

## When position matters – Different photophysical properties of two tetracyclic imidazo[4,5-*b*]pyridine regioisomers



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Nitrogen-containing heterocycles are, besides their well-known biological features, recognized as an interesting class of organic fluorescent sensors present in a wide range of (bio)chemical and environmental processes. Due to their excellent spectroscopic properties and diverse spectral responses, such derivatives offer promising applications in optoelectronics as optical lasers, fluorescence probes, organic luminophores and fluorescent dyes.[1]





Condensation of 2-cyanomethylimidazo[4,5-*b*]pyridine **3** with 2-chlorobenzoyl chloride **4** offered an acyclic precursor **5**. Then, a two-step thermic cyclization led first to chloro-substituted tetracyclic precursors **7** and **8**, and, then, to both amino substituted regioisomers **9** and **10** through the uncatalyzed microwave assisted amination. Structures of prepared systems were confirmed by <sup>1</sup>H i <sup>13</sup>C NMR, as well as MS spectrometry, while both regioisomers were structurally identified through 2D NMR spectroscopy.

Fig. 4. Emission pH titrations of 9 (left) and 10 (right)





Spectroscopic titrations were performed to determine a potential application of both regioisomers as pH sensors. Experimental  $pK_a$  values (2.8 for **9** and 3.2 for **10**) are found in a very good agreement with computations that predicted 3.5 and 4.1 by the (SMD)/B3LYP/6–31+G(d) model, respectively.

DFT analysis showed that, under normal conditions, both systems exist as monocations protonated at chain amines. Above pH = 8.7, they convert to unionized neutrals, yet without any notable change in the UV/Vis spectra, leaving this process hidden to this technique. In contrast, below  $pH \approx 3$  both systems exchange to dications, with 9 most preferably protonated on imidazole, while 10 on pyridine. As such, different dications give dissimilar UV/Vis responses, with computed absorption maxima and shifts induced by this exchange found in excellent quantitative agreement with experiments. These results highlight the profound influence of the pyridine nitrogen position within regioisomers, which allows a fine-tuning of their spectral properties and promotes these systems as promising pH-sensing materials.







