Spectroscopic properties and immobilization of fluorescent amino substituted benzimidazo[1,2-*a*]quinolines

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Recently, one of the extensively studied classes of organic fluorescent sensors is that based on benzimidazole nuclei. Due to the highly conjugated planar chromophore, cyclic benzimidazole derivatives offer promising applications in optical lasers, fluorescence probes, organic luminophores and optoelectronics.

The compounds 1-4 were designed as fluorescent sensors for pH determination over a wide pH scale. In order to determine the structure-property relations, modifications on tetracyclic core were made by changing the position and structure of the amino substituents.

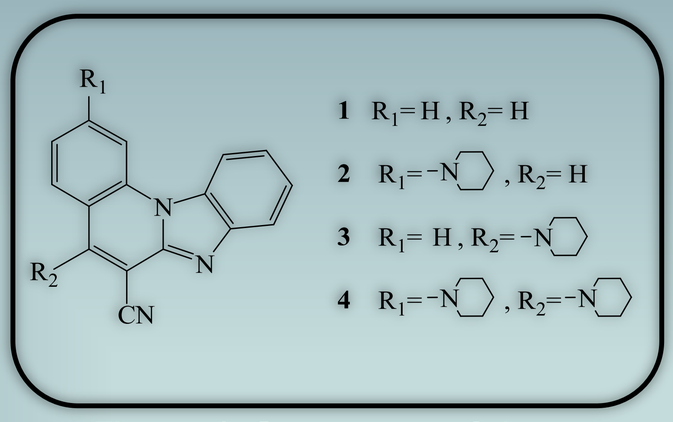

Figure 1. Structures of the benzimidazo[1,2-a]quinoline derivatives 1-4.

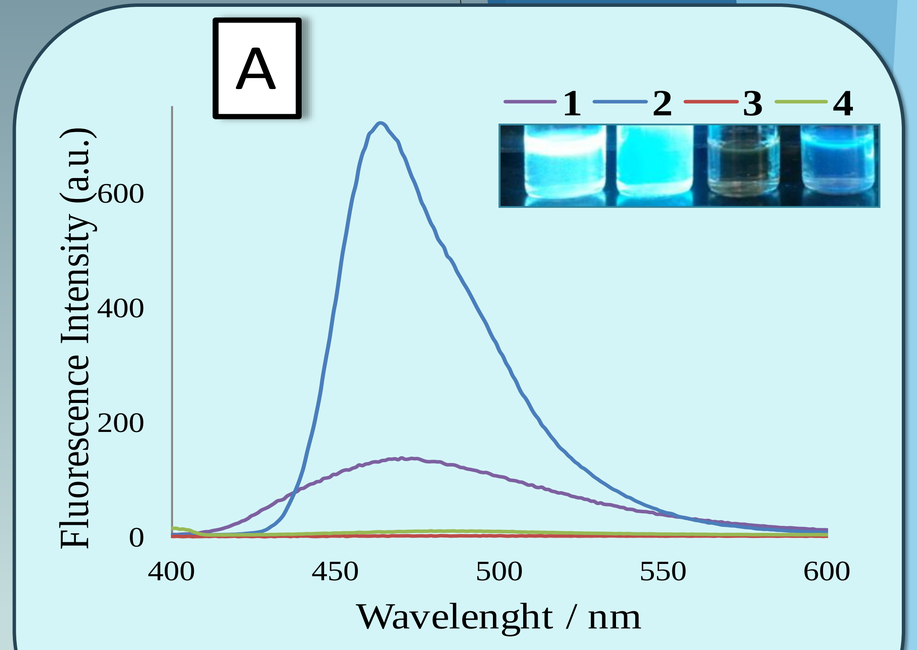

Figure 2. Effect of piperidine position on the emission properties (c = 5 ×10^{-7} M).

