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SPECTRAL ANALYSIS OF N-METHYL 6-HYDROXY QUINOLINIUM AND THEIR SALTS

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INTRODUCTION

M6HQ is a type of super photo acid because its acidity in the excited state is significantly higher than in the ground state. All of the **M6HQ** derivatives synthesized show spectroscopically sufficient solubility in the shorter-chain alcohols, water, DMSO and acetonitrile. None of these salts are soluble in non-polar solvents which are immiscible with water, except for the few which were soluble in long-chain alcohols. Further details can be seen several salts of the N-methyl-6-hydroxyquinolinium cation **(M6HQ)** were investigated via spectroscopic and chemical means. The goals of these experiments were twofold: to create a compound exhibiting a large pK_a drop upon photoexcitation (ideally greater than 10 units), and to investigate the interplay between the cation and its conjugate base in the excited state

KEY WORD: M6HQ N-Methyl 6-Hydroxy Quinolinium

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UV-Visible Spectroscopy

Ultraviolet and visible spectra were acquired with a spectrometer equipped with UVW in Lab acquisition software. All samples were prepared in the highest quality spectral-grade solvents. Solvents were examined prior to use, and were found to have no fluorescent contaminants and a low water concentration.

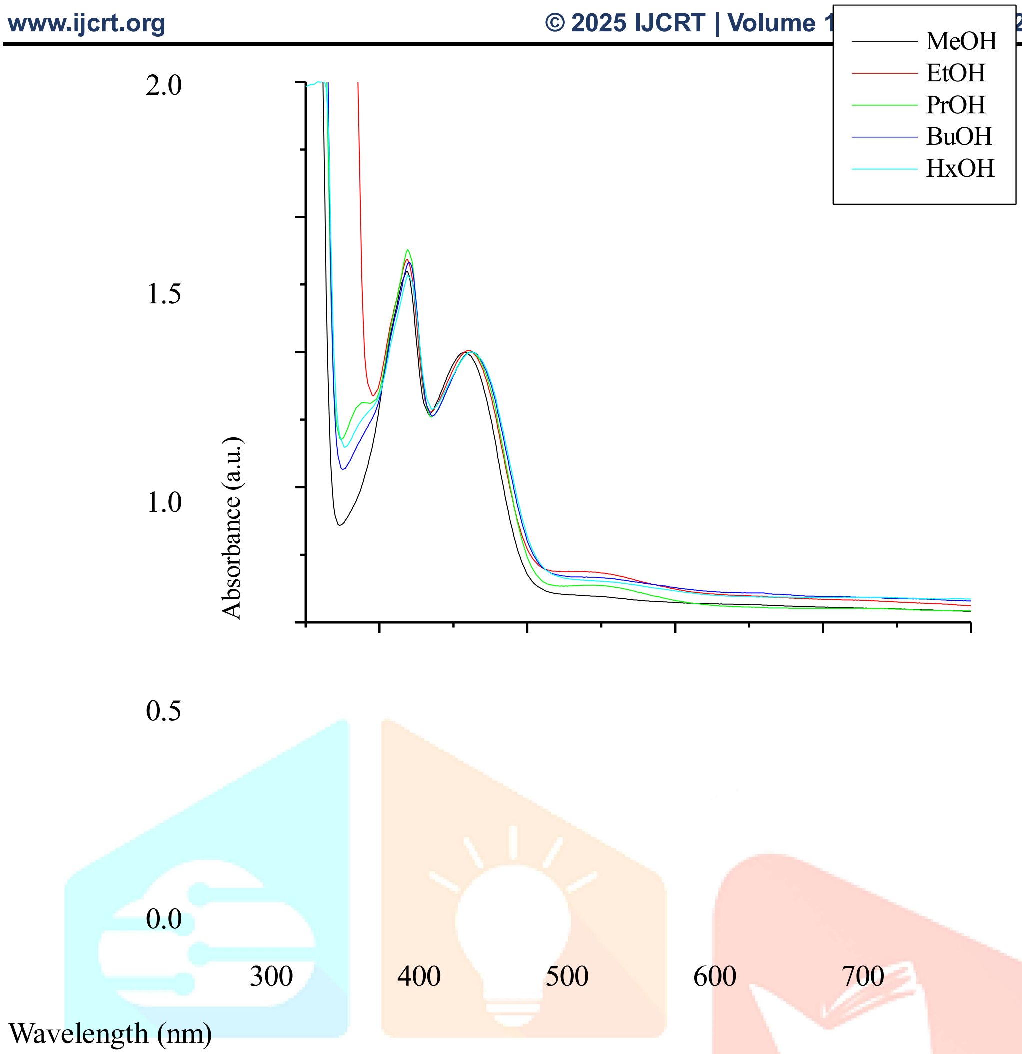


Figure 1.1 Absorbance Spectra have been normalized at the lowest energy absorbance (358-364 nm)

Table 1.1 Solvatochromism of **M6HQ** (all salts) in alcohols C_1-C_6.

