Journal of Photochemistry and Photobiology A: Chemistry 150 (2002) 249–255

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Short communication

Synthesis and fluorescence behaviour of crown and azacrown ethers carrying the dansyl fluorophore as a pendant in acetonitrile solution

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Received 4 February 2002; accepted 12 February 2002

Abstract

The influence of Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Al^{3+} ions on the spectroscopic properties of the dansyl group covalently linked to crown ether or diazacrown ethers was investigated by means of absorption and emission spectrophotometry. Interaction of the alkali metal ions with all fluoroionophores studied is weak, while alkaline earth metal ions interact strongly causing about 50% quenching of dansyl fluorescence of A21C5-Dns and $A_2$18C6-Dns. The Cu^{2+}, Pb^{2+} and Al^{3+} cations interact very strongly with dansyl chromophore regardless the crown ether type, causing a major change in absorption spectrum of the chromophore and forming non-fluorescent complexes. The Co^{2+}, Ni^{2+}, Zn^2, Mg^{2+} and Ag^+ cations interact moderately with all fluoroionophores studied causing about 20% of fluorescence quenching of dansyl, except for a strong dansyl fluorescence quenching of 15C5-Dns by Co^{2+} ion. The quenching efficiency of didansylated fluoroionophores by the alkali metal ions and alkaline earth metal ions is weaker than monodansylated ones.

Keywords: Fluorescence probes; Dansyl; Azacrown ether; Diazacrown ether

1. Introduction

Detecting cations is of great interest to many scientists, including chemists, biologists, clinical biochemists and environmentalists. Among the numerous analytical methods that are available for the detection of cations, the methods based on fluorescent sensors offer several distinct advantages in terms of sensitivity, selectivity, response time and local observation [1–4]. Therefore, considerable efforts are being made to develop selective fluorescence sensors for cation detection.

Owing to their great structural variety, crown ethers are suitable for selective complex formation. Introduction of a pendant chromophore or fluorophore to the macrocyclic ring offers a potential for the use of such compounds in qualitative and quantitative analysis of metal ions in solution by means of absorption or emission spectroscopy [5,6]. In the last few years an enormous interest in dansyl derivatives as a potential fluorophore has been observed, especially in molecular recognition [7] and in the detection of metal ions [5,8–14]. Usually, dansyl group Dns is introduced into the structure via a sulfonamide bond with a primary amino group of polyamines [15]. This yields the ligands which could interact with metal ions by coordination of the amino group,

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Abbreviations: Dansyl or Dns, 1-dimethylaminonaphthalene-5-sulfonyl; Dma-Dns, 1-dimethylaminonaphthalene-5-sulfonic acid dimethylamide; Dns-Cl, 5-dimethylamino-1-naphthalenesulfonyl chloride; A12C4-Dns, *N*-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,7-trioxa-10-azacyclododecane; A21C7-Dns, *N*-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,7,10,13,16-hexaoxa-19-azacycloheneicosane; 15C5-Dns, *C*-[*N*-(5-dimethylamino-1-naphthalenesulfonylo)-aminomethyl]-1,4,7,10,13-pentaoxacyclopentadecane; $A_2$15C5-Dns, 7-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10-trioxa-7,13-diazacyclopentadecane; $A_2$15C5-$(Dns)_2$, 7,13-bis-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10-trioxa-7,13-diazacyclopentadecane; $A_2$18C6-Dns, 7-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane; $A_2$18C6-$(Dns)_2$, 7,16-bis-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

