2nd
European Union Science Olympiad
in Groningen, Netherlands

TASK B

Task B

Task B is about the production of light and divided into two seperate parts.

Part B.1 Chemiluminescence

The production of light ('luminescence') from a chemical reaction is called chemiluminescence. In such reactions, one of the products of the reaction is formed in an electronically 'excited state'. This means that the electrons of the molecule are in a state of higher energy, compared to the normal situation (the 'ground state' of the molecule). When the molecule relaxes from the excited state back to its ground state, the released energy is emitted in the form of a light particle, a 'photon'. The colour of the light is determined by the energy difference between the excited and the ground state of the molecule. Each kind of molecule has a specific set of energy levels for its electrons.

Many living organisms produce light through chemiluminescent reactions. This is called 'bioluminescence'. You may have seen the beach glowing greenish at night when walking along the shoreline. This light is produced by microorganisms. Other well-known bioluminescent organisms are fireflies. Fewer people know that there is a great variety of luminescent fish in the oceans.

In the experiment with glucose, we used a bioluminescence reaction in order to measure the activity of the enzyme hexokinase.

In this experiment you are going to make this form of chemical light happen. First, you prepare the chemiluminescent compound called adamantylideneadamantane-1,2-dioxetane from adamantylideneadamantane (abbreviated as 'ad=ad') by having it react with a reactive form of oxygen. This product was made for the first time in Groningen in 1973. It is one of the very few known 1,2-dioxetanes that are stable. Then you will heat this 1,2-dioxetane at ~200 C. At this temperature, the compound rapidly falls apart into two halves and light is emitted from one of them.

Note: The assistant marks during the experiments.

Material and equipment

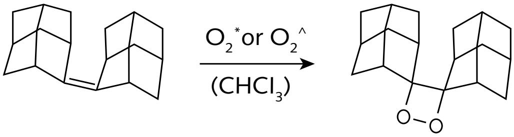
For Task B.1

- 500 mg ad=ad
- Chloroform solvent
- Methylene blue
- 1,2-dioxetane (adamantylideneadamantane-1,2-dioxetane)
- n-hexane
- 9,10-diphenylantharacene
- Rubrene
- Active carbon
- Three-necked flask
- Condenser
- Gas inlet tube, connected to an oxygen cylinder
- Glass stopper
- 250 ml glass beaker
- Erlenmeyer flasks
- Funnel
- Filter paper
- Lamp
- Red plastic shield
- Magnetic stirrer with stirring bar
- Pipette
- 3 TLC-plates
- Hot plate
- Rotary evaporator

For Task B.2

- Multimeter
- Piece of glass with one side coated with indium tin oxide
- Poly-phenylene vinylene
- THF
- Toluene
- Acetone
- Cyclohexanone
- Liquid indium-tin alloy
- Pipette
- Power supply
- Photo-diode
- Glass beakers

Synthesis of adamantylideneadamantane-1,2-dioxetane



ad-ad ad-ad-diox

Adamantylideneadamantane-1,2-dioxetane is made in the presence of methylene blue. Methylene blue is used in this reaction as a sensitizer. A sensitizer is a dye molecule that can transfer the energy of absorbed light *from the sodium lamp* to an oxygen molecule. By taking up the absorbed energy from the dye, the oxygen molecule in turn is excited to a high-energy form, which makes the reaction of the oxygen molecule with ad=ad happen.

Experimental procedure

- Take a three-necked flask and provide it with one condenser on the middle neck. In one of the side necks, put a gas inlet tube, connected to an oxygen cylinder by a flexible tube. Close the third neck with a glass stopper.
- Connect the condenser with a tap water outlet in the proper way: water inlet to the bottom, outlet to the top of the condenser.

Have the assistant control your experimental setup.

- Put 500 mg ad=ad in a 250 ml glass beaker and add 100 ml of chloroform solvent. Use gloves!
- Now add 10 mg methylene blue

Have the assistant control your experimental setup again.