Solvatochromism

Solvent	λ_{max} (nm)
Methanol	358
Ethanol	362
Propanol	362
Butanol	364
Pentanol	364
Hexanol	364

Representative ultraviolet-visible absorbance measurements are shown in **Figure 1.1**. Although ground-state deprotonation should not occur in alcoholic solvents due to **M6HQ**'s ground state pK_a below that of the alcohols tested, a small amount is seen regardless.

Ground-state deprotonation is evidenced by a broad absorption centered near 420 nm, and a narrow feature at approximately 275 nm. In all cases and in all future fluorescence studies examining the effects of proton transfer, the ground-state deprotonation was considered, and never exceeded 1%. Ground state deprotonation in alcohols seems to be correlated with the concentration of the sample.

SPECTROSCOPY OF M6HQ DERIVATIVES

Fluorescence spectroscopy has historically been the principal method in the study of ESPT, so it is a logical starting point for the photophysical investigations of fluorescent photoacids. Initial investigations into the photochemistry of **M6HQ** were undertaken in alcohols for several reasons. Despite acting having a comparable nucleophilicity to water, alcohols are less capable of accepting protons resulting from ESPT. This partially due to the larger steric bulk of the alcohols compared to water; the bulkier alkyl chains slow proton transfer times due to increased solvent reorganization times while the photoacid is undergoing a light-induced geometric change. Thus, proton transfer can be observed on the picosecond, rather than the femtosecond timescale. This was necessary due to equipment limitations. All of the **M6HQ** derivatives synthesized show spectroscopically sufficient solubility in the shorter-chain alcohols, water, DMF, DMSO and acetonitrile. None of these salts are soluble in non-polar solvents which are immiscible with water, except for the few which were soluble in long-chain alcohol sited state!

FLUORESCENCE EXPERIMENT

First, three salts of the **M6HQ** class with immensely different fluorescence spectra were examined via spectroscopic means; nonaflate, tetrafluoroborate and hexafluoroantimonate were examined due to their differences in steady-state fluorescence and time-resolved decays. Dilution studies were examined at four different concentrations in methanol and at one concentration in DMSO. In DMSO, all **M6HQ** salts share similar steady-state fluorescence spectra, suggesting excellent excited-state . However, the fluorescence spectra in methanol show a large discrepancy. Both solvents are capable of receiving a proton, but the proton transfer is inefficient for methanol, depending on the counterion.