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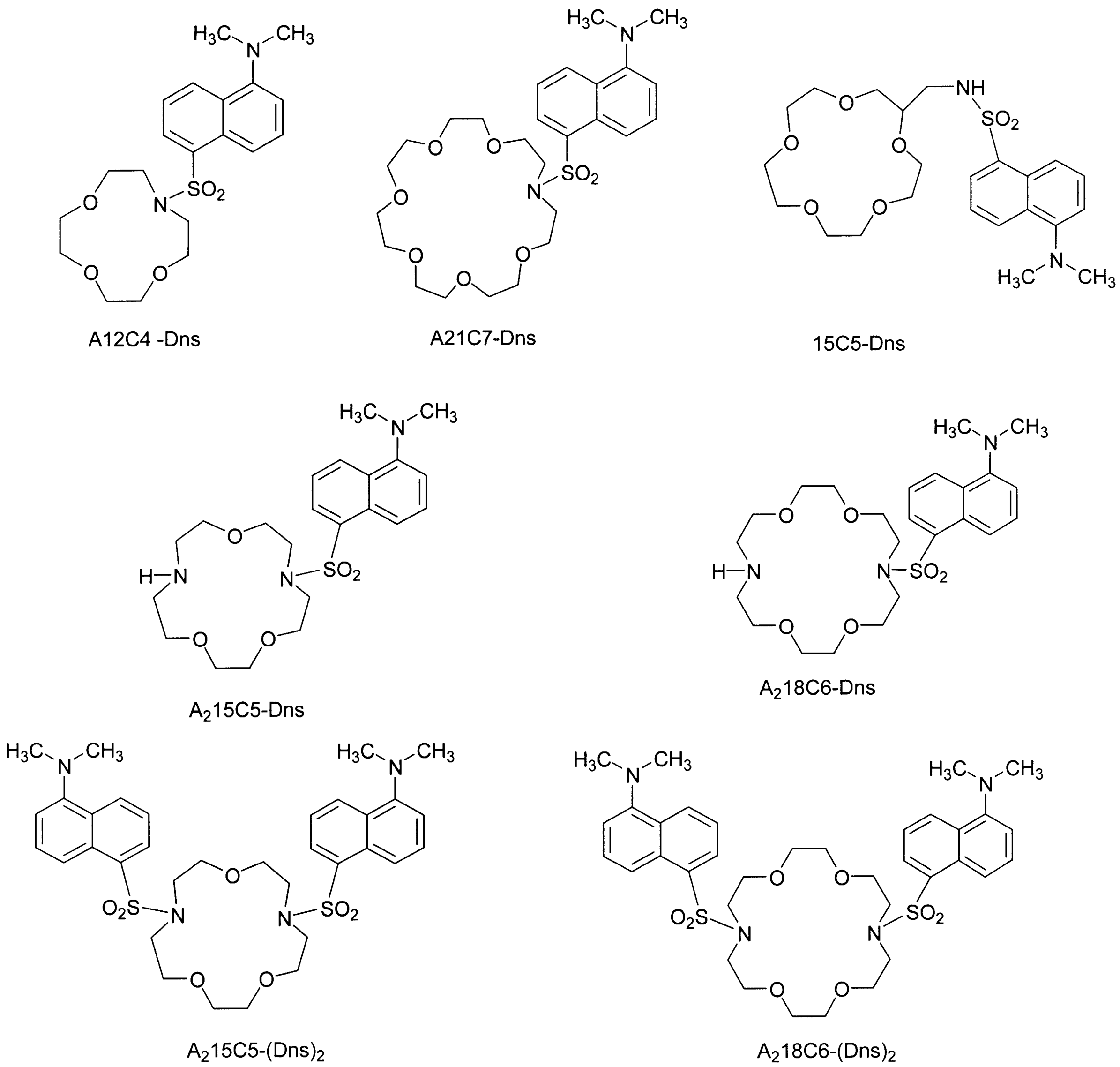
1010-6030/02/$ – see front matter
PII: S1010-6030(02)00090-4



A12C4 -Dns A21C7-Dns 15C5-Dns

$A_2$15C5-Dns $A_2$18C6-Dns

$A_2$15C5-$(Dns)_2$ $A_2$18C6-$(Dns)_2$

Fig. 1. Line drawing structures of fluoroionophores studied.

followed by abstraction of the sulfonamide hydrogen atom [8]. This type of interaction can cause important changes in the absorption or emission spectrum of the dansyl chromophore [8,12,16].

In this paper we report the synthesis and fluorescence properties of azomacrocycles comprising one or two Dns substituents linked directly to macrocyclic nitrogen atom (monoaza: A12C4-Dns, A21C7-Dns; diaza: $A_2$15C5-Dns, $A_2$15C5-$(Dns)_2$, $A_2$18C6-Dns, $A_2$18C6-$(Dns)_2$) or via aminomethyl bridge (15C5-Dns) (Fig. 1). The usage of the mono- and diazacrown ethers as a matrix binding the metal ions enabled us to analyse how the properties of both metal ion (radius, charge) and monoaza and diaza crown ether (cavity size and pedant arm) as well as the presence of an additional Dns substituent affected the spectral properties of dansyl chromophore studied in acetonitrile solution by means of absorption and fluorescence spectroscopy. The results of our studies concerning the interaction of alkaline and alkaline earth metal cations (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and non-transition metal cations (Pb^{2+}, Al^{3+}) with fluoroionophores are reported.

