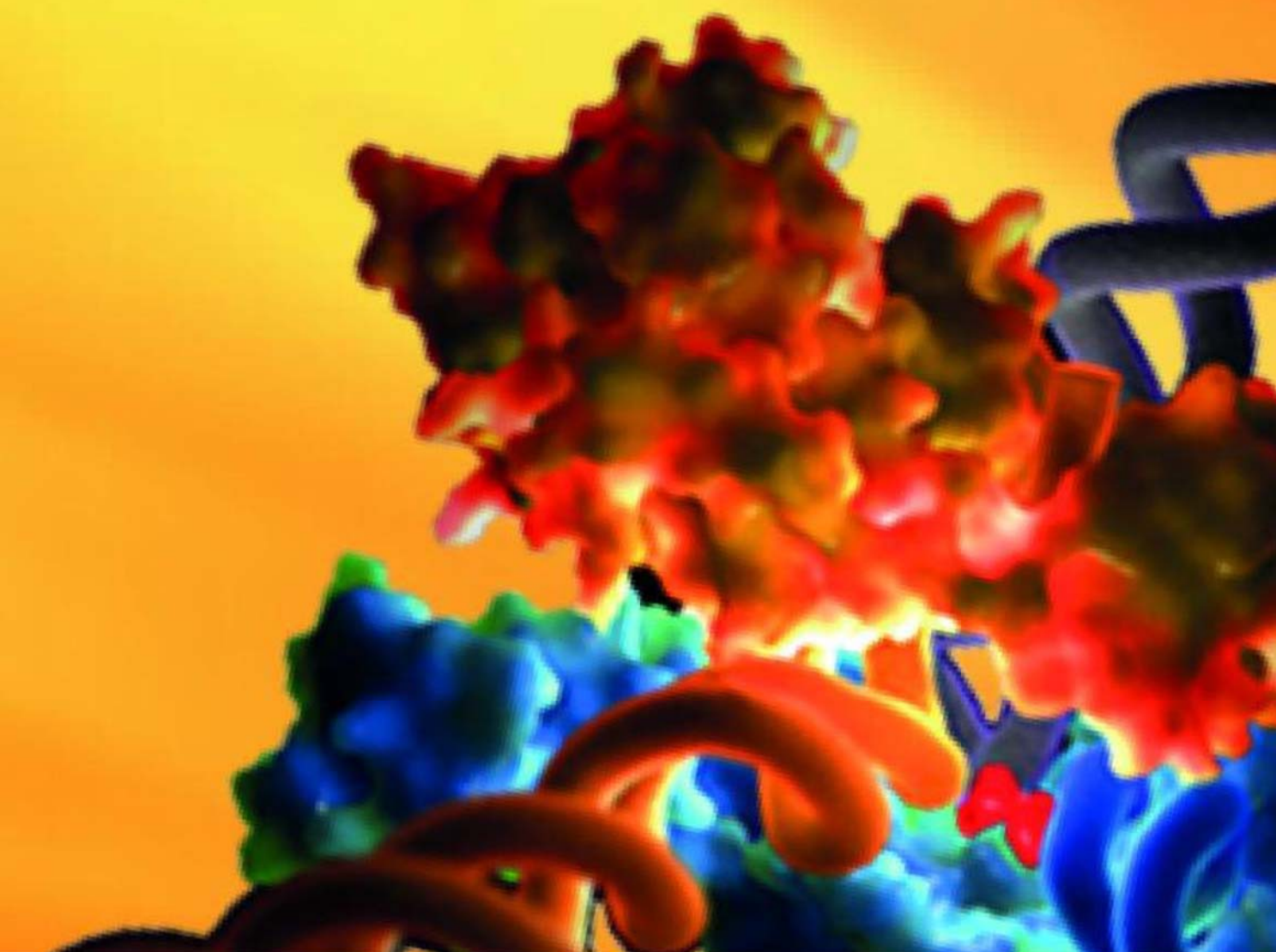


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BOOK OF ABSTRACTS

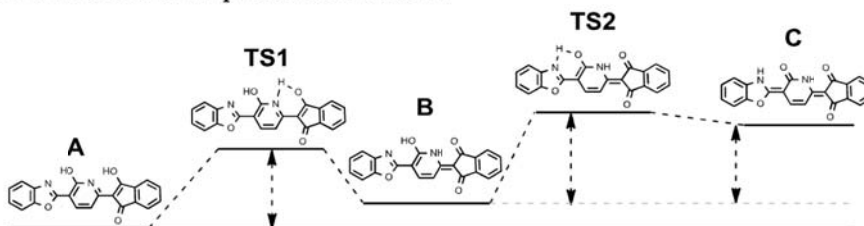
MOLECULAR WIRES BASED ON PROTON-COUPLED ELECTRON TRANSFER

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The assumption of Aviram and Ratner [1] that a single molecule could perform as a current rectifier may be regarded as the beginning of molecular electronics. The main requirement in the design of molecular wires is to provide high conductivity and fast electron transfer between donor-acceptor molecular units. In order to fulfill these conditions the structural characteristics of the wire should exhibit strong electronic coupling between donor and acceptor units. In contrast to currently known molecular wires in which high conductivity is basically due to extended π -electronic conjugation of bridge units that promotes strong coupling between donor-acceptor pairs, we suggest a new molecular wire based on a different concept of achievement of the above mentioned characteristics. They can be attained by tautomeric conversion accomplished by a fast proton transfer reaction between keto and enol tautomeric forms, each of them with distinct molecular properties. An important feature in this reaction mechanism is the coupling between the proton motion and the electron density redistribution known as Proton Coupled Electron Transfer (PCET). The conceptual idea of wire based on this transfer is presented below:



The proposed structure is designed in such a way that the electron transfer is accompanied by the cooperative proton motion. This proton transfer may produce a reversible color or/and dipole moment change.

Theoretical investigation of the proposed molecular wire was carried out at the MP2/6-31G** level by considering the influence of the external electric field. It demonstrates that many molecular features are sensitive to the electric field applied.

References:

1. A. Aviram, M.A. Ratner, (1974) Chem. Phys. Lett., 29: 277-283

TAUTOMERIC EQUILIBRIA OF 5-FLUOROURACIL (5FU) IN WATER. 5FU-LOADED NANOPARTICLES.

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It has long been postulated that rare tautomeric or ionized forms of nucleic acid bases may play a role in mispair formation. Therefore *ab initio* quantum chemical investigations on the tautomeric equilibrium in 5-fluorouracil (**5FU**) and its anions (deprotonated from **N1**, **AN1**, and from **N3**, **AN3**) and their tautomeric forms in water were performed. The effect of the water as solvent was introduced using solute-solvent clusters (4 water molecules). The influence of the water molecules on the tautomeric reactions between different forms was considered by multiple proton transfer mechanism. In water solution 5-fluorouracil exists mainly in 