

Report on the AKTION Project: No.: 63p20

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1. Mutual visits**Pardubice group:**

Dr. Numan Al Monasy - 9.-13. July 2012, **Activities undertaken: lecture** "Synthesis and photophysical properties of bichromophoric systems based on polycyclic aromatic amines."
 Prof. Radim Hrdina - 3.-7. December.2012, **Activities undertaken: lecture** "High performance (HP) pigments, preparation, properties and application"

Dr. Numan Al Monasy, 3.-7. December.2012, **Activities undertaken: measurements**
PhD student, Ing. Hana Přichystalova - 9.-13. July 2012, **Activities undertaken:** Measurements of fluorescence lifetime

Graz Group:

Prof. Günter Grampp – 7.-8. November 2012, **Activities undertaken:** Discussion of obtained results.

Dr. Kennett Rasmussen - 7.-8. November 2012, **Activities undertaken:** lecture "Application of ESR spectroscopy to polymer research: Stability tests of polymers used in space"

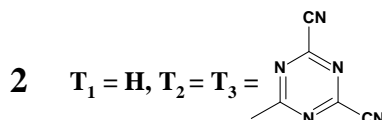
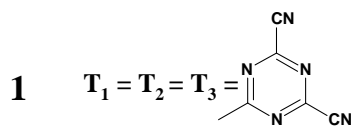
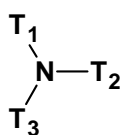
Prof. Günter Grampp- 18-19 December, **Activities undertaken:** lecture "Magnetic Field Effects in Chemistry: How does an external magnetic field influence a chemical reaction?"

2. Summary of the investigations**a. The compounds prepared according to the project purpose:****Synthesis of tetracyano-1,4-hydroquinone (TCNHQ)**

TCNHQ was prepared in two stages process. In the first stage, the oxidative bromination of hydroquinone with hydrobromic acid and hydrogen peroxide mixture was performed to obtain bromanil. In the second stage, the bromanil reacted with sodium cyanide to create the final product.

Synthesis of 2,4,6-tricyanotriazine (TCTA)

To prepare TCTA by the reaction of cyanuric chloride with sodium cyanide, several experiments have been performed. However, instead of the target product, the compounds **1** and **2** were obtained. Although the process of the preparation of TCTA has not been successful, the new compound **1** has very good chance for its use as a potential system for photoinduced electron transfer (PET) reaction. Nonetheless, due to time constraints this compound has not yet been prepared in pure form.



Synthesis of 4,5-dicyanoimidazoles derivatives (DQI)

Three DQI compounds were synthesized. The study of the photoinduced electron transfer reaction of these compounds is now in progress.

b. The compounds prepared beyond of the project purpose

Synthesis of π -conjugated acetylene derivatives

A series of push-pull π -conjugated acetylene derivatives were prepared. The UV/Vis absorption, fluorescence and excitation spectra and fluorescence quantum yields of the prepared compounds were measured by the group of Dr. Almonasy in Pardubice. The fluorescence lifetimes were measured by the group of Prof. Grampp in Graz. Currently we are working on a manuscript for publication of the obtained results in an impacted journal.

Steady-state absorption and fluorescence emission properties of TCNHQ:

The absorption and fluorescence emission properties (in steady-state) of **TCNHQ** and its deprotonated forms have been investigated in different media (aqueous and non-aqueous). The protolytic equilibria in ground and excited states have been investigated for the aqueous solution of **TCNHQ**. We observed two ground state pK_a -values at 0.9 and 3.9 but only one pK_a^* value -1.1 in water. **TCNHQ** is a strong acid and has a capacity to donate its proton to the solvent very efficiently. The pK_a^* value for the **TCNHQ** ($pK_a^* = -1.1$) suggest it to be classified as “super” photo-acid. Normally, photoacids are categorized into two groups based on their excited-state acidity constants (pK_a^*). Photoacids with pK_a^* greater than zero are called normal photoacids and photoacids with pK_a^* value less than zero are named as “super” photoacids. The absorption spectra of **TCNHQ** were measured in the binary mixture of acetonitrile/water and DMSO/water.

The absorption and emission spectra of **TCNHQ** in H_2O at different concentration disclosed the highly acidic nature of **TCNHQ**. The presence of cyano-groups enhance the acidic properties of the parent hydroquinone many folds as can be seen by comparing pK_a and pK_a^* values for hydroquinone and cyano-substituted hydroquinones.

Due to the presence of four cyano groups, the aromatic ring is highly electron deficient and very much willing to donate its hydroxyl proton. **TCNHQ** exists in three distinct forms, i.e. **TCNHQ**, **TCNHQ**⁻ and **TCNHQ**⁻², at different pH/ H_0 values as well as in different solvents.