2. Experimental

Absorption spectra of fluoroionophores at concentration about 2×10^{-5} M in acetonitrile solution containing 50 M equivalents of appropriate metal perchlorate salt were measured on a Perkin-Elmer Lambda 18 spectrophotometer using 1 cm absorption cell. Fluorescence spectra of the same solutions were measured on a Perkin-Elmer LS-50B spectrofluorimeter using 340 nm excitation wavelength in a range 400–750 nm with spectral band width

4.5 nm for excitation and emission at 20 °C. ^{1}H NMR spectra were measured at 400 MHz on a Varian Mercury 400 BB spectrometer in $CDCl_3$. The chemical shifts were expressed in ppm units using tetramethylsilane as an internal standard. Elemental analyses were performed on a CARBO ERBA Instruments CHNS-O EA1108 Elemental Analyser.

2.1. Synthesis

2.1.1. Synthesis of N-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,7-trioxa-10-azacyclododecane (A12C4-Dns)

A total of 0.3 g (1.91 mmol) aza-12-crown-4 (1,4,7-trioxa-10-azacyclododecane, A12C4, Aldrich) and 0.54 g (2.0 mmol) 5-dimethylamino-1-naphthalenesulfonyl chloride (Dns-Cl, Fluka, puriss p.a.) were dissolved in 10 ml acetonitrile (LabScan, HPLC grade). Then 0.652 g (2.0 mmol) cesium carbonate (PPH POCh Gliwice) was added to the solution. The mixture was heated in a closed capsule at 50 °C for 3 h. The progress of the reaction was controlled by TLC on silica gel (Merck, Silica Gel 60 F_{254}) using methylene chloride:methanol (5:0.05). After completion of the reaction, the solution was purified by filtration, the residue washed with methylene chloride and the combined solutions were concentrated. The resulting brown oil was redissolved in methylene chloride, the solution washed 3 × 100 ml aqueous solution of tetrabutylammonium hydroxide (PPH POCh Gliwice), and dried over magnesium sulfate (PPH POCh Gliwice). The crude product was purified by column chromatography on silica gel (Merck, Kieselgel 60, 0.040–0.063 mm) with methylene chloride:methanol (5:0.1) as eluent to give one fraction 0.48 g (69%) of A12C4-Dns as brown oil.

A12C4-Dns: ^{1}H NMR ($CDCl_3$) 2.88 (s, 6H, CH_3); 3.55–3.79 (m, 16H, crown); 7.17 (d, 1H, $J = 7.6$ Hz, aromatic H^6); 7.52 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 7.2$ Hz, aromatic H^3); 7.55 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 7.6$ Hz, aromatic H^7); 8.18 (d, 1H, $J = 7.2$ Hz, aromatic H^2); 8.32 (d, 1H, $J = 8.4$ Hz, aromatic H^8); 8.51 (d, 1H, $J = 8.8$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{20}H_{28}N_2O_5S$: C 58.80%, H 6.91%, N 6.86%, O 19.58% and S 7.85%. Found: C 58.92%, H 6.79%, N 6.84%, O 19.57% and S 7.88%.

2.1.2. Synthesis of N-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,7,10,13,16-hexaoxa-19-azacycloheneicosane (A21C7-Dns)

A21C7-Dns was prepared and purified as described for A12C4-Dns starting with 0.10 g (0.325 mmol) aza-21-crown-7 (1,4,7,10,13,16-hexaoxa-19-azaheneicosane, A21C7, Aldrich) and 0.09 g (0.333 mmol) Dns-Cl. The desired compound was obtained as brown solid with total reaction yield 60% (0.12 g).

A21C7-Dns: ^{1}H NMR ($CDCl_3$) 2.87 (s, 6H, CH_3); 3.49–3.67 (m, 28H, crown); 7.16 (d, 1H, $J = 7.6$ Hz, aromatic H^6); 7.49 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 7.2$ Hz, aromatic H^3); 7.54 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 7.6$ Hz, aromatic H^7); 8.16 (d, 1H, $J = 7.2$ Hz, aromatic H^2); 8.31 (d, 1H, $J = 8.8$ Hz, aromatic H^8); $\delta = 8.49$ (d, 1H, $J = 8.8$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{26}H_{40}N_2O_8S$: C 57.76%, H 7.46%, N 5.18%, O 23.67% and S 5.93%. Found: C 57.66%, H 7.50%, N 5.24%, O 23.70% and S 5.90%.

2.1.3. Synthesis of C-[N-(5-dimethylamino-1-naphthalenesulfonylo)-aminomethyl]-1,4,7,10,13-pentaoxacyclopentadecane (15C5-Dns)

15C5-Dns was prepared and purified as described for A12C4-Dns starting with 0.30 g (1.2 mmol) 15-crown-5-meNH_2 (*C*-aminomethyl-(1,4,7,10,13-pentaoxacyclopentadecane, 15C5meNH_2, Aldrich) and 0.32 g (1.2 mmol) Dns-Cl. The desired compound was obtained as brown solid with total reaction yield 66% (0.38 g).

