

Effect of potassium ion on switching of photoinduced electron transfer in inclusion dyads formed by crown ether-porphyrins and an ammonium cation-fullerene[†]

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Abstract : Reversible switching of electron transfer paths in supramolecular donor-acceptor dyads formed by complexing benzo-18-crown-6 appended porphyrins and fulleropyrrolidine appended with an alkyl ammonium ion is demonstrated. The intra-supramolecular to intermolecular switching is achieved by the addition of K⁺ which dissociates the crown ether-alkyl ammonium complex, while intermolecular to intra-supramolecular switching was achieved by the addition of 18-crown-6 to extract the potassium ions of the porphyrin-crown entity. The employed porphyrin-fullerene donor-acceptor pairs were proved to be especially suitable for the generation of relatively long-lived charge-separated states which allows easy observation of switching and monitoring of such processes. In the absence of K⁺, the charge-separation takes place within the inclusion complex via the excited singlet state, generating the radical ion pair with the lifetime of 20–60 ns. On addition of K⁺, the inclusion complexes between the porphyrins and C₆₀ moieties are dissociated, favoring intermolecular electron transfer via the excited triplet state. Further addition of benzo-18-crown-6 to the solution extracts the K⁺ from the crown-ether appended porphyrin and regenerates the inclusion complex with the functionalized fullerene capable of undergoing intra-complex charge separation. The observed phenomena afford concerted metal ion sensing with photoinduced electron transfer in inclusion complexes.

Keywords : Sensor, porphyrin, fullerene, photoinduced electron transfer, laser flash photolysis.

Optical properties of sonochemically synthesized dysprosium doped CdO nanoparticles[†]

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Abstract : The undoped and dysprosium-doped CdO nanoparticles were prepared by sonochemical method in aqueous media and characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Vis diffuse reflectance spectrum, and photoluminescence spectra. The results of XRD indicated that the obtained CdO : Dy³⁺ nanoparticles were well crystallized with a cubic phase. The TEM image illustrated that the CdO : Dy³⁺ nanoparticles were spherical with an average size around 40 nm. Under irradiation of UV light, the emission spectrum of CdO : Dy³⁺ nanoparticles exhibited along with the host emission, the characteristic line emissions arising from the ⁴F_{9/2} ® ⁶H_J (J = 13/2, 15/2) transitions of the Dy³⁺ ions, with the dominating emission centered at ~580 nm. The optimum doping concentration for CdO : Dy³⁺ nanoparticles was determined to be 3 mol%.

Keywords : CdO, nanoparticle, dysprosium dopant, sonochemical synthesis, photoluminescence studies.

Studies on the dissociation constants and solubility of amino acids in water + urea mixtures at 298 K, interaction of urea with amino acids and the role of urea in the denaturation of proteins in terms of structural aspects of water†

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Abstract : The first and second dissociation constants of amino acids (glycine, L-proline, L-valine, α-alanine, β-alanine, L-asparagine, L-methionine, L-leucine, L-threonine, L-glutamine, L-serine and L-histidine) were determined pH-metrically in water + urea (0–8 M urea) mixtures at 298 K. Solubilities of amino acids in water + urea mixtures and the interaction constants of amino acids with urea were also determined pH-metrically.

The Gibbs energies of transfer DG_t^0 (1) and DG_t^0 (2) for the reactions,



and



were coupled with Gibbs energies of transfer for neutral amino acids [DG_t^0 (RH^\pm)] and H^+ -ions [DG_t^0 (H^+)] (determined previously) to get the Gibbs energies of transfer of RH_2^+ [DG_t^0 (RH_2^+)] and R^- [DG_t^0 (R^-)] from water to water+urea mixtures. DG_t^0 (H^+) were also calculated directly and utilized. DG_t^0 (RH_2^+) and DG_t^0 (R^-) are negative and positive respectively. These give the quantitative measure of ion-solvent interactions of the cations and anions of the amino acids. The interaction constants of amino acids with urea were calculated. The results were discussed in terms of structural changes of water in presence of urea in water + urea mixtures, changed basicities of the solvent mixtures and solute-solvent interactions. However interaction of urea with amino acids appears not to be responsible for the denaturation of proteins but the destruction of the tetrahedral structure of H_2O by urea is responsible for the alteration of protein folding and protein structure leading to denaturation.

Direct mechanism involving microscopic properties suggests that no structure breaking of water by urea but a number of indirect evidences suggest urea to be the structure breaker of water.