2,4-dioxo form (A). We propose that the populations of the 2-hydroxy-4-oxo (B) and 4-hydroxy-2-oxo (D) tautomers are 4.2×10^{-4} % and 3.1×10^{-4} %, respectively. The fluorescence spectrum of 5-fluorouracil in water confirms the presence of the hydroxy tautomer. All calculations of the solute-water complexes were carried out at an MP2 level of theory and supplemented with correction for higher order correlation terms at CCSD(T) level, using the 6-31+G(d,p) basis set. The *ab initio* calculated frequencies and Raman intensities of **5FU** and its anions **AN1**, **AN3** and dianion are in good agreement with the experimental Raman frequencies in aqueous solution at different pH. In order to establish the pH induced structural transformation in the molecule of **5FU**, further ¹H, ¹⁹F and ¹³C NMR spectra in water solution for pH = 6.9-13.8 were acquired and the chemical shift alterations were determined as a function of pH. On the basis of NMR spectroscopic data obtained for **5FU** in aqueous solution at alkaline pH, we suggest the existence of a mixture of the anionic tautomeric forms predicted by our theoretical calculations.

The presence of 5FU (as saline solution, pH 10–11) in the polymerization medium affected the polymerization as well as the nanoparticle formation by influencing the initiation of the polymerization reaction. 5FU acted as an initiator in the anionic polymerization of *n*-butylcyanoacrylate monomer through its nucleophilic nitrogen centers.

Acknowledgements

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MICROSTRUCTURE OF DAUNORUBICIN-LOADED POLY(BUTYL- α -CYANOACRYLATE) NANOPARTICLES

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The design, preparation and characterization of poly(butyl- α -cyanoacrylate) nanoparticles as a drug-delivery system for daunorubicin is reported. ¹H nuclear magnetic resonance (¹H NMR) and quantum chemical techniques have been employed for the physicochemical characterization of drug-loaded nanoparticles. Nuclear magnetic resonance (NMR) and quantum chemical calculations were applied for structural characterization and determination of the preferred stereochemical sequence distribution of the monomer units in the homopolymer chains of poly(butyl- α -cyanoacrylate) nanoparticles as well as daunorubicin-loaded poly(butyl- α -cyanoacrylate) nanoparticles. The stereochemical sequence distribution of the monomer units was defined by analysis of their high-resolution 1D ¹H and ¹³C NMR and 2D J-resolved, ¹H/¹³C HSQC and ¹H/¹³C HMBC NMR spectra. The results were verified by employment of B3LYP/6-31G(d) calculations and are consistent with the preferred tendency of polymer chains of poly(butyl- α -cyanoacrylate) nanoparticles to adopt syndiotactic placements.

Acknowledgements

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