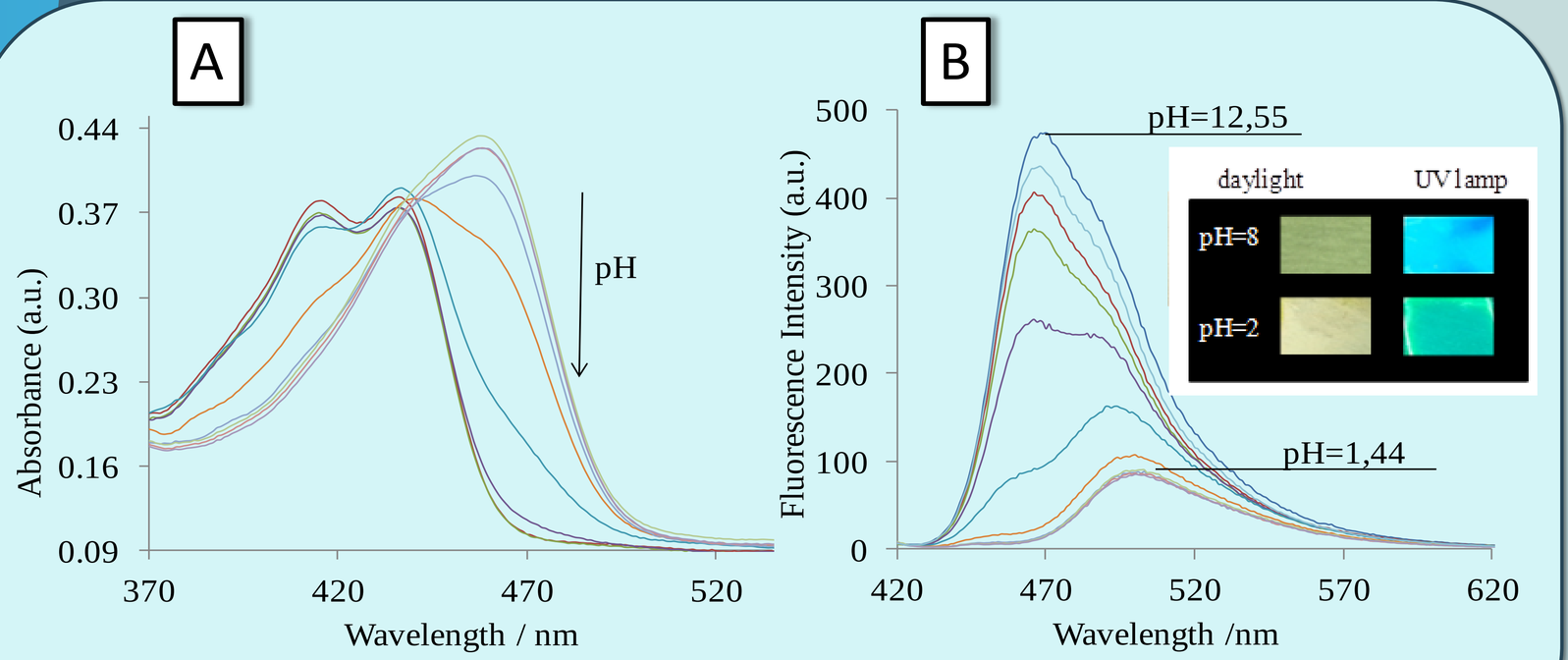

Figure 1. Effect of pH on A) absorption and B) fluorescence spectra of compound 2 immobilised in plasticised PVC films. Inset: thin film observed by daylight and under UV lamp.

The studied derivatives enable internal charge transfer (ICT) interactions, causing expressed pH sensing properties. It is proven that substituent on the position 5 of tetracyclic skeleton radically disrupt charge transfer within the aromatic core and decrease fluorescence intensity. Moreover, upon acidification, the push - pull character of the ICT transition is enhanced in all aminated fluorescent dyes. The emission band is batochromicly shifted and fluorescence is quenched.

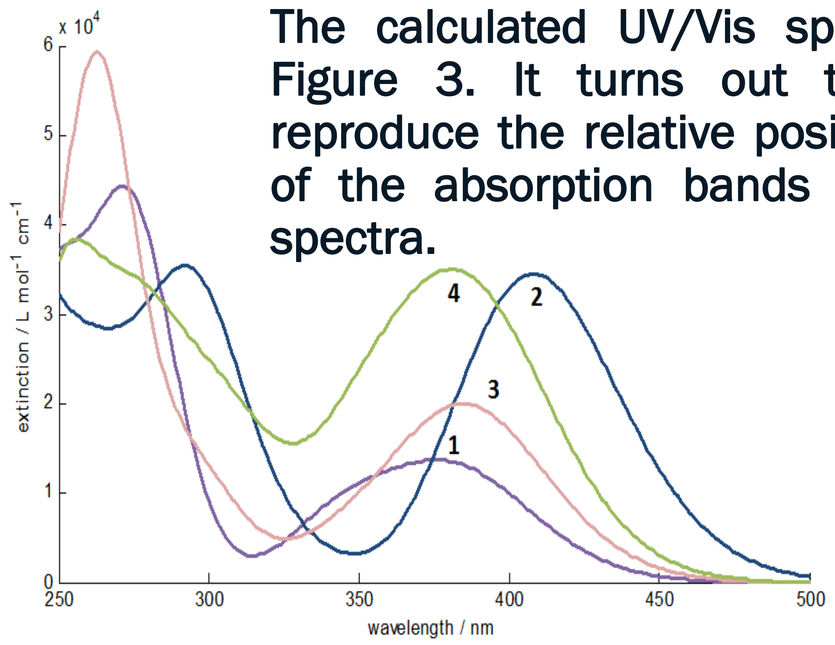

Figure 3. The calculated UV/Vis spectra of 1–4 in water, obtained with TD–DFT approach utilizing (SMD)/M06/6–311++G(2d,2p) methodology

