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Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

EVIDENCE FOR A FLUORESCENCE ENHANCEMENT OF SOME DANSYL AND STILBENE DERIVATIVES USED AS OPTICAL CHEMOSENSORS

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Three novel fluorescent derivatives, 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (F-1), 5-dimethylamino-1-(β-methacryloyloxyethylcarbamoyloxyethyl)-N-methylsulfonamidonaphthalene (F-2), (S)-N-acryloylphenylalanine-4-styrybenzyl ester (F-3) were discussed in the light of fluorescent properties which may recommend them as "turn on" chemosensors for acid type analytes (F-1 and F-2) or for nucleobases (F-3).

INTRODUCTION

Synthesis and characterization of fluorescent chemosensors is currently an important area of modern research because of their potential applicability in a large range of disciplines, such as medical diagnostics and physiological imaging (neurobiology, for example), biochemical investigations, environmental monitoring, biotechnology, drug discovery and cell biology.[1] However, a fluorescence chemosensor results from combining a binding site and one or more fluorescence probes which afford the fluorescence properties, often the target compound being a metal ion, anion or organic molecule. As result of the interaction with the target, the sensor will exhibit a different fluorescence behavior for which a number of fluorescence signaling modes such as quenching, enhancement, the excimers or exciplex formation, modifications of lifetimes or anisotropy are important considerations for sensing. The analysis of these changes offers valuable information on the type of interaction between the sensor and the target compounds as well as the effect of various external factors (solvent, pH, temperature, light, etc) on the resulting systems. Generally, the fluorescence efficiency can be associated with many structural factors of such chemicals including π-π* and n-π* transitions, structural rigidity, noncovalent interactions (*e.g.*, hydrogen bonds, π-π interactions, and hydrophilic and hydrophobic interactions), intra- or intermolecular energy transfers, and photoinduced electron transfers.[2] On this line, numerous literature reports use the fluorescence quenching ("turn-off" sensing) as a readout mechanism for the sensing response to the detriment of the fluorescence enhancement ("turn-on" sensing). As a practical extension of this approach, it should be noticed that the main advantage of "turn-on" sensors related to "turn-off" sensors is the simplicity of measuring low concentrations relative to a "dark" background.[3] Despite this benefit that would reduce the possibility of false positive signals resulted from contaminants which may quench the fluorescence,[4] unfortunately, to our knowledge, there are no many examples of sensors in which the binding of an ion causes an increase in the fluorescence. [5]

In the last few years much attention has been dedicated to the investigation of dansyl derivatives, particularly in molecular recognition[6] and in the detection of both metal cations[7] and anions,[8] as well as in supramolecular structures like dendrimers.[9] For instance, the 5-dimethylamino-1-naphthalenesulfonate, known as dansyl, is one of the most well-known fluorophore that is strongly

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sensitive to local polarity because of its charge transfer structure, which allows a modulation of the performance of materials by changing the environmental conditions, quality extensively exploited in the area of fluorescent sensors for organic molecules. Moreover, such structure shows strong absorption bands in the near UV and also an intense fluorescence in the visible region.[10] These characteristics, associated with the synthetic flexibility of the sulfonic acid group from the dansyl molecule, have encouraged the incorporation of dansyl fluorophore as core-structure in many fluorescent sensors.

Another class of highly sensitive compounds which has attracted significant interest owing to their various biological including antimicrobial and antitumor[11] or insecticidal activity,[12] together with the fact that they represent essential constituents of optical brighteners and laser dyes,[13] photoresists, photoconductive devices or electroluminescent materials,[14] are stilbene derivatives. The stilbene (fluoro)chromophore is one of the most widely explored conjugated organic systems because it presents not only spectroscopic accessibility but also a specific photochemistry that includes reversible *trans-cis* isomerization, cyclization to dihydrophenanthrene or dimerization to yield tetraphenylcyclobutane products.[15] Considering the stilbene photophysics, related to the excimer fluorescence emission observed in many stilbene derivatives, the excimer formation in solutions, which is governed by diffusion-controlled factors, has been proposed as an intermediate during the dimerization process.[16] More recently, it was found that the stilbene molecule can be used to study antibody-based photochemical sensors for diagnosis and clinical applications[17] or in the field of molecular machines.[18]

