New ESIPT fluorescent aldehydes as building blocks for organic photoactive compounds

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INTRODUCTION

2-(2'-Hydroxyphenyl)benzazoles are highly fluorescent compounds whose applications are widely applied in the field of the material chemistry.[1] The well-known large Stokes' shift in these dyes can be attributed to an excited state intramolecular proton transfer (ESIPT), a phenomena that occurs between an acidic phenol and basic azolic sites.[1] This particular behavior makes this kind of compound suitable as building blocks for new fluorescent molecules.[2] In this work we have developed a method for selective formylation of a 2-(2'-hydroxyphenyl)benzoxazole (HBO) derivative and its photophysical profile were investigated by UV-Vis absorption and fluorescence emission.

RESULTS AND DISCUSSION

Since Duff's hexamethylenetetramine (HMTA) formylation of salicylic acid leads to unselective 3 and 5-formyl products, we have decided to obtain the benzoxazole derivative (3) starting from the condensation of *o*-aminophenol (1) and the corresponding 3-methylsalicylic acid (2) in polyphosphoric acid (PPA) at 170º for 5h,[3] yielding the corresponding methyl derivative (58%). The next step was carried out in presence of HMTA excess in PPA leading to the aldehyde (4) after 2 hours in 28%. An inverse method was also tested with formylation of (2) prior to condensation with (1), leading to (4) in lower yield.

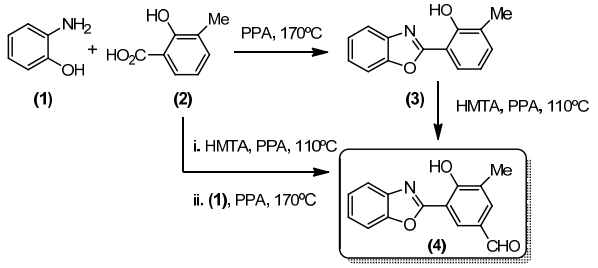

Figure 1. Synthesis of ESIPT fluorescent benzoxazoles

Since it is well-known that the ESIPT mechanism is solvent dependent,[4] the absorption and emission spectra were recorded in 1,4-dioxane and ethanol and compared to the unsubstituted HBO. All compounds absorb in the UV region (~332 nm) with electronic transitions ascribed to $^{1}\pi\pi^{*}$ transitions (ε ~10^4 $M^{-1}\cdot cm^{-1}$). The introduction of a methyl and/or formyl group does not affect significantly the photophysical properties of the compounds (Table 1). The high energy band can be related to normal emission from the enol conformer (E*) and the low energy band to the keto tautomer (K*).

Table 1. Photophysical data of HBO and its derivatives.

Comp.	Solvent	λ_{abs} (nm)	λ_{em} (nm)		$\Delta\lambda_{ST}$ [a] (nm)	
			E*	K*	E*	K*
HBO	1,4-Dioxane	330	367	490	37	160
3		331	368	498	37	167
4		335	-	493	-	158
HBO	Absolute Ethanol	331	363	479	32	148
2		333	372	490	39	157
3		334	428	487	94	153

[a] Stokes' Shift: $\Delta\lambda_{ST}=\lambda_{em}-\lambda_{abs}$.

The methodology was also extended to benzothiazole and benzimidazole derivatives, providing new photoactive building blocks with tailored fluorescence emission.

CONCLUSION

It was successfully synthesized a new fluorescent building block derivative 2-(2'-hydroxy-3'-methyl-5'-formylphenyl)benzoxazole. The methyl, as well as the formyl moieties does not affect on the photophysics, retaining the characteristics of the precursor HBO. These compounds absorb in the UV region and present fluorescence in the blue-green region.

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REFERENCES

1. Kwon, J.E.; Park, S.Y. *Adv. Mater*. **2011**, 23(32), 3615.

2. Lakowicz, J.R. (Editor). In: *Topics in Fluorescence Spectroscopy, Vol. 4: Probe Design and Chemical Sensing*. Publisher: Springer; **1994** edition.

3 Barni, E.; Savarino, P.; Marzona, M.; Piva, M. *J. Heterocycl. Chem.*. **1983**, *20*, 1517.

4. Rodembusch, F.S.; Campo, L.F.; Leusin, F.P.; Stefani, V. *J. Lumin.* **2007**, *126*, 728.