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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.
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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

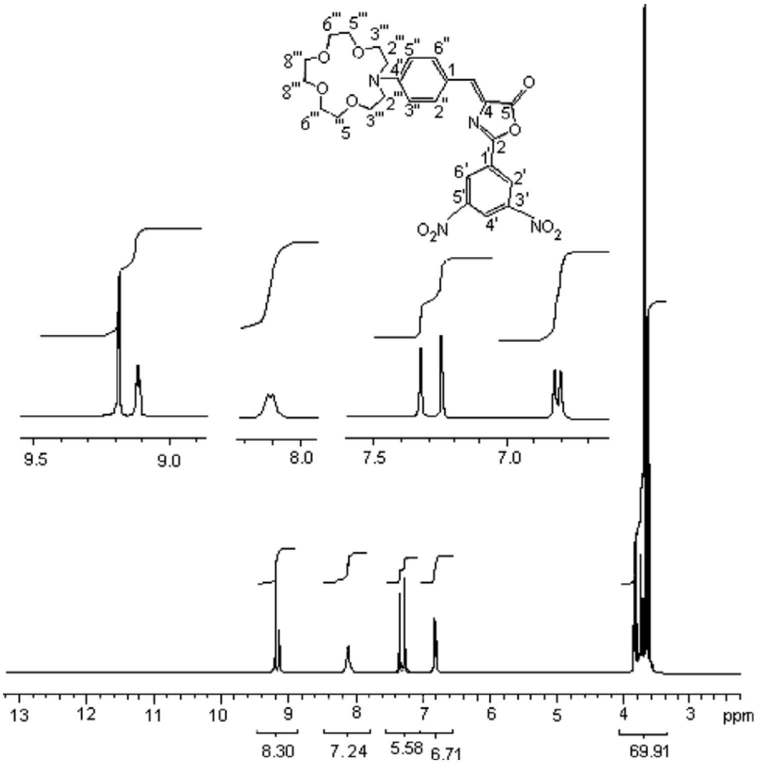

Figure 1. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of pure **1b**.

Keywords: 5-Oxazolones; *N*-phenyl-aza-15-crown-5; Fluorophores.

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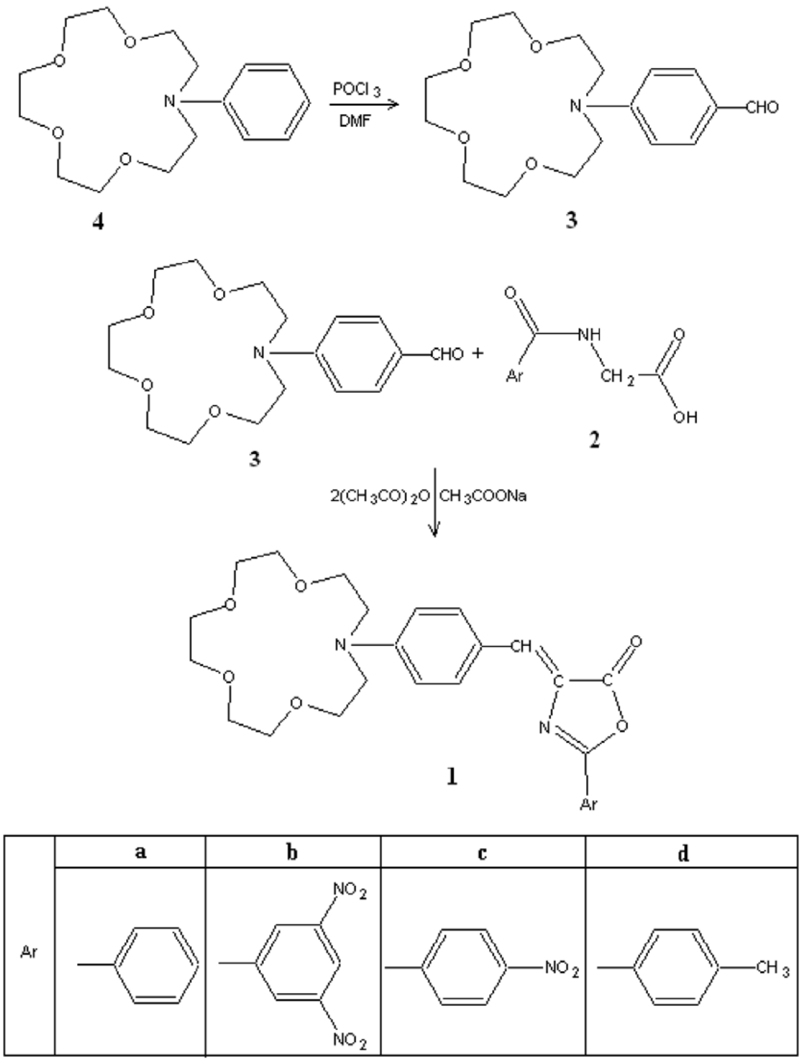
incorporating different chromo- and fluorophores is due to their applications as alkaline and alkaline earth ion sensors in biochemical analysis, medical diagnostics, separation of metal ions and small molecules, supramolecular chemistry, host–guest chemistry and phase transfer catalysis.[6–10]