The calculated UV/Vis spectra are shown in Figure 3. It turns out that they very well reproduce the relative positions and intensities of the absorption bands in the experimental spectra.

The lowest four excited states have $\pi-\pi^*$ character as indicated by the nodal molecular plane and the isodensity surfaces similar to those of the π-molecular orbitals (Figure 4).

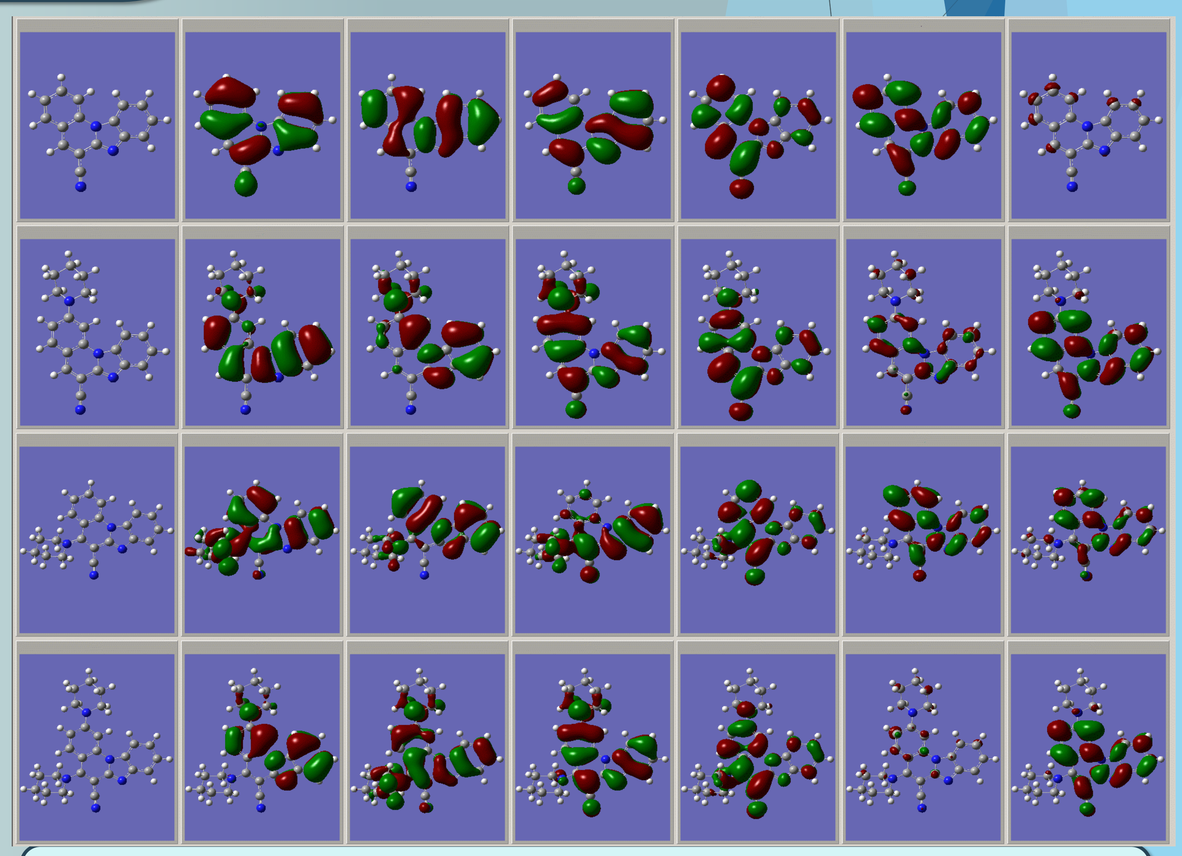

Figure 4. The frontier molecular orbitals of 1–4 (from left to right: HOMO–2, HOMO–1, HOMO, LUMO, LUMO+1, and LUMO+2).

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