15C5-Dns: ^{1}H NMR ($CDCl_3$) 2.92 (s, 6H, CH_3); 3.66 (d, 2H, CH_2); 3.46–3.63 (m, 19H, crown); 5.30 (s, 1H, NH); 7.21 (d, 1H, $J = 7.6$ Hz, aromatic H^6); 7.54 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 7.2$ Hz, aromatic H^3); 7.57 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 7.6$ Hz, aromatic H^7); 8.25 (d, 1H, $J = 7.2$ Hz, aromatic H^2); 8.34 (d, 1H, $J = 8.4$ Hz, aromatic H^8); 8.54 (d, 1H, $J = 8.4$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{23}H_{34}N_2O_7S$: C 57.24%, H 7.10%, N 5.80%, O 23.21% and S 6.64%. Found: C 57.20%, H 7.14%, N 5.82%, O 23.20% and S 6.63%.

2.1.4. Synthesis of 7-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10-trioxa-7,13-diazacyclopentadecane ($A_2$15C5-Dns) and 7,13-bis-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10-trioxa-7,13-diazacyclopentadecane ($A_2$15C5-$(Dns)_2$)

$A_2$15C5-Dns and $A_2$15C5-$(Dns)_2$ ware prepared and purified as described for A12C4-Dns starting with 0.50 g (2.35 mmol) diaza-15-crown-5 (1,4,10-trioxa-7,13-diazacyclopentadecane, $A_2$15C5, Merck) and 0.64 g (2.37 mmol) Dns-Cl. Finally two products were obtained: $A_2$15C5-$(Dns)_2$ (0.25 g with 15% yield) as a yellow solid and $A_2$15C5-Dns (0.21 g with 20% yield) as a dark yellow oil.

$A_2$15C5-Dns: ^{1}H NMR ($CDCl_3$) 2.88 (s, 6H, CH_3); 3.49–3.73 (m, 20H, crown); 7.17 (d, 1H, $J = 7.6$ Hz, aromatic H^6); 7.50 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 7.6$ Hz, aromatic H^3); 7.56 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 7.6$ Hz, aromatic H^7); 8.12 (d, 1H, $J = 7.6$ Hz, aromatic H^2); 8.31 (d, 1H, $J = 8.8$ Hz, aromatic H^8); $\delta = 8.51$ (d, 1H, $J = 8.4$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{22}H_{33}N_3O_5S$: C 58.51%, H 7.37%, N 9.31%, O 17.71% and S 7.10%. Found: C 57.40%, H 7.48%, N 9.25%, O 17.74% and S 7.13%.

$A_2$15C5-$(Dns)_2$: ^{1}H NMR ($CDCl_3$) 2.86 (s, 12H, CH_3); 3.44–3.65 (m, 20H, crown); 7.15 (d, 2H, $J = 7.2$ Hz, aromatic H^6); 7.48 (dd, 2H, $J_1 = 8.4$ Hz, $J_2 = 7.6$ Hz, aromatic H^3); 7.53 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 7.2$ Hz, aromatic H^7); 8.12 (d, 2H, $J = 7.6$ Hz, aromatic H^2); 8.28 (d, 2H, $J = 8.8$ Hz, aromatic H^8); 8.50 (d, 2H, $J = 8.4$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{34}H_{44}N_4O_7S_2$: C 59.63%, H 6.48%, N 8.18%, O 16.35% and S 9.36%. Found: C 59.60%, H 6.51%, N 8.18%, O 16.35% and S 9.36%.

2.1.5. Synthesis of 7-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane ($A_2$18C6-Dns) and 7,16-bis-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane ($A_2$18C6-(Dns)$_2$)

$A_2$18C6-Dns and $A_2$18C6-(Dns)$_2$ were prepared and purified as described for A12C4-Dns starting with 0.50 g (1.9 mmol) diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, $A_2$18C6, Fluka) and 0.54 g (2.0 mmol) Dns-Cl. As for the synthesis mentioned above two products were obtained: $A_2$18C6-(Dns)$_2$ (0.41 g with 30% yield) as a dark yellow solid and $A_2$18C6-Dns (0.35 g with 37% yield) as a brown oil.

