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An experimental and TD-DFT theoretical study on the photophysical properties of Methylene Violet *Bernthsen*

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ABSTRACT

We revisited the photophysics the Methylene Violet (MV) Bernthsen dye in aprotic solvents to rationalize both its peculiar solvatochromism, which cannot be explained by the standard solvatochromic empirical models, and the large dependence of its excited states decay kinetics upon changes on the polarity of the medium.

To this end, MV singlet and triplet excited states were characterized by stationary and time-resolved absorption and emission techniques. The experimental information was combined with a detailed theoretical study using TD-DFT to characterize not only the emitting states but also all dark states which would play a role in determining the fate and properties of the experimentally populated excited states. It is concluded that owning to both the high permanent dipole and polarizability of MV, singlet and triplet excited states are stabilized by the medium to a very different extent, leading to an unusual solvatochromism and decay kinetics.

1. Introduction

Methylene Violet *Bernthsen* (MV, Scheme 1) is a (neutral) synthetic dye that belong to the family of the phenothiazines. Several biological and technological applications for this dye have been reported. Among these, MV has been investigated as a potential photosensitizer for "*in situ*" inactivation of viruses, bacteria and parasites in blood [1–3]. The viability of the cells was also investigated using MV stain which apparently is able to penetrate only dead cells [4]. On the other hand, MV has been used for the amperometric detection of hydrogen peroxide and nicotinamide adenine dinucleotide (NAD) [5] and as an effective inhibitor of steel corrosion in acid media [6].

Several years ago, Otsuki et al. [7,8] reported a study on the photophysical properties of MV (and two closely related derivatives) in aprotic solvents and dioxane-water mixtures. According to these studies, the photophysics of MV is certainly unusual. For instance, a typical Lippert–Mataga plot constructed from the experimental Stokes shifts ($\Delta\nu$) measured in aprotic of low and medium polarity solvents shows a negative slope. Clearly, this behavior cannot be explained in the framework of the current solvatochromic theories. In analogy with the ICT-TICT model [9], Otsuki and col. proposed that MV may exist in (both) the ground and singlet excited states as two conformers, which can rapidly isomerize by means of the rotation of the amine-aromatic ring bond. The fluorescence of the dye arising from two different excited state species (whose predominance could depend on the solvent polarity) may explain the observed anomalies. Recently, Ronzani et al. [10] revised some aspects of MV's photophysics. However, these studies did not provide additional experimental evidence that could be use to confirm Otsuki's hypothesis.

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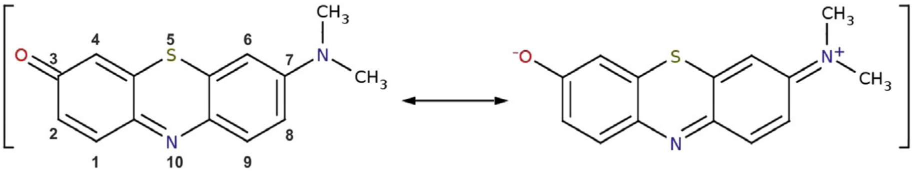

Scheme 1. Methylene Violet (*Bernthsen*) or 3H-phenothiazin-3-one, 7-dimethylamin (MV).

The main aim of this study is to rationalize the sharp dependence of MV photophysics on the nature of the media and to explain its apparent solvatochromic anomalies. Thus, MV singlet and triplet excited states were experimental and theoretically characterized in a series of aprotic solvents covering a broad range of polarities. A simple analysis of the molecular structure of MV shows that it has an electron donor (amino) group coupled to an electron acceptor (carbonyl) group through a conjugated π system. This structure is typical of push–pull chromophores. Although push–pull chromophore have attracted the attention of many researchers because their interesting nonlinear optical properties [11], only few experimental and theoretical studies aimed to achieve a better understanding of the photophysics of this kind of compounds have been reported [12,13].

2. Experimental

2.1. Materials

Methylene violet (Bernthsen) was purchased from Aldrich. The dye content of commercial sample is ~80%, the $-NH_2$ and $-NH(CH_3)$ derivatives being the major impurities [14]. Purification of dye was achieved by flash chromatography on silica (230–400 mesh) using methanol/chloroform 10% v/v as eluent. The purity obtained was >99.9% according HPLC analysis.