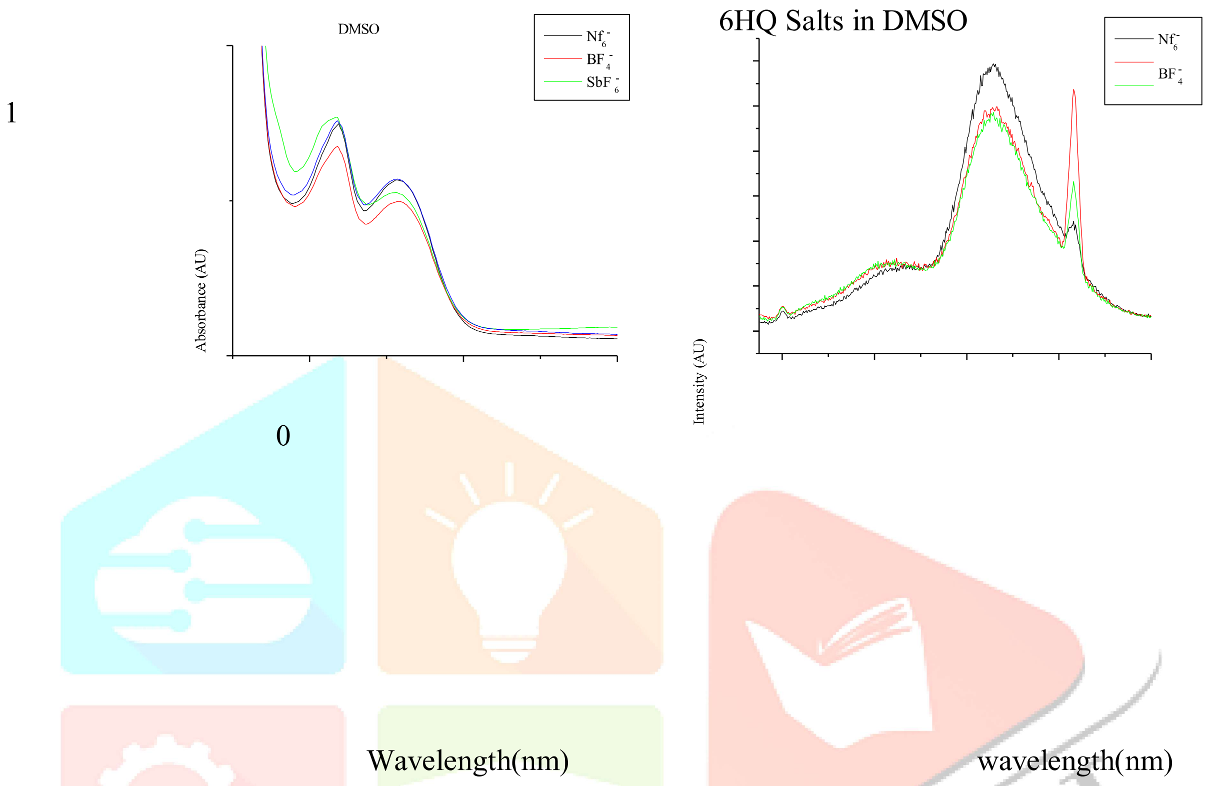
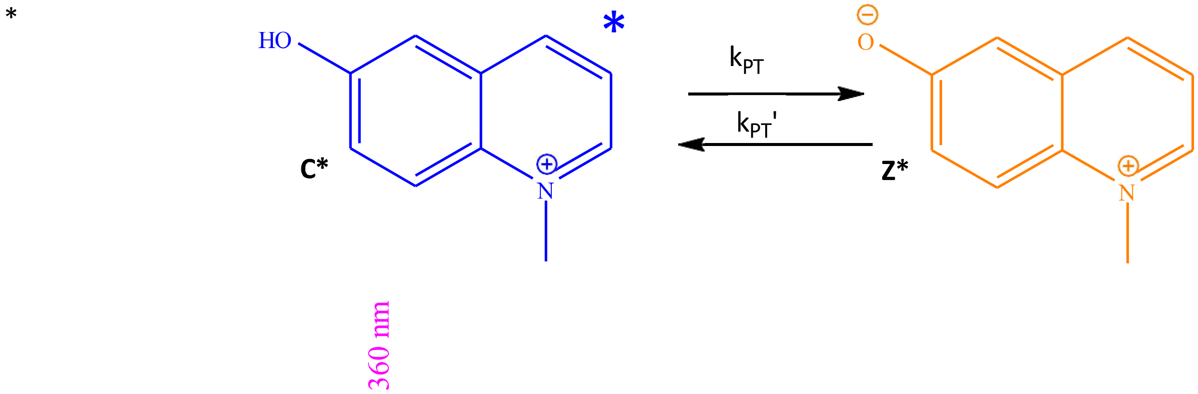