$A_2$18C6-Dns: ^{1}H NMR ($CDCl_3$) 2.88 (s, 6H, CH_3); 3.52–3.76 (m, 24H, crown); 7.17 (d, 1H, $J = 7.2$ Hz, aromatic H^6); 7.50 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 7.2$ Hz, aromatic H^3); 7.55 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 7.2$ Hz, aromatic H^7); 8.14 (d, 1H, $J = 7.2$ Hz, aromatic H^2); 8.28 (d, 1H, $J = 8.8$ Hz, aromatic H^8); 8.51 (d, 1H, $J = 8.4$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{24}H_{37}N_3O_6S$: C 58.16%, H 7.52%, N 8.48%, O 19.37% and S 6.47%. Found: C 58.06%, H 7.57%, N 8.53%, O 19.34% and S 6.50%.

$A_2$18C6-(Dns)$_2$: ^{1}H NMR ($CDCl_3$) 2.87 (s, 12H, CH_3); 3.48–3.60 (m, 24H, crown); 7.15 (d, 2H, $J = 7.6$ Hz, aromatic H^6); 7.48 (dd, 2H, $J_1 = 8.4$ Hz, $J_2 = 7.2$ Hz, aromatic H^3); 7.53 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 7.6$ Hz, aromatic H^7); 8.12 (d, 2H, $J = 7.2$ Hz, aromatic H^2); 8.28 (d, 2H, $J = 8.8$ Hz, aromatic H^8); 8.50 (d, 2H, $J = 8.4$ Hz, aromatic H^4).

Elemental analysis: calculated for $C_{36}H_{48}N_4O_8S_2$: C 59.32%, H 6.64%, N 7.69%, O 17.56% and S 8.80%. Found: C 59.30%, H 6.65%, N 7.70%, O 17.52% and S 8.84%.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of all fluoroionophores studied in acetonitrile solution are very similar to the absorption spectrum of dansyl amide reported in our previous paper about the interaction of monoaza crown ethers with covalently linked dansyl as a fluorophore (A15C5-Dns, A18C6-Dns) [14]. Such spectral similarity indicates the absence of significant interactions between the nitrogen atom of diazacrown ether moiety and dansyl chromophore. All compounds studied possess two absorption bands, one with a maximum at about 336 nm and the second one with a maximum at 253 nm. The molar absorption coefficients are very close for all these compounds except the ones possessing two dansyl chromophores for which the molar absorption coefficient was twice as high as in the case of monodansylated compounds. The similar pattern of absorption spectrum observed for mono- and disubstituted fluoroionophores indicates that there is no ground-state interaction between two dansyl moieties. The interaction of the fluoroionophore with metal ion causes changes in the absorption spectrum of the chromophore similar to published previously for A15C5-Dns and A18C6-Dns [14]. The changes of long-wave absorption band of dansyl chromophore attached to the different ionophore moieties upon influence of Ba^{2+} ion are shown in Fig. 2.

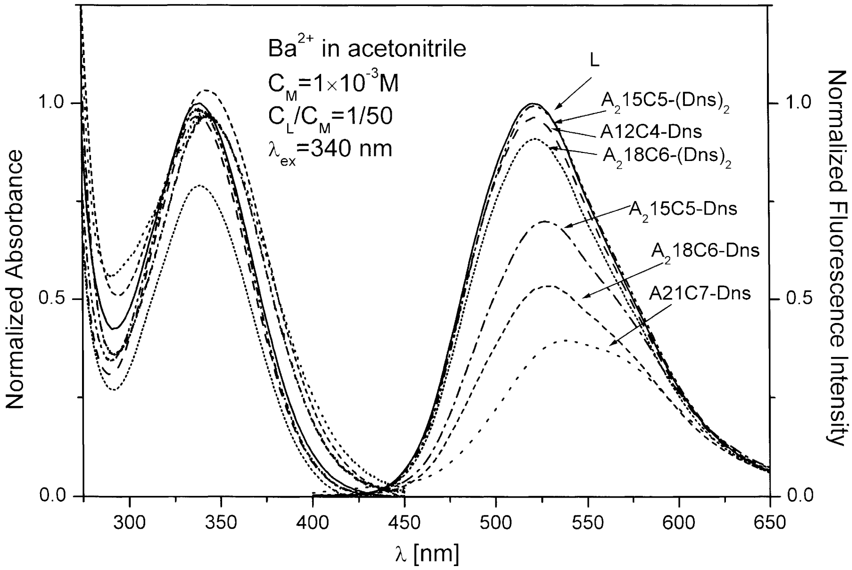


Fig. 2. Absorption (left) and fluorescence spectra (right) of the complexes of Ba^{2+} with the fluoroionophores in acetonitrile.

