

**I.** The glass slides coated with ITO are cleaned with Ethanol and a fluffless cloth. The ITO is masked at two opposite lying sides with a 5mm wide strip of Scotch tape.

**II. $TiO_2$-film deposition**

1. Slurry : 6,0 g $TiO_2$ (Degussa $TiO_2$ P25)
   20 mL $H_2O$
   2-3 mL TritonX
   2 mL PEG 20000 (0,1 g /mL $H_2O$)
   1 mL Acetylacetone

2. Apply a few drops of the slurry on the conductive side of the ITO and spread it to a transparent film with the help of a glass bar.

3. Remove the tape and heat the ITO at 460°C for 30 min. starting at room temperature.

4. Let it slowly cool down in the furnace.

**III. Dye application**

Drop the dye onto the $TiO_2$ film and dry it carefully with a hairblower.

**IV.Graphite electrode**

An ITO-sized white paper is coated with a graphite pencil and cut out.

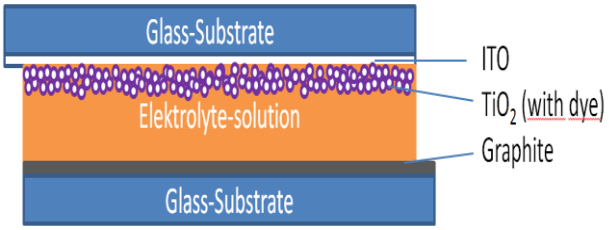
**V. Electrolyte application**

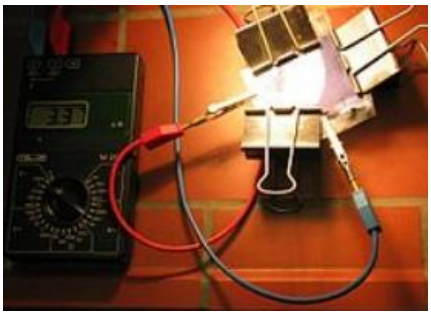
Solution: 4,15 g KJ
0,51 g $I_2$ in 50 mL $H_2O$

Sprinkle the solution on both sides of the graphite electrode and also 1-2 drops on the $TiO_2$ film.

**VI. Grätzel cell assembly and measurement**

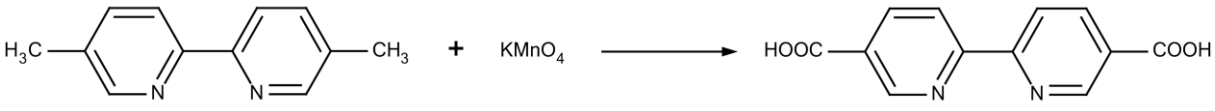
1. Fix both glass plates with two clamps.
2. Connect the wiring to the gauge (Keithley) and contact the ITO and the graphite layer
3. Irradiate the Grätzel cell with „cold light“ and note the values.



# Preparation of 5,5`-Dicarboxyl-2,2`-bipyridine ligand

Chemicals: 5,5`-Dimethyl-2,2`-bipyridin (Dbp)
Formula: $C_{12}H_{12}N_2$
Molecular weight. 184,237 g/mol
4 mol/L $H_2SO_4$
Cooling bath (Ice/$NH_4Cl$)
$KMnO_4$
$Na_2CO_3$-solution 1 mol/L
Mixture of glacial acetic acid / HCl (1:1)




5,5'-Dimethyl-2,2'-dipyridin 5,5'-Dicarboxyl-2,2'-dipyridin

Synthesis:

**Day 1:**

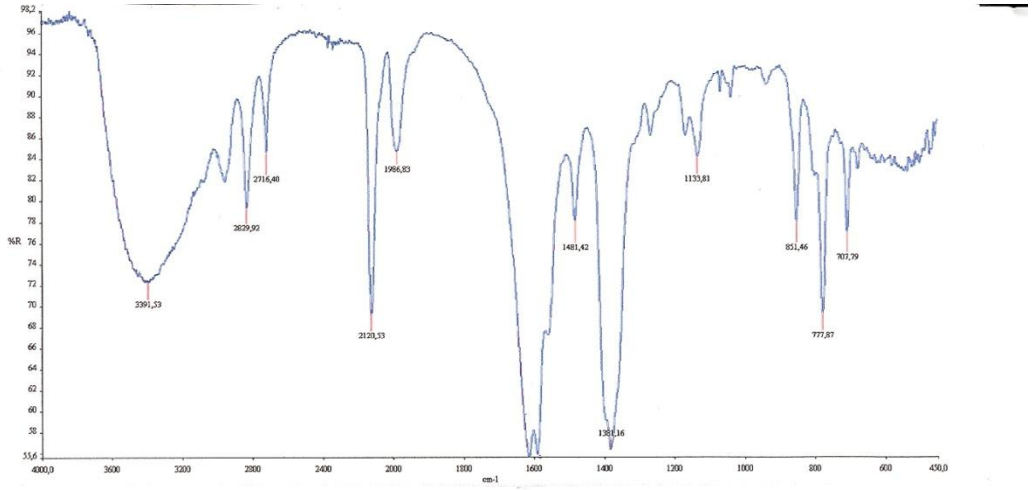
3 g of Dbp are dissolved in 160 ml $H_2SO_4$ and cooled down to -5°C. Over a period of 10 min. 6,4g solid $KMnO_4$ is added in six portions under stirring. Continue stirring for 30 min. at low temperature. Additional 6,4g $KMnO_4$ is added as before. The solution is then refluxed for another 5 h.

**Day 2:**

The suspension is sucked off via Büchner funnel ( Filter 602H) and the precipitate is dissolved in 200 ml $Na_2CO_3$-solution and stirred for additional 15 min. Subsequently the solution is sucked off again under the same conditions. Adjust the pH of the filtrate to <2 by slow addition of the above mentioned acid mixture and then suck off the white precipitate .

The product is to be characterized by IR-spectroscopy.

## IR-spectrum of cis $Ru^{II}(dcbpy)_2(NCS)_2$




## Position of absorption bands depending on the solvent:

| Lösungsmittel | λ(π→π*)/nm | λ(MLCT)/nm | λ(MLCT)/nm |
|---|---|---|---|
| $H_2O$ | 308.1±0.4 | 371.8±0.9 | 502.8±0.8 |
| $C_2H_5OH$ | 313.2±0.2 | 396.3±0.2 | 536.0±0.5 |
| DMF | 317.0±0.5 | 403.8±0.9 | 545.8±0.5 |
| DMSO | 319 | 404 | 549 |