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A high sensitive ion pairing probe (the interaction of pyrenetetrasulphonate and methyl viologen): Salt and temperature dependences and applications

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ABSTRACT

The interaction between pyrenetetrasulphonate (PTS) and methyl viologen (MV^{2+}) leads to a 1:1 charge transfer complex (CTC) in the concentration range below mmol L^{-1} of the ligands. Quantum mechanical calculations show the 1:1 complex having the planar moiety of PTS and the charges of the sulfonate groups stabilized by the twisted rings of the positively charged MV^{2+} species. The peculiar nature of PTS includes high fluorescence quantum yield (~1), clear specular UV–vis spectra and fluorescence emission images, as well similar $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions as those of $S_1 \leftarrow S_0$, all of them exhibiting well resolved vibrational structure. MV^{2+} has well known electron-accepting properties that favor the complexation. These features were studied as a function of salt concentration and temperature dependences allowing a detailed comprehension of static and dynamic association processes. Quantum mechanical calculations show the 1:1 stabilization of PTS/MV^{2+}. In addition the effect of urea on the CTC equilibrium is presented, as expected the additive acts towards the non-complexed species (solvated free ions). The fluorescence quenching of MV^{2+} over PTS highlights is one of the applications of this effect for giant vesicles characterization.

1. Introduction

Planar aromatic molecules are known to make π-interactions that can lead to molecular agglomeration as in π-stacking effects and as well in J and H aggregates [1]. Drive force for the stacking is originated from the overlap of carbon π orbitals and partial electron transfer conferring a charge transfer (CT) character to the bond. Aromatic carbon rings as pyrene, perylene and several others are candidates to present these interactions that are strong functions of solvent parameters and how the molecules are solvated [1,2].

Previous studies with a pyrene derivative (8-hydroxy-1,3,6-pyrenetrisulphonate, pyranine) (e-donor) and methyl viologen (MV^{2+}) (e-acceptor) and as well with PTS and butyl viologen showed the CT character of the ion-pairing complex formation from the appearance of new absorption bands [3]. This study also showed the participation of static and dynamic components in the fluorescence quenching of pyranine by MV^{2+} [3]. The partial electron transfer in the CT complex could be further exploited by laser flash photolysis studies where intense and large pulses promote the photoredox process [3,4].

The special spectral features of these ions as their high absorption coefficients and clear separation of the more prominent bands and as well high fluorescence yields of the pyrene derivative prompted us to pursue further with the characterization and applications of these properties.

In this study we selected a "simpler" probe the 1,3,5,8-pyrenetretasulphonate (PTS) for the absence of photoacid effects, to characterize the photophysical effects derived from the stacking

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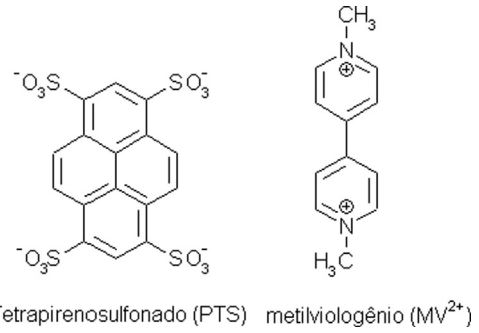

Fig. 1. Chemical structures of(please clarifiy with MC coz check instruction) betetrapyrenesulphonate (PTS) and methyl viologen (MV^{2+}).

(dimer) formation with MV^{2+}. As PTS and MV^{2+} (Fig. 1) are soluble in water and have opposite charges the screening effect of salts is also investigated. From spectrophotometric and fluorimetric determinations, ground and excited states dimer formation is observed. The effect of urea on the ion pairing destabilization is also highlighted [5]. To demonstrate one of the pair formation applications the effect on vesicles characterization is also highlighted.

2. Materials and methods

2.1. Materials

Pyrenetetrasulphonate (Sodium salt, Eastman Kodak) (PTS) was used as received due to the absence of detectable impurities on TLC plates [3]. Methyl viologen (MV^{2+}) (Aldrich) was recrystallized twice from cold acetone/methanol (85/15 v/v). Stock solutions of these compounds were freshly prepared and kept refrigerated in dark. Urea (Carlo Erba) was recrystallized from hot ethanol; 6 mol L^{-1} solutions gave an electrical conductivity of 18 μS showing the lack of ionic contaminants. Electrolyte solutions were prepared from well dried solids from the best analytical available salts. Water was doubly distilled and further purified and deionized with a Mill-Q system.