The majority of ions studied in this paper caused only minor changes in the molar absorption coefficients of the long- and short-wave absorption bands in the spectrum of dansyl chromophore. Such changes can be explained by the modification of environment polarity caused by the excess salt added and interaction of metal ions with fluoroionophores [8]. The influence of the environment polarity on the absorption and emission spectra of the dansyl chromophore is well known [17–19]. On the other hand, Al^{3+}, Cu^{2+} and Pb^{2+} ions caused disappearance of the characteristic dansyl absorption spectrum for all compounds studied as it was observed previously [14] but small changes of the dansyl absorption spectrum by acid impurity present in this salts cannot be excluded. The appearance of a new, short-wave absorption band with maximum at about 280 nm indicates a strong interaction between the ions and the dansyl chromophore alone.

3.2. Emission spectra

Emission spectra of all fluoroionophores studied (Figs. 2 and 3) are typical of dansyl emission in organic solvent with maximum at about 520 nm [14,17–19]. Incorporation of the ionophore moiety does not change the shape and position of dansyl amide fluorescence spectrum (Figs. 2 and 3). An addition of metal ions causes the decrease of dansyl fluorescence intensity and simultaneously a small batochromic shift of the fluorescence spectrum compared to the free ligand as shown in Fig. 2 for different fluoroionophores and Ba^{2+} ion and in Fig. 3 for 15C5-Dns and different ions. The quenching efficiency of a number of metal ions on the fluorescence intensity of all fluoroionophores studied are shown in Fig. 4.

Quenching efficiency of metal ions studied depends on the kind of metal ion as well as the properties of macrocycle moiety: cavity size, number of nitrogen atoms and number of dansyl substituents. Cu^{2+}, Al^{3+} and Pb^{2+} ions totally quench the fluorescence of all fluoroionophores studied, regardless of the kind of macrocycle and number of fluorophores, because of the interaction with dansyl amino group [14]. The quenching efficiency of others ions depends on size of macrocyclic moiety, as well as on the of metal (Fig. 4).

For ions Li^+, Na^+, K^+, Cs^+, Ag^+ and Mg^{2+} only a weak quenching of dansyl fluorescence (not higher than a several percent) is observed. Generally the quenching is higher for monodansylated macrocycle than didansylated ones. These ions practically do not quench the dansyl fluorescence of A12C4-Dns, except for Ag^+ ion (few percent only). This fluoroionophore (A12C4-Dns) possessing the smallest macrocyclic cavity is also not quenched by alkaline earth metal ions studied. Only Co^{2+}, Ni^{2+}, Zn^{2+} ions interact with this fluoroionophore moderately. For the alkaline ions studied the highest quenching efficiency is exhibited by Li^+ ion towards $A_2$15C5-Dns, whereas the most diversified quenching is observed for Cs^+ and K^+ ions, which interact more strongly with fluoroionophore possessing the biggest cavity size. Ag^+ and Mg^{2+} ions interact weakly with all fluoroionophores studied, however, Ag^+ interacts moderately with monodansylated diazacrown ethers ($A_2$15C5-Dns and $A_2$18C6-Dns), whereas Mg^{2+} with 15C5-Dns derivative. The highest selectivity and quenching efficiency is exhibited by alkaline earth metal ions (Ca^{2+}, Sr^{2+} and Ba^{2+}). The quenching efficiency of A21C7-Dns is about 60% for Ba^{2+}, 55% for Ca^{2+} and more than 40% for Sr^{2+}. Lowest (less than 50%) and less diversified quenching efficiency is observed for $A_2$18C6-Dns and 15C5-Dns (20–30%). More diversified quenching efficiency (from 10 to 30%) for this ions are also observed for $A_2$15C5-Dns. The didansylated fluoroionophores ($A_2$18C6-$(Dns)_2$ and $A_2$15C5-$(Dns)_2$) are quenched weakly, about 10% for $A_2$18C6-$(Dns)_2$ and only