Figure 1.2 Absorbance and fluorescence of samples in DMSO



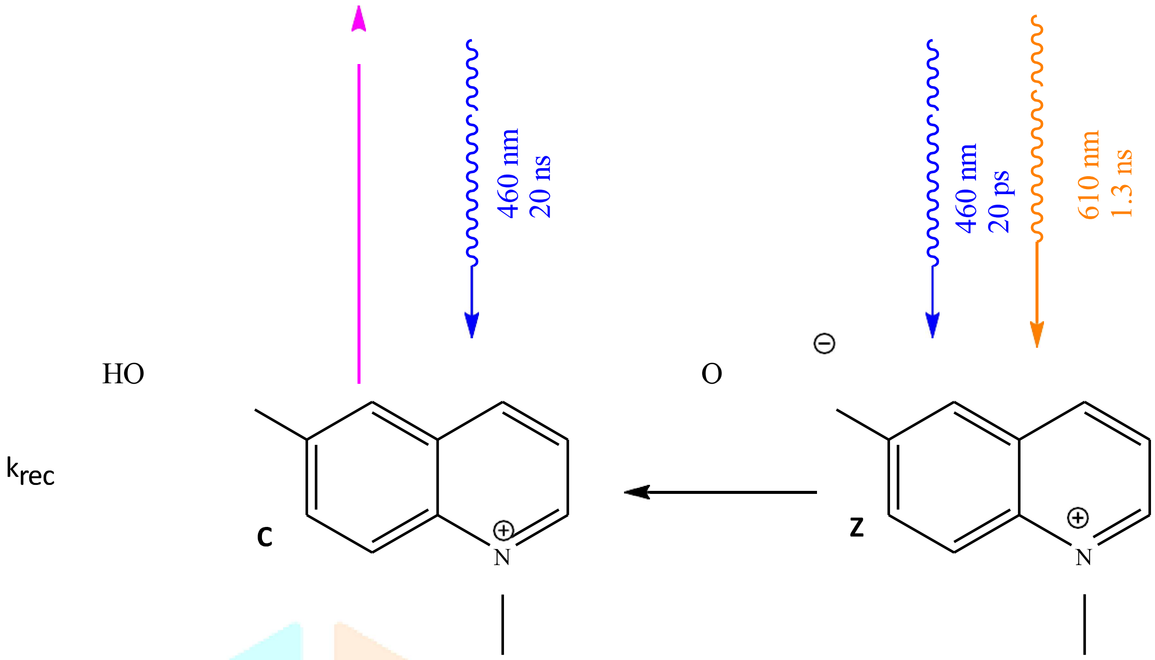


Figure 1.3 proton transfer and recombination and fluorescence decay process for **M6HQ**.

***N*-Methyl 6-Hydroxyquinolinium Tetrafluoroborate (M6HQ-BF4).** *N*-Methyl-6- hydroxyquinolinium iodide (0.235 g, 0.819 mmol) was dissolved in water (15 mL).

Silver tetrafluoroborate (0.197 g, 1.01 mmol) was likewise dissolved in water (15 mL). After addition of the two solutions, silver iodide precipitated immediately, and the solution was stirred for ten minutes. The resulting solid was filtered and discarded. The

mother liquor was concentrated by rotary evaporation and dissolved in 15 mL EtOH. After a hot-filtration with 15 mg activated charcoal, the product was precipitated with Diethyl ether, filtered, and recrystallized from an ethnol-ether mixture. After drying at 110 °C in vacuo over P_2O_5, the desired product (0.154 g, 0.622 mmol, 75.9% yield) was recovered as white needles, mp 151-152°C. ^{1}H NMR (300 MHz, Acetone) δ 10.09 (s, 1H), 9.34 (d, J = 5.0, 1H), 9.10 (d, J = 8.5, 1H), 8.54 (d, J = 9.5, 1H), 8.11 (dd, J = 5.7, 8.5, 1H), 7.92

(dd, J = 2.8, 9.6, 1H), 7.75 (d, J = 2.7, 1H), 4.84 (s, 3H). EIMS, m/z 160.1 (M^+, 24%), 145.1 (100%), 89.1, 63.1; MS (EI, m/z), calcd. for $C_{10}H_{10}NO$: 160.076. Found: 160.1.

***N*-Methyl-6-Hydroxyquinolinium Hexafluoroantimonate (M6HQ-SbF6).** *N*-methyl- 6-hydroxyquinolinium iodide (0.123 g, 0.429 mmol) was dissolved in water (15 mL).

Silver hexafluoroantimonate (0.223 g, 0.651 mmol) was likewise dissolved in water (15 mL). After addition of the two solutions, silver iodide precipitated immediately, and the solution was stirred for ten minutes. The resulting solid was filtered and discarded. The mother liquor was rotovapped and dissolved in 15mL EtOH. After a hot-filtration with 10mg activated charcoal, the product was precipitated with Diethyl ether, filtered, and recrystallized from an ethnol-ether mixture. After drying at 110 ºC in vacuo over P_2O_5, the desired product (0.135 g, 0.342 mmol, 79.7% yield) was recovered as a tan-white powder, mp 195-197 ºC. ^{1}H NMR (300 MHz, Acetone) δ 10.09 (s, 1H), 9.34 (d, J = 5.0, 1H), 9.10 (d, J = 8.5, 1H), 8.54 (d, J = 9.5, 1H), 8.11 (dd, J = 5.7, 8.5, 1H), 7.92 (dd, J = 2.8, 9.6, 1H), 7.75 (d, J = 2.7, 1H), 4.84 (s, 3H). EIMS, m/z 160.1 (M^+, 24%), 145.1 (100%), 89.1, 63.1; MS (EI, m/z), calcd. for $C_{10}H_{10}NO$: 160.076. Found: 160.

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Results and discussion

As discussed previously, the M6HQ emission in pure alcohols, including MeOH, exhibits dual emission: the band at 460 nm and the red-shifted band at 610 nm. Two fluorescence bands, indicating that the ESPT reaction occurs under these conditions. The C* maximum is at 445 nm which shifts to longer wavelengths with increasing temperature, while the Z* maximum shows no shift with temperature. The overall emission in the system decreases with increasing temperature. In DMSO, all **M6HQ** salts share similar steady-state fluorescence spectra, suggesting excellent excited-state . However, the fluorescence spectra in methanol show a large discrepancy.

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