In aqueous solution, neutral form of **TCNHQ** was only observed at lower pH (highly acidic). **TCNHQ** behaves as an extremely strong acid in the electronically excited state that makes it impossible to observe the steady-state emission spectra of the neutral **TCNHQ** in highly acidic water. The absorption spectra in different organic solvents showed that **TCNHQ** was present in one form (neutral **TCNHQ**) in solvents with very little polarity like ethers (DEE and NBE) and two forms of **TCNHQ** (neutral and mono anionic) were detected in moderately polar solvents such as acetone and acetonitrile. In strongly polar solvent like water and DMSO, no neutral **TCNHQ** was observed. Only the dianionic form [**TCNHQ**]²⁻ was present in very dilute solutions in DMSO and water. Ethers are the only solvents that contain just the neutral **TCNHQ** in the ground state. **TCNHQ** behaves like such strong acid in the excited state that it donates the proton as is seen in the fluorescence spectra of **TCNHQ** in ethers. Investigations performed in the binary mixture have further strengthened the idea about the existence of three different species of **TCNHQ** in various solvents. The increasing share of the water content in the binary mixture led to the formation of mono-anion and/or di-anion of **TCNHQ** by giving an opportunity to donate the proton(s) to water molecules.

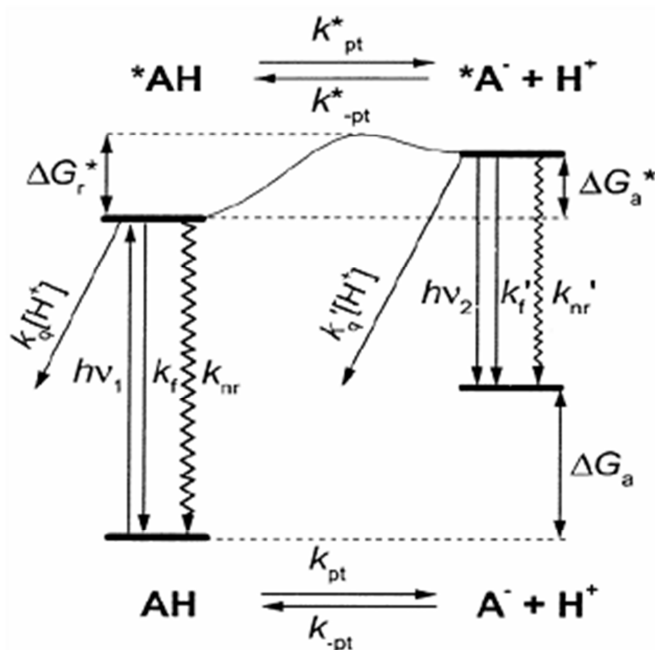
Fluorescence emission spectra in various solvents suggested an ultrafast excited state proton transfer to solvents. Present findings about absorption and fluorescence emission **TCNHQ** will provide a strong base for the investigation of proton transfer kinetics in various solvents.

Future Interests

We have explored only the steady-state absorption and steady-state emission properties of different forms of **TCNHQ** and found very interesting absorption and fluorescence emission properties for **TCNHQ** in aqueous and non-aqueous media. These properties suggest an ultrafast proton transfer in the excited state. In order to have the insight of this proton transfer mechanism, the kinetics of the de-excitation (radiative and non-radiative) of various protonated and deprotonated forms the **TCNHQ** have to be investigated thoroughly.

Therefore, the time-resolved fluorescence emission properties including the ultrafast proton transfer kinetic studies in an excited state through Time Correlated Single Photon Counting (TCSPC) are very important. The ultrafast excited-state proton transfer kinetics of **TCNHQ** will also depend upon the medium used. The effect of a medium on excited state proton transfer will also be studied by using solvents as well as binary mixtures of varying acidity, basicity, and polarity.

Possible quenching phenomenon studies of **TCNHQ** and its deprotonated forms by proton-accepting solvents (or external quencher) have yet not been explored. The following scheme shows the various decays and proton transfer process in ground and excited state protolytic equilibrium:



Scheme 1:

Protolytic equilibrium in the ground and excited state

In order to understand the ground and excited state proton transfer equilibrium, it is important to determine the kinetic and thermodynamic parameters of the various processes by using a combination of steady-state and time-resolved spectroscopic techniques.

Moreover, we have the intention to continue on the research of synthesis of **TCTA** in order to get it in pure form and investigate its photoinduced electron-transfer reactions. The photoinduced electron-transfer reactions will also be studied for imidazol derivatives, for which it was not done during the project solution because of lack of time.