2. Pour the solution in the three-necked flask and carefully open the oxygen cylinder to give a slow stream of gas bubbles (approximately 1 bubble / 3 seconds).
- Turn on the cooling water
3. Put the lamp in position and turn it on (be careful with the tubes).
4. Put a protecting red plastic shield in front of the setup
5. **Let the reaction happen for at least 2½ hours**
6. Pour the reaction mixture into an Erlenmeyer (conical flask)
7. Add 3 slices active carbon, add a stirring bar, and stir for 10 minutes on a magnetic stirrer.
8. Filter the suspension.

9. Concentrate the filtrate very carefully (under the supervision of the assistant) on the rotary evaporator at about 40 °C.

Have the assistant check your product.

Chemiluminescence

- Put 25 mg of the 1,2-dioxetane (adamantylideneadamantane-1,2-dioxetane) in a glass beaker and add a minimum amount of n-hexane to obtain a clear solution.
- Suck the solution into a pipette and impregnate three TLC plates in an even way. Dry the TLC plates with a stream of air.
- Leave TLC A for control.
- Subsequently impregnate the second TLC plate with a solution of 9,10-diphenyl-antharacene (a dye) in toluene and dry the plate with a stream of air. (=B)
- Similarly impregnate the third TLC plate with a solution of rubrene (another dye) in toluene and dry. (=C)
- Bring the three dried TLC plates to the dark room and put them on a hot plate (~220 °C) one after the other. Observe what happens and fill out the table in question 3 in the answer sheet.

Part B.2 – Plastic light emitting diodes

Nowadays conventional insulating polymers (or plastics) are widely used as substitutes for traditional materials like wood and metal, because of their high strength, light weight, ease of chemical modification, and processability at low temperatures. Since the 1950s, the study of semiconducting organic materials focused on small organic molecules in the crystalline state. However, due to their poor semiconducting characteristics, organics were mostly considered as exotic materials with little potential for applications. The first highly conducting organic polymer, chemically doped polyacetylene, was reported in 1977. Polyacetylene is an example of a so-called conjugated polymer, it consists of alternating single and double bonds between the carbon atoms (Fig. 1). For this invention the Nobel prize for chemistry was awarded in 2000.

Alternating single and double bonds

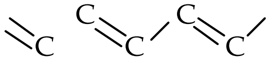


Figure 1: (trans) polyacetylene

The interest in polymeric semiconductors revived at the end of the 1980s as a result of (i) the report of field-effect transistors made from polythiophene, and (ii) the discovery of electroluminescence from a poly-phenylene vinylene (PPV) conjugated polymer-based diodes at Cambridge University. The schematic structure of such a polymeric light-emitting diode (PLED) is shown in Figure 2.

Polymer Light-Emitting Diode (PLED)

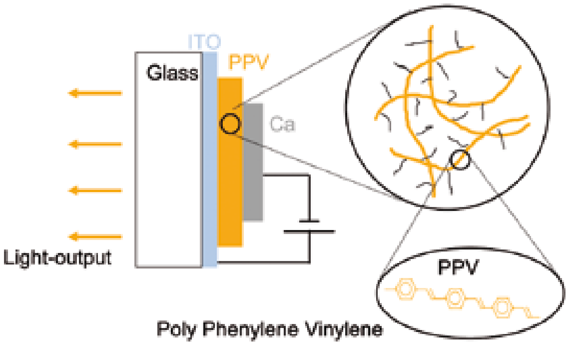


Figure 2: Structure of a polymer light-emitting diode (PLED). ITO is indium tin-oxide. PPV equals poly-phenylene vinylene.

A typical PLED consists of a thin layer of conjugated polymer sandwiched between two electrodes on top of a glass substrate. Experimentally, attention has especially been focused on PLEDs that contain the conjugated polymer poly-phenylene vinylene (PPV) or its derivatives. The PPV is spin-coated on top of a patterned indium-tin-oxide (ITO) bottom electrode which forms the anode. The cathode on top of the polymer consists of a (evaporated) metal layer, for which often Ca is used.

Why are polymers so attractive for applications? By adding side-chains to the main-chain of the polymer it can be made soluble in common organic solvents. As a result the material is available as a liquid, meaning that electronic components are available in a bottle!

Under forward bias electrons and holes are injected from the cathode and the anode, respectively, into the polymer, as schematically indicated in Fig. 3. Driven by the applied electric field, the charge carriers move through the polymer over a certain distance until recombination takes place. The device operation of a PLED is thus determined by three processes: charge injection, charge transport, and recombination.