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.

Table 1. Absorption and fluorescence emission data for compounds **1a–d**

Compound	Solvent	$\lambda_{\max}^{\text{abs}}$	$\varepsilon_{\max}$	$\lambda_{\max}^{\text{emis}}$	$\Delta\lambda$
1a	Xylene	473	63,000	502	29
	Toluene	473	60,000	507	34
	Chloroform	475	60,000	517	42
	Ethyl acetate	469	58,000	517	48
	Dimethylformamide	478	56,000	541	63
	Dichloromethane	472	76,000	524	52
	Acetonitrile	469	88,000	536	67
	Tetrahydrofuran	472	127,000	516	44
1b	Xylene	517	60,000	580	63
	Toluene	518	64,000	584	66
	Chloroform	524	70,000	580	56
	Ethyl acetate	506	63,000	653	147
	Dimethylformamide	512	52,000	560	48
	Dichloromethane	517	520,000	570	52
	Acetonitrile	504	557,000	554	50
	Tetrahydrofuran	509	571,000	558	49
1c	Xylene	508	96,000	600	92
	Toluene	508	56,000	603	95
	Chloroform	516	49,000	654	138
	Ethyl acetate	505	52,000	689	184
	Dimethylformamide	515	44,000	572	57
	Dichloromethane	515	463,000	669	154
	Acetonitrile	505	478,000	675	170
	Tetrahydrofuran	510	403,000	663	153
1d	Xylene	472	96,000	496	24
	Toluene	471	66,000	498	27
	Chloroform	473	91,000	513	40
	Ethyl acetate	467	94,000	515	48
	Dimethylformamide	476	89,000	537	61
	Dichloromethane	474	754,000	523	49
	Acetonitrile	468	687,000	533	65
	Tetrahydrofuran	472	724,000	520	48

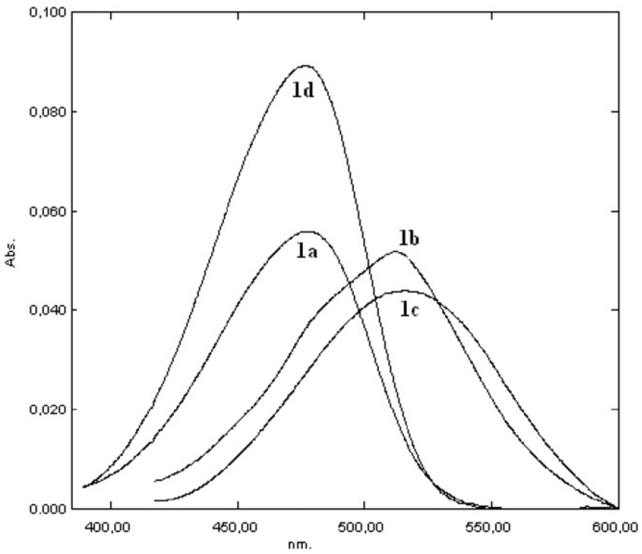


Figure 2. Absorption spectra of compounds **1a**–**d** measured in dimethylformamide.

ture.[19] After purification and crystallization from ethanol, 2-aryl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone derivatives were obtained as orange (**1a**, 21%), claret red (**1b**, 53%), dark lilac (**1c**, 46%) and yellow (**1d**, 27%) crystals and were identified by FT-IR and NMR (^{1}H and ^{13}C) spectroscopy. The presence of the imino, C=N group was confirmed by FT-IR, which shows a band at 1639 (**1a**) and 1643 (**1b–d**) cm^{-1}. The carbonyl group, which shows a strong band at 1661 cm^{-1} for **2**, appeared at 1764 (**1a**), 1781 (**1b**), 1771 (**1c**) and 1763 (**1d**). The ^{1}H NMR spectrum of pure **1b** is presented in Figure 1. The signals of the crown ether moiety for **1b** were in the range of 3.58–3.85 ppm. The signals for the =CH—Ar protons appeared at 7.19, 7.33, 7.26 and 7.16 ppm for **1a**–**d**, respectively, (Scheme 1).