2.1.1. Quantum mechanical calculations

Molecular dynamics calculations have been performed with the Gaussian 09 package [14]. The molecular geometry optimizations of the PTS, viologen and complex (PTS/MV^{2+}) were performed using the Kohn–Sham density functional theory (DFT) [15] with the Becke three-parameter hybrid exchange–correlation functional known as B3LYP [16,17] along with the basis set 6-31G(d) [18]. Vibrational frequencies were calculated from analytic second derivatives to check the minimum on the potential energy surface. Zero-point vibrational energies were added on the basis of B3LYP frequency calculation (uncalled) using the same basis set as for the geometry optimizations. The polarizable continuum model (PCM) [19] is employed to optimize the structures in a cavity created via a series of overlapping spheres simulating the water solvation. The PCM is based on a description of the solvent as macroscopic continuum medium having suitable properties (dielectric constant, thermal expansion coefficient, *etc.*). In this procedure, the solute is embedded in a cavity in the dielectric medium and the solute–solvent interactions are described in terms of the reaction field due to the presence of the dielectric medium, which acts as perturbation on the Hamiltonian of the solute through its reaction potential [19].

2.2. Giant vesicles preparation

The phospholipid 1,2-dioleoyl-sn-glycero-3-phosphatidylcholine (DOPC, Avanti Polar Lipids) was used without further purification. Sucrose and glucose (SigmaAldrich). GUVs were obswerved in a 100 uL cuvette. Typically, Giant Unilamellar Vesicles (GUVs) were formed in a solution containing 5×10^{-3} mol L^{-1} PTS. For monitoring, an aliquot of 50 μL of the vesicle suspension was mixed with the same volume of a solution containing 5×10^{-3} mol L^{-1} MV^{2+}. MV^{2+} suppresses PTS fluorescence outside vesicles. Once PTS, MV^{2+} and PTS/MV complexes do not permeate through the bilayer permeable observed fluorescence arises from free unquenched PTS [6].

GUVs of DOPC were generated using the electroformation method [7] between two parallels Pt electrodes in a Teflon custom chamber. The chamber consists of a block of Teflon with a slot sufficiently large to submerge the two electrodes in the formation medium with a 1 mm gap in between. Before use, the Teflon chamber and the electrodes are thoroughly cleaned with solvents and copious amounts of deionized water.

Briefly, 5 μL of a 1 mg mL^{-1} lipid chloroform solution was spread in the electrodes. The lipid film in the electrodes is left to dry in a vacuum chamber for 2 h to remove all traces of the organic solvent. The chamber was filled with 0.1 mol L^{-1} sucrose solution having PTS 5×10^{-3} mol L^{-1}. The electrodes were connected to a sinusoidal function generator and an AC current of 3 V with a 10 Hz frequency was applied for 2 h. The vesicle suspension was transferred to an Eppendorf tube.

GUVs were observed in a 100 μL fluorescence cuvette, extensively washed before experiments. Typically, 50 μL of vesicle suspension was mixed with an equal volume of 0.1 mol L^{-1} glucose solution creating a sugar asymmetry between GUVs interior and exterior. Density gradient causes vesicles to sediment in the observing chamber for easy observation, while refraction

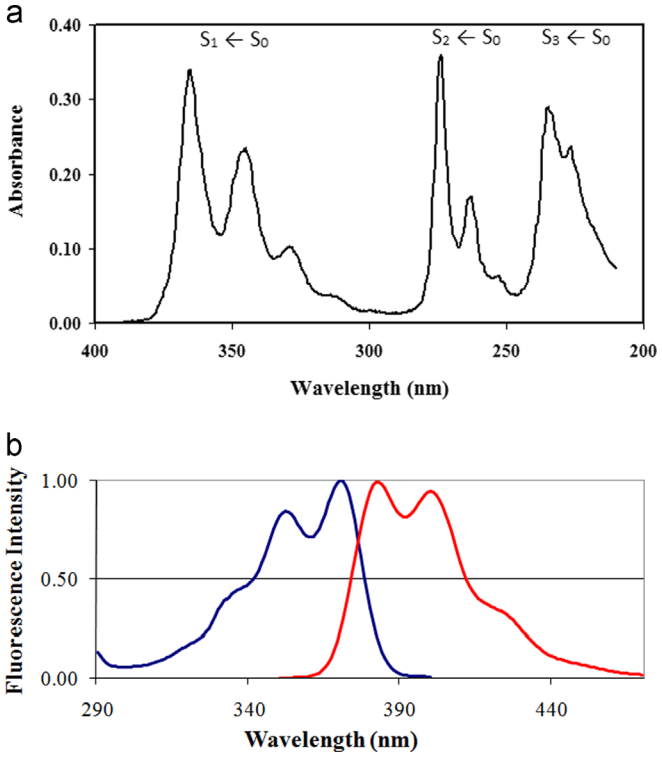

Fig. 2. (a) UV–vis spectrum of [PTS] = 1×10^{-5} mol L^{-1} in H_2O. (b) Normalized uncorrected fluorescence spectra of [PTS] = 1×10^{-5} mol L^{-1} in H_2O, excitation spectra (λ_{em} = 430 nm), and emission spectra (λ_{ex} = 365 nm) (excitation and emission slits = 10 mm, T = 25 °C).