Keywords : Amino acids, urea + water mixtures, solubility, dissociation constants, free energy of transfer of single ion values, binding constant, Gibbs energy of H^+ .

NMR advances towards structural characterization of huge protein assemblies†

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Abstract : A majority of cellular functions are mediated through protein-protein interaction/association. However, large assemblies of megadalton size pose a great challenge to

structural investigations either by X-ray crystallography or by NMR; they may, in fact, be termed as 'black holes' so far as NMR measurement is concerned. This is due to the fact that the line widths in the NMR spectra of such huge assemblies are extremely large and often the signals are buried in the noise. In this article, we review some of the recent efforts in overcoming these problems. Firstly, there are efforts to narrow down lines by relaxation optimization, both by appropriate sample preparation and by the design of NMR pulse sequences. These direct methods aim at observing signals directly from the assemblies. Recent efforts in our laboratory have presented an alternate and indirect NMR approach, which derives its success from the NMR methods, developed for studying unfolded, partially folded and properly folded proteins with similar ease. This involves a bottom-up strategy of denaturation-dissociation followed by systematic refolding-association, wherein the observations made on the monomer carry valuable information with regard to the structural detail of the molecules in the assembly. Naturally, this approach is not limited by the size of the assembly. We have used this approach to characterize a megadalton size protein assembly, the largest ever handled by NMR till date.

Keywords : NMR, large assemblies, HNN, spin relaxation, GED.

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Kinetics of the peroxomonosulfate oxidation of sulfur(-II) compounds : thioacetamide, dithiooxamide and thiourea[†]

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Abstract : Kinetics of relatively faster oxidation of thioacetamide (TA), dithiooxamide (DTO) and thiourea (TU) by peroxomonosulfate (PMS) has been studied spectrophotometrically under pseudo order condition by keeping oxidant in excess. Under these conditions, the sulfur(-II) compounds are oxidized to corresponding S-dioxides. The kinetics rate law for the oxidation of TA and TU both is eq. (A) and for the oxidation of DTO is eq. (B).

$$\frac{d[S(-II)]}{dt} = \frac{kK [PMS] [S(-II)]}{1+K [H^+]} \quad (A)$$

$$\frac{d[DTO]}{dt} = k [DMS] [DTO] \quad (B)$$

The values of rate constant, *k*, at 30 °C were 3.4 (DTO), 44 (TA) and 3.4 L mol⁻¹ s⁻¹ (TU) and those of protonation constants, *K*, were 3.2 (TU) and 19 (TA). A comparative rate analysis showed oxidation by PMS to be much faster than with H₂O₂.

Keywords : Peroxomonosulfate, thiourea, thioacetamide, dithiooxamide, oxidation, kinetics.

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Nanometer-nanosecond dynamics in laser-induced expansion/contraction and ablation of polymer films[†]

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Abstract : In this account we have summarized our systematic studies on laser ablation and related phenomena of polymer films by utilizing time-resolved absorption spectroscopy and nanosecond interferometry. Polystyrene, poly(methyl methacrylate), poly(methyl acrylate), azobenzene-substituted urethane-urea copolymer, nitrocellulose, triazene polymer, polyurethane, and polyimide were examined, and their expansion and contraction dynamics were confirmed directly at the laser fluence below the ablation threshold. The molecular species which are formed by intense laser excitation are identified by absorption spectroscopy and correlated to the morphological changes. We proposed the cyclic multiphotonic absorption mechanism and explained well the ablation and related phenomena in terms of photophysics and photochemistry.

Keywords : Polymer film, laser, dynamics, nanosecond.

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Chemistry of lapachol – Syntheses of some new biogenetically related naphthoquinones, naphthoquinone dimers, naphthaquinoxaline and naphtha-azaquinoxaline derivatives from lapachol[†]

