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Synthesis and spectroscopic properties of new 5-oxazolone derivatives containing an *N*-phenyl-aza-15-crown-5 moiety

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Abstract—Novel 5-oxazolone derivatives containing an *N*-phenyl-aza-15-crown-5 moiety were synthesized for the first time. The structures of the new derivatives were confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR. In addition, evaluation of the visible absorption and emission properties of the structures were carried out in eight different solvents. The products show intense visible absorption maxima in the range 467–524 nm, and fluoresced strongly, with emission maxima from 496 to 689 nm in all the solvents tested.

There has been increasing interest in fluorescent chromophores in life sciences, particularly for applications in detection, labelling, diagnosis and analysis.[1–5] The recent increase in the synthesis of crown ether derivatives

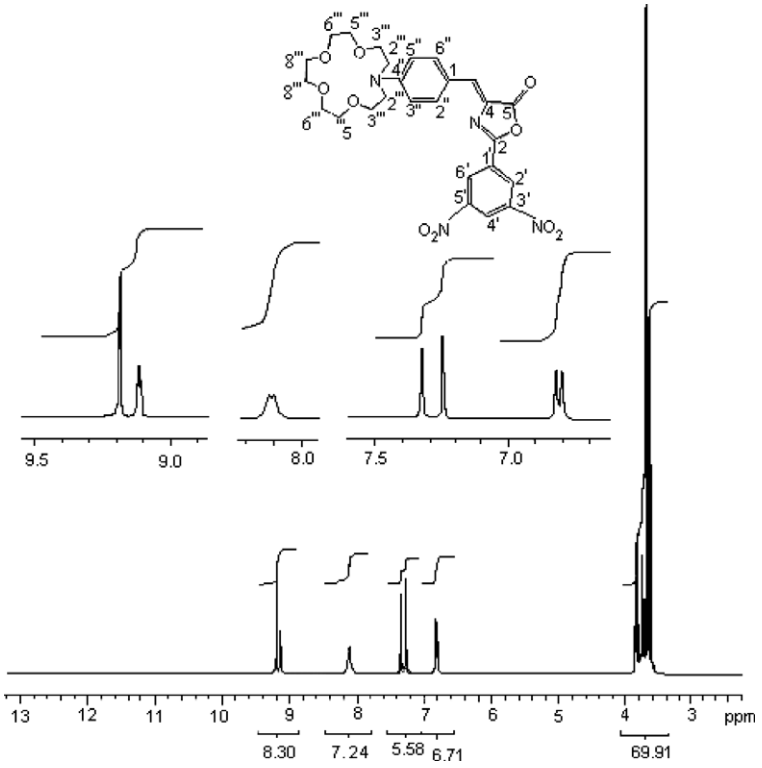

Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of pure **1b**.

Keywords: 5-Oxazolones; *N*-phenyl-aza-15-crown-5; Fluorophores.
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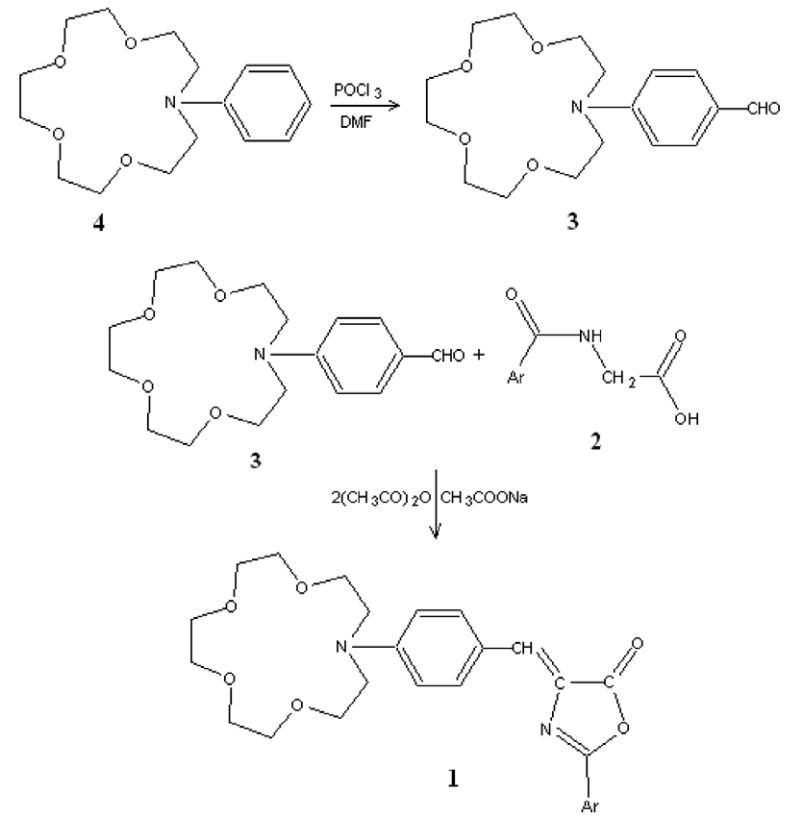
incorporating different chromo- and fluorophores is due to their applications as alkaline and alkaline earth ion sensors in biochemical analysis, medical diagnostics, separation of metal ions and small molecules, supramolecular chemistry, host–guest chemistry and phase transfer catalysis.[6–10]

5-Oxazolones have a wide range of applications including their use in semiconductor devices such as electrophotographic photoreceptors, and in non-linear optical materials because of their promising photophysical and photochemical activities.[11]

We recently synthesized several 5-oxazolone derivatives and investigated their basic photophysical properties and sensor characteristics using UV–vis and fluorescence spectroscopy.[11–17] Following our previous work with 5-oxazolone derivatives, we have now prepared novel 5-oxazolone derivatives, which contain an *N*-phenyl-(aza-15-crown-5) moiety. Thus, we aimed to combine the advantages of crown ether structures and 5-oxazolone derivatives. The present work describes the synthesis of 2-phenyl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone **1a**, 2-(3,5-dinitrophenyl)-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone **1b**, 2-(4-nitrophenyl)-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone **1c** and 2-(4-tolyl)-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone **1d** and their photophysical characterization in eight different solvents: xylene, toluene, chloroform, ethyl acetate, dimethylformamide, dichloromethane, acetonitrile and tetrahydrofuran. The effect of the polarity of the solvents on the fluorescent properties of 5-oxazolone derivatives were investigated. We also tried to examine the correlation between the molecular structures and fluorescent properties.

2-Aryl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)-benzylidene]-5-oxazolone dyes **1** were prepared by the cyclization of 4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzaldehyde **3** with benzoylglycine derivatives **2** in the presence of acetic anhydride.[18] The 4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzaldehyde **3** was synthesized by reaction of *N*-phenyl-(aza-15-crown-5) **4** with $POCl_3$ in dimethylformamide as described in the litera-



Scheme 1.