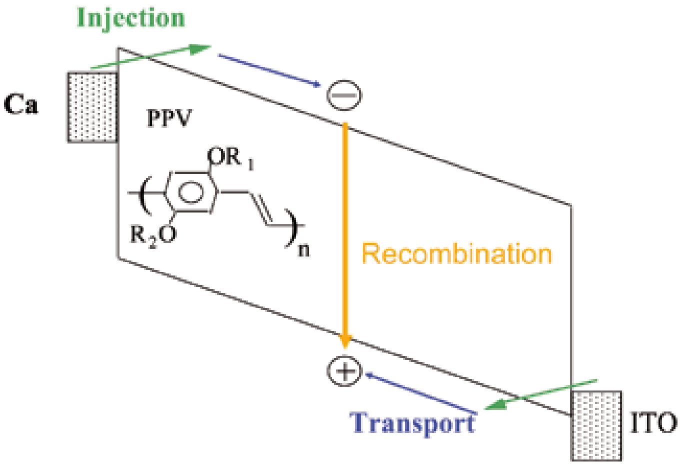


Figure 3: Schematic device operation of a PLED.

Instead of calcium we use indium tin alloy.

Experimental procedure

Preparation of an Organic Light Emitting Diode

"Solid-State Organic Light-Emitting Diodes Based on PPV"

1. Identify the conducting side of an indium tin oxide-coated piece of glass by using a multimeter to measure resistance.

   Determine the resistance of the conducting side.

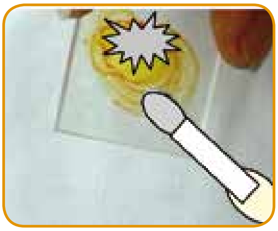
2. Dissolve 10 mg PPV in 5 ml of THF, and stir at 60 degrees until the PPV is dissolved (takes about 30 minutes). Add successively 5 ml of toluene and ca. 2 ml of acetone until the solution is clear. Finally add 1 ml of cyclohexanone (film-forming properties).

   Show your final solution to the assistant for inspection.

3. In order to be sure that the PLED will work we use the standard solution. Add a few drops of the standard solution to the conducting side of a tin-oxide coated piece of glass.

   In a fume hood, evaporate the solution to dryness (takes about 15–30 minutes). Use a pipette to drop cast with liquid indium-tin alloy, heated at 150 °C, to add an active metal electrode (This mixture of indium-tin is a liquid above 100 °C). Casting is more easily done if the coated glass is warm. (100 °C). Be careful not to scrape aside the PPV to produce a direct connection or short between the indium tin oxide and the indium-tin.

   Measure the resistance of the PLED.



4. Touch the positive lead of a volt power supply to the tin-oxide glass (not the PPV coating). Gently touch the negative lead to the indium-tin. Increase the voltage ***slowly*** from zero until the PLED gives light. Failure to follow this may result in catastrophic failure of your PLED. Make sure you do not exceed 20V. If your PLED doesn't work first try again if that doesn't work either then ask one of the assistants for a working one.

Measure voltage and current, and calculate the absorbed electrical power.

5. A photo-diode is used to measure the amount of light released by the PLED. The voltage reading from the diode is proportional to the light intensity.

   Make a series of measurements to determine the dependence of the emitted light intensity of the PLED as a function of the absorbed electrical power. Present your data in a table and a graph.

Task B

B.1 Chemilumescence – Answer sheet

1. Quality of experimental setup *5 Marks*
2. Quality of filtrate *5 Marks*
3. Fill out the following table, concerning your observations. *5 Marks*

Colour of light	TLC A	TLC B	TLC C
Purple			
Dark blue			
Bright blue			
Red			
Yellow			

4. Explain the origin of the various colours. Tick maximum three true statements *5 Marks*

☐ Heating creates a new compound
☐ Heating splits the dioxetane into two parts in the ground state
☐ Heating splits the dioxetane into two parts with one in the excited state
☐ The dye causes a colour change in dioxetane
☐ The dye absorbs the emitted light
☐ The dye is ineffective
☐ A photon is emitted when an excited molecule makes a transition to the ground state
☐ The heat absorbed by the dye is converted to a photon