All the solvents employed were HPLC grade. The absence of spurious solvent emission was used as purity criterion.

2.2. Methods

UV/Vis absorption spectra were obtained using a Shimadzu UV-2401 spectrophotometer. Steady-state fluorescence measurements were performed on a Fluoromax Spex spectrofluorometer. Freshly prepared MV solutions were used for each measurement and the concentration of the dye adjusted to an absorbance <0.1 to avoid distortion of the spectra due to reabsorption of the emission light. No changes in the absorption or emission spectra and fluorescence lifetimes were observed in the concentration range of 1×10^{-7}–3×10^{-5} M, confirming that the dye does not aggregate at the concentrations used.

Fluorescence quantum yields were determined by integration of the (corrected) emission spectrum using cresyl violet in methanol as fluorescence standard. The reported emission quantum yield of cresyl violet in methanol is 0.54 ± 0.03 [15].

Fluorescence-lifetime measurements were performed with an Edinburgh Instruments OB 900 time-correlated single-photon counting fluorometer. The excitation of the samples was carried-out with a PicoQuant PLS600 diode with emission centered at ~600 nm. The emission wavelengths were selected near maximums of fluorescence bands in each particular solvent. In all cases, the fluorescence lifetimes could be fitted to monoexponential decays, optimizing χ^2, residuals and standard deviation parameters. The lifetimes were independent of the emission and excitation wavelengths.

Transient absorption measurements were carried-out using a laser-flash photolysis equipment. A Spectron SL400 Nd:YAG laser generating 532 nm laser pulses (~18 ns pulse width) was used for sample excitation. The laser beam was defocused in order to cover all the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The detection system comprises a PTI monochromator coupled to a Hamamatsu R666 PM tube. The signals were captured by an HP54504 digitizing oscilloscope, averaged and finally transferred to a computer for storage and analysis. Measurements were performed in samples deoxygenated by continuous argon bubbling at (25 ± 0.5) °C.

Values of relative permittivities (ε_r), refraction index (n_D), and empirical parameter $E_T(30)$ of pure solvents were obtained from literature [16–18].

2.3. Quantum mechanics calculations

For the Quantum Mechanics calculations, a series of functionals and methodologies were tried for modeling the effect of the solvent. Most calculations were done using the hybrid gradient generalized functionals PBE0 [19], B3LYP [20,21] and its correction proposed by Yanai et al. for accounting the true asymptotic behavior at long interelectronic distances, the CAM-B3LYP [22]. The vertical excitations were computed using the TD-DFT implementation of Gaussian 09 [23]. The state-specific (SS) and linear response (LR) version of the IEFPCM continuum solvation model [24–27] as implemented in Gaussian 09 were applied for modeling heptane, benzene, acetyl acetate and acetonitrile. In all cases the combination of the LR-IEFPCM at the B3LYP/6-311 + G(d,p) level yielded the closer results compared with the experiments and details concerning the other functionals are available as Electronic Supporting Information (ESI). Electrostatic potential and its derived charges as well as the permanent and transition dipole moments computed with CAM-B3LYP and the usual uncorrected form of the functional were practically indistinguishable even though we [28] and other authors [29,30] have observed discrepancies in the charge distribution for systems with much important charge separation and bigger delocalized systems.

The conformational search and optimization of the minima on both the surface of the ground singlet, first triplet and singlet excited states were done the standard procedure by characterizing the stationary points using the diagonalization of the Hessian matrix and harmonic frequencies analysis. The linear response implementation of the IEFPCM was used for all excited states geometry optimizations. The permanent dipoles, electrostatic potentials, total electron density and spin distribution of the electronic states were done and plotted using the LR generalized CI density matrix using Molden [31] and VMD 1.8.9 [32] graphical packages.

3. Results and discussion

3.1. Ground and singlet excited states properties

The absorption and (corrected) emission spectra of the MV were acquired in a series of aprotic solvents covering a wide range of solvent polarities (Table 1). The absorption and emission spectra of