The absorption and emission spectral data are given in Table 1 and show that the nature of the substituent groups on the aryl group influences the absorption and fluorescence emission maxima. In all of the solvents employed, the excitation wavelengths were chosen as 445, 485, 495 and 450 nm for **1a**–**d**, respectively, and the emission spectra were recorded. In the absorption and emission spectra of **1** a well shaped absorption and emission maxima were observed. The UV–vis absorption spectra of the 5-oxazolone derivatives show one characteristic band in all the solvents examined. There were no considerable changes observed in the absorption maxima of each derivative due to the solvent polarity. In contrast to their absorption spectra, as a result of interaction of the molecules in their excited states with the solvents, considerable shifts were observed in their emission maxima. The Stokes' shift values increased in polar solvents. While **1a** and **1d** show the longest wavelength absorption maxima in dimethylformamide (Fig. 2), **1b** and **1c** show the longest wavelength absorption in acetonitrile. Amongst derivatives **1**, **1c** had the longest wavelength emission at 689 nm (ethyl acetate). This can be attributed to enhanced conjugation in **1c**, due to the nitro group on the phenyl ring.

In conclusion, four different 5-oxazolone derivatives, containing an *N*-phenyl-aza-15-crown-5 moiety were synthesized for the first time and their structures confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy. All the derivatives displayed strong fluorescence maxima in the range of 496–689 nm. Considering the absorption and fluorescence emission maxima, derivatives **1** are expected to be good probes for biological applications. Our next goal is to investigate their performance as ion sensors for biological applications.

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18. Typical procedure for the syntheses of **1a**–**d** (described for **1b**): A solution of 4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzaldehyde **3** (1 g; 3.1 mmol), 3,5-dinitrobenzoylglycine (0.83 g; 3.1 mmol), acetic anhydride (1.17 mL, 6.2 mmol) and sodium acetate (0.41 g; 3.1 mmol) was heated until the mixture just liquified, and then heating was continued for a further 2 h. After completion of the reaction (determined by thin-layer chromatography), ethanol (20 ml) was added and the mixture was kept at room temperature for 18 h. The solid product thus obtained was purified by washing with cold ethanol, hot water and then a small amount of hexane. The solid was recrystallized from hot ethanol to afford pure crystals of **1b**. Mp 179 °C. FT-IR (KBr): $\nu_{\max}$ 1762 (—O—*C*=*O*), 1163 (*O*—*C*=O), 1126 (CH_2–$\mathit{CH_2}$–*O*–), 1643 (—C=N—), 1602 (–C–N), 1345–1520 (–NO_2) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 3.59–3.85 (m, 20H, $H_{2'''}$, $H_{3'''}$, $H_{5'''}$, $H_{6'''}$, $H_{8'''}$); 6.81 (d, $J = 8.9$ Hz, 2H, $H_{3''}$, $H_{5''}$); 7.33 (s, 1H, =CH—Ar); 8.11 (d, $J = 7.6$ Hz, 2H, $H_{2''}$, $H_{6''}$); 9.13–9.14 (m, 1H, $H_{4'}$); 9.19 (d, $J = 2.1$ Hz, 2H, $H_{2'}$, $H_{6'}$). ^{13}C NMR ($CDCl_3$, 75 Hz, δ (ppm)): 53.4 (1C, $C_{2'''}$); 68.4 (2C, $C_{3'''}$); 70.3 (2C, $C_{6'''}$); 70.6 (2C, $C_{8'''}$); 71.5 (2C, $C_{5'''}$); 112.2 (2C, $C_{3''}$,$C_{5''}$); 120.7 (1C, $C_{1''}$); 121.3 (1C, $C_{4'}$); 126.3 (1C, $C_{2'}$); 126.8 (1C, $C_{6'}$); 128.4 (2C, $C_{2''}$, $C_{6''}$); 130.2 (1C, $C_{1'}$); 136.0 (1C, C_4); 137.2 (1C, =CH—Ar); 149.0 (2C, $C_{3'}$, $C_{5'}$); 151.5 (1C, $C_{4''}$); 155.9 (1C, C_2); 166.9 (1C, C_5). ESIMS: *m*/*z* calcd for $C_{26}H_{29}N_4O_{10}$ (M^++H) = 557.529; found, 557.188.
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