

Structure-Fluorescence Relationships in Antimicrobial Fluoroquinolones (AMFQs)

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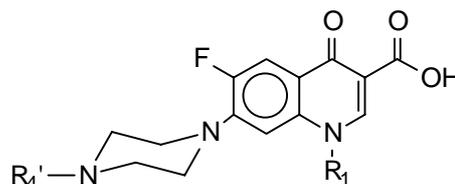
Abstract: The analysis of fluorescence spectra of a set of structurally related AMFQ let to identify the effects of structural changes and the presence of electric charge generated by acid-base reaction on the emission spectra.

Introduction

The fluorescence produced by quinolone ring has been extensively used in analytical determination of AMFQs in biological fluids and bacterial uptake studies.

It is well known the effect of polarity and pH on both intensity and wavelength of the emission of some AMFQs like norfloxacin (**I**) and ciprofloxacin (**II**). Variation of the emission of **I** and **II** as a consequence of pH changes is related to the variation in the proportions of the species (+0), (00), (+-), and (0-).

Compound	R ₁	R' ₄
I	-C ₂ H ₅	H
II	c-C ₃ H ₅	H
III	-C ₂ H ₅	-I(CH ₃) ₂
IV	-C ₂ H ₅	-CO-CH ₃
V	-C ₂ H ₅	SO ₂ -C ₆ H ₄ -NH ₂
VI	-C ₂ H ₅	SO ₂ -C ₆ H ₄ -NH-CH ₃
VII	-C ₂ H ₅	SO ₂ -C ₆ H ₄ -N-(CH ₃) ₂
VIII	c-C ₃ H ₅	SO ₂ -C ₆ H ₄ -NH ₂
IX	c-C ₃ H ₅	SO ₂ -C ₆ H ₄ -NH-CH ₃
X	-C ₂ H ₅	SO ₂ -C ₆ H ₄ -CH ₃
XI	c-C ₃ H ₅	SO ₂ -C ₆ H ₄ -CH ₃



In order to identify the main factors that affect light emission in aqueous solution, a set of 11 structurally related compounds was used (table I). Compounds **V-XI** are new active AMFQs synthesized in our laboratory.

Emission spectra were recorded at two pHs (4.8 and 8) which were selected taken into account the pKa of the ionizables groups.

Results and Discussions

The analysis of such results let to relate the emission parameters with both presence and type of electric charge in the molecules.

Com- pound	Excitation	Emission				U.V. Absortion Coefficients
	λ_{\max} (pH= 4,8 - 8)	Intensity (pH = 4,8)	λ_{\max} (pH = 4,8)	Intensity (pH = 8,0)	λ_{\max} (pH = 8,0)	ξ ($L \cdot mol^{-1} \cdot cm^{-1}$)
I	272 nm	5040	444 nm	2402	415 nm	32400
II	270 nm	5885	447 nm	3074	417 nm	28800
III	278 nm	6968	440 nm	2634	409 nm	33846
IV	272 nm	600.0	443 nm	3085	435 nm	35733
V	272 nm	540.3	445 nm	2178	427 nm	54900
VI	274 nm	664.0	440 nm	833.5	424 nm	53430
VII	272 nm	589.7	443 nm	625.2	420 nm	49252
VIII	272 nm	659.8	442 nm	1788	431 nm	41000
IX	270 nm	874.9	444 nm	763.8	426 nm	48700
X	274 nm	-----	-----	3388	428 nm	33900
XI	276 nm	-----	-----	3950	431 nm	42200

Emission at pH 4.8. In this condition ${}^+HBH$ is the prevalent species of **I** and **II**, their spectra exhibit a higher intensity and a emission λ_{\max} shifted to the red with respect to that recorded at pH 8. A similar behavior is observed with **III**, in which the prevalent species is ${}^+BH$ and exhibits the highest intensity registered. On the other hand, compounds **IV-IX** exhibit emission λ_{\max} which are not significantly different from those of their zwitterionic analogs **I-III**, however, their quantum yields are 8 to 10 times lower.

Emission at pH 8. The ionization of 3-COOH yields zwitterionic and/or anionic species. Thus, at pH 8 the proportion of prevalent species of **I** or **II** are in the order ${}^+HB^- > B^- \geq BH^{00}$; the resulting λ_{em} are shifted 30 nm to the blue and quantic yields lowered with respect to pH 4.8. A similar change oc-

curs with **III** also, which is essentially as ${}^+B^-$ in this condition and it λ_{em} is 409 nm.

Compounds **IV-XI** are essentially as B^- , their λ_{em} lie in the range 420-435 nm, that is, at higher wavelengths than **I-III**. Therefore, it seems that the emission of fluorescence of zwitterionic species ${}^+HB^-$ and ${}^+B^-$ occurs at lower wavelengths than that of anionic species B^- .

In summary: a) cationic species ${}^+HBH$ exhibit the higher fluorescence intensity; b) the emission of zwitterionic species ${}^+HB^-$ and ${}^+B^-$ is about a half of that of the formers; c) the emission of anionic species B^- is highly variable, ranging from ones even higher than that of zwitterions to others sensible lower; d) neutral species BH exhibit the lower emission.

References and Notes

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