In the present paper the results concerning modulation of fluorescence signaling for three new fluorescent derivatives prepared in our group, namely 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (F-1), 5-dimethylamino-1-(β-methacryloyloxyethylcarbamoyloxyethyl)-N-methylsulfonamidonaphthalene (F-2), (S)-N-acryloylphenylalanine-4-styrybenzyl ester (F-3), after adding various types of analytes of proton donor type (for dansyl derivatives) or nucleobases (for stilbene derivative) are described. Until now, the experimental findings sustains that in such systems is possible to induce fluorescence enhancement rather than quenching, a challenging task in the development of "turn-on" fluorescent chemosensors.[19]

RESULTS AND DISCUSSION

Details of synthesis for 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (F1), 5-dimethylamino-1-(β-methacryloyloxyethylcarbamoyloxyethyl)-N-methylsulfon-amidonaphthalene (F-2) and (S)-N-acryloylphenylalanine-4-styrybenzyl ester (F-3) have been reported in our prior publications. [17, 20] The molecular structure of the fluoroprobes used in this study is given in Figure 1.

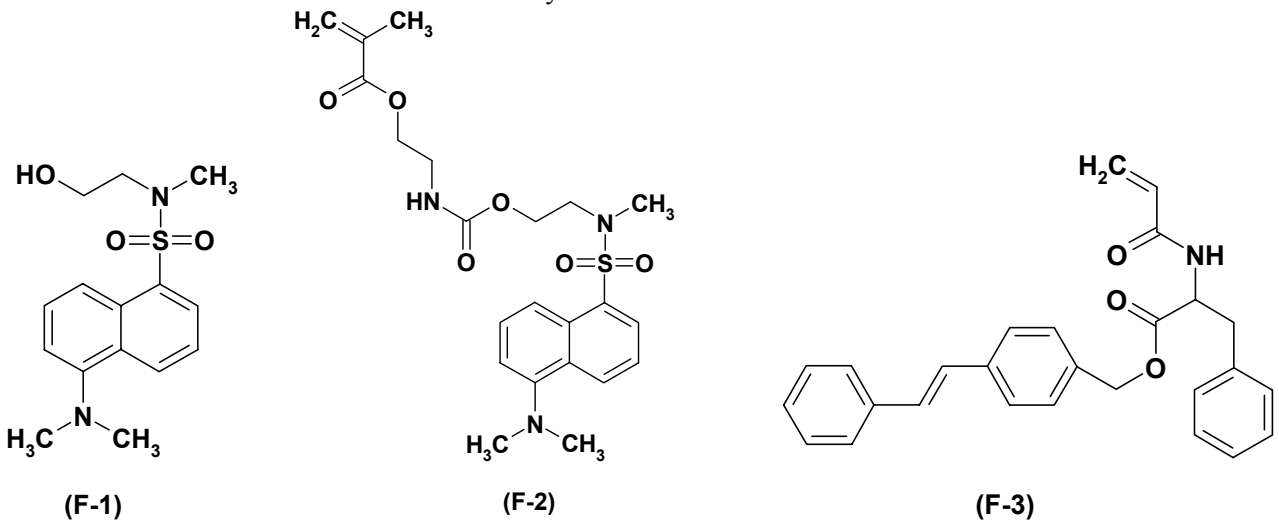

Fig. 1 – Structure of 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (F1), 5-dimethylamino-1-(β-methacryloyloxyethylcarbamoyloxyethyl)-N-methylsulfon-amidonaphthalene (F-2) and (S)-N-acryloylphenylalanine-4-styrybenzyl ester (F-3).

The chemical structure and the purity of the above compounds were confirmed by spectral methods, respectively IR, ^{1}H NMR, and UV spectroscopy. A summary of the characteristics of the fluorophores is shown in Table 1.

Table 1

Spectral characteristics of fluorescent derivatives, F-1