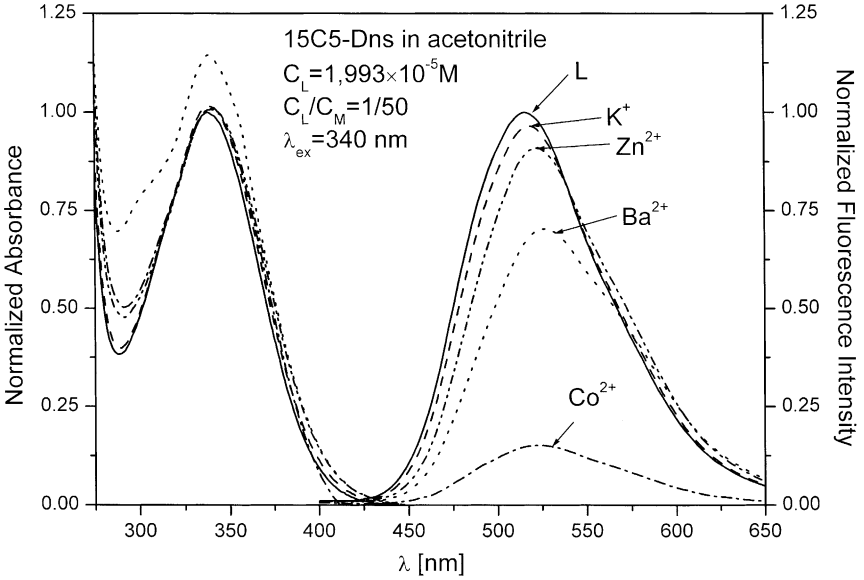


Fig. 3. Absorption (left) and fluorescence spectra (right) of 15C5-Dns and its complexes with metal ions in acetonitrile.

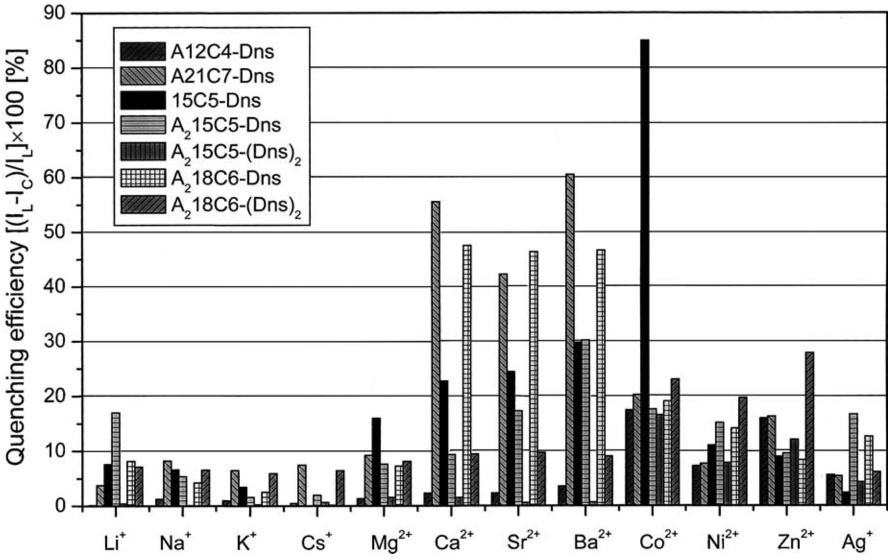


Fig. 4. A bar chart of dansyl fluorescence quenching at 520 nm resulted by the addition of metal ions to the fluoroionophores solution.

few percent for $A_2$15C5-$(Dns)_2$; much weaker than monodansylated derivatives reported in our previous paper [14]. Thus, the quenching efficiency of dansyl fluorophore attached to the macrocycle moiety by alkaline earth metal ions depend not only on the cavity size of macrocycle, but also on the kind and number of nitrogen atoms in the macrocyclic moiety. The fluorescence of A15C5-Dns is quenched by Ba^{2+} ion by 50%, A18C6-Dns by 85% [14], whereas A21C7-Dns by 61% and A12C4-Dns by 3% only. Taking into account the mutual relation between the radius of the ions (Ca^{2+} 1.00 Å, Sr^{2+} 1.16 Å, Ba^{2+} 1.36 Å) [20] and the radius of the cavity of the crown ether (A15C5 0.85 Å, A18C6 1.38 Å, A21C7 1.7 Å, A12C4 0.6 Å) [21] one can notice that matching of the ion radius and macrocycle cavity radius is important for strong interaction and dansyl fluorescence quenching, but exact matching is not important (small differences of quenching efficiency between these ions). The replacement of an oxygen atom by a nitrogen one in the macrocyclic moiety causes substantial decrease of dansyl efficiency quenching by alkaline earth metal ions (e.g. from 85% for A18C6-Dns to 48% for $A_2$18C6-Dns and from 50% for A15C5-Dns to 30% for $A_2$15C5-Dns for Ba^{2+} ion). The quenching efficiency of dansyl fluorescence by alkaline earth metal ions decreases subsequently for didansylated fluoroionophores: for $A_2$18C6-$(Dns)_2$—less than 10%, while for $A_2$15C5-$(Dns)_2$—few percent only. The lower quench-