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Abstract : The present short review focus on chemical transformations of lapachol to a large number of biogenetically related lapachol congeners, dimers and heterocyclic analogues that have been achieved in our laboratory during more than two decades. Conversion of lapachol to stenocarpoquinone-B, rhinacanthin-A, b-(1-hydroxyisopropanyl)- dihydrofurano-1,2-naphthoquinone, stenocarpoquinone-A, dehydro-a-lapachone and dehydro-b-lapachone by the reaction with *m*-chloroperbenzoic acid; dehydroiso-a-lapachone, dehydroiso-b-lapachone, dehydro-a-lapachone, a-lapachone and b-lapachone by the reaction with aqueous NaNO₂ and glacial AcOH; adenophyllone, quadrilone and dehydro-a-lapachone by the reaction with boiling pyridine; naphthaquinoxaline and naphtha-azaquinoxaline derivatives by the reaction with 1,2-diamines and dialkyltin dilapacholates by the reaction with dialkyltin diisopropoxides have been accomplished. Notably the syntheses of rhinacanthin-A, b-(1-hydroxyisopropanyl)-dihydrofurano-1,2-naphthoquinone, dehydroiso-a-lapachone, dehydroiso-b-lapachone, adenophyllone and quadrilone have been reported for the first time from our group starting from lapachol. The synthesis of novel naphthaquinoxaline and azaquinoxaline derivatives from lapachol has been additional interesting results of this investigation.

Keywords : Lapachol, lapachol congeners, rhinacanthin-A, adenophyllone, quadrilone, naphthaquinoxaline and azaquinoxaline derivatives.

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Design of novel, potent neuraminidase inhibitor for H5N1 avian influenza using molecular docking, multinuclear NMR and DSC methods[†]

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Abstract : To probe more effective inhibitors for neuraminidase subtype N1, four potential inhibitors were synthetically designed by substitution at the C5 position of oseltamivir to provide additional interaction with the 150-cavity, a well-known active site in the neuraminidase subtype N1. Molecular docking with H5N1 and intermolecular interaction with model membrane to predict their drug effectiveness have been carried out. A comparison of four potential inhibitors with oseltamivir indicates that the glyceryl derivative of oseltamivir has the most profound effects on the membrane, compared to the other derivatives. It seems to be the most promising derivative for further pharmacological evaluation as an neuraminidase inhibitor.

Keywords : Neuraminidase, oseltamivir, molecular docking, model membranes, NMR, DSC.

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Modeling and simulation of unstirred dead end ultrafiltration of macromolecules[†]

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Abstract : A mass transfer model based on unsteady state component balance over the concentration boundary layer has been developed in the present study. The model uses semi-infinite consideration in order to solve the governing partial differential equation by Laplace transform that gives an analytical expression for the concentration profile. During the solution procedure, pseudo steady state assumption has been used, as a consequence of which permeate flux and membrane surface concentration have been taken constant over any small time interval. Once the expression for concentration profile is known, a time evolution loop has been developed to simulate the permeate flux, membrane surface concentration and permeate concentration under specified operating conditions of transmembrane pressure drop and bulk concentration. The prediction of the proposed model was found to be in good agreement with experimental results obtained during unstirred dead end ultrafiltration of polyethylene glycol (of average molecular weight 6000) solution using a cellulose acetate membrane of 5000 Da molecular weight cut-off.

Keywords : Ultrafiltration, permeate flux, membrane, simulation.

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Magnetic field effect in homogeneous medium for triplet born radical ions : a way for assessment of inter-radical distance in intermolecular photoinduced electron transfer[†]

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Abstract : Photoinduced electron transfer (PET) reaction involves excitation of either donor or acceptor prior to electron transfer. The PET reaction might occur in the singlet or in the triplet electronic state of the chromophore. These reactions could be influenced by the presence of internal or external magnetic field since radical ions with free electrons are generated as intermediates. Magnetic field effect (MFE) in homogeneous medium could be observed on exciplex luminescence, however the change is very small as the rate of recombination is very high owing to the singlet spin correlation of the geminate radical ion pair (RIP). On the other hand for the triplet born RIPs the detection of MFE needs confinement of the triplet species because at ambient temperature the lifetime of the solvent cages containing spin correlated RIP in homogeneous solvent is 10^{-10} s whereas the rate of intersystem crossing is 10^{-8} s. It is possible to confine the triplet born radicals by using organized assemblies like micelles, reverse micelles, etc., highly viscous solvents at low temperature or long chain biradicals which help to reduce fast escape and thus retain the spin-correlation between the partners of the geminate RIP. MFE is a composite of diffusion dynamics, spin dynamics leading to intersystem crossing and recombination of free ion formation. The effect is optimized only when the inter-radical distance through diffusion becomes sufficient to make exchange interaction between free electrons negligible retaining the original spin-correlation in the solvent cage. In this review we would like to highlight a few systems where MFE for the triplet born radicals could be observed even in homogeneous media due to some specific interactions other than covalent linking, which also helps to assess the inter-radical distance in such intermolecular PET, which is very rare.

Keywords : Magnetic field effect, triplet radical, electron transfer.