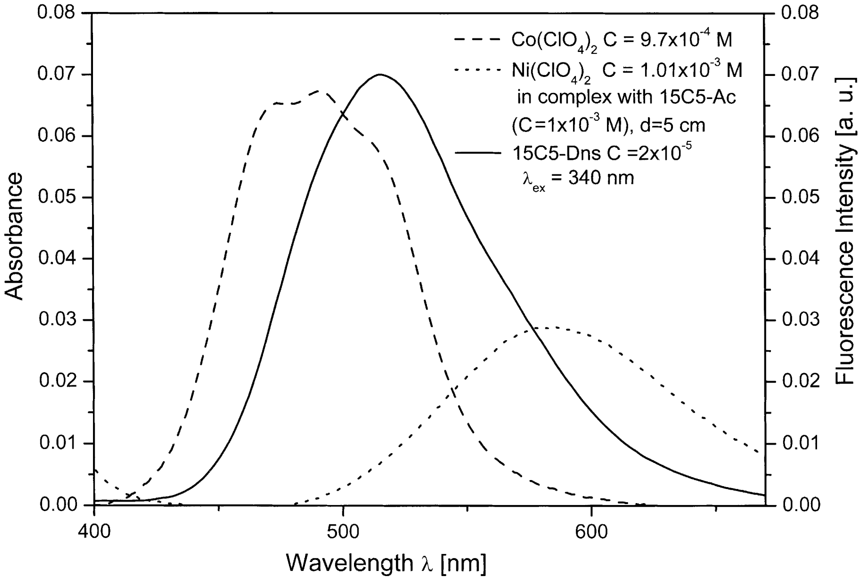


Fig. 5. The absorption spectra of Co^{2+} and Ni^{2+} ions in the presence of 15C5-Ac, and emission spectrum of 15C5-Dns in acetonitrile.

ing effect of the dansyl fluorescence of monodansylated diazacrown ether by alkaline earth metal ions is in conformity with general observations that saturated nitrogen atom displays lower affinity toward alkali and alkaline earth metal ions compared to the affinity displayed by oxygen [22]. An attachment of the second dansyl fluorophore to diazacrown moiety by forming the sulfonamide bond substantially decreases the affinity of nitrogen atom and changes the geometry and flexibility of the crown ether cavity [22,23]. Such structural changes of ionophore moiety results in low binding ability of metal ions and consequently small quenching efficiency of dansyl fluorescence.

The divalent ions Co^{2+}, Ni^{2+} and Zn^{2+} interact moderately with all fluoroionophores studied, however, the fluorescence efficiency quenching for $A_2$18C6-$(Dns)_2$ is higher than 20%. The quenching of dansyl fluorescence intensity of 15C5-Dns by Co^{2+} is extraordinary exception. For this particular fluoroionophore the quenching efficiency by Co^{2+} is about 85%. A large difference between dansyl fluorescence quenching of 15C5-Dns caused by Co^{2+} and Ni^{2+} indicates on the different mechanism of interaction of these ions with fluorophore though both ions have similar radius (Co^{2+} 0.57 Å, Ni^{2+} 0.69 Å) lower than cavity radius of crown ether cavity size (0.9 Å). As suggested by Prodi et al. [8] a dansyl-to-Co^{2+} energy transfer mechanism (which is strongly distance dependent [24]) can be invoked to explain the observed fluorescence quenching by Co^{2+}. The radiationless energy transfer process from dansyl (energy donor) to Co^{2+} ion (energy acceptor) is highly probable because is fulfilled a basic requirement of this process, a strong overlap of emission spectrum of dansyl and absorption spectrum of Co^{2+} ion (Fig. 5) [24]. In the case of Ni^{2+} ion a lower overlap of the emission and absorption spectra causes a lower quenching of dansyl fluorescence by this ion. The lower quenching efficiency of dansyl fluorescence of the other fluoroionophores by Co^{2+} as well as Ni^{2+} ions arises probably from the larger distance between an energy donor and acceptor than in the case of Co^{2+}–15C5-Dns complex.

4. Conclusions

A new crown and azacrown ethers carrying dansyl fluorophore have been synthesised and characterised, and the results compared with dansyl monoazacrown ethers. The dansyl fluorescence quenching efficiency of metal ions depend on the cavity size of ionophore moiety as well as on the kind of donor atom in the macrocyclic ring. The replacement of an oxygen atom by a nitrogen one decreased the quenching efficiency of fluoroionophores by alkaline earth metal ions. An introduction on the second dansyl fluorophore on the nitrogen atom of diazamacrocycle moiety causes a substantial decrease of dansyl fluorescence quenching efficiency. The crown ether containing pendant fluorophore, 15C5-Dns, exhibits interesting properties as a potential selective receptor for Co^{2+} cation at low concentration of this metal ion.

Acknowledgements

This work was financially supported by the Polish State Committee for Scientific Research (KBN) under Grant nos. BW/8000-5-0022-1 (T.O.) and DS-8351-4-0132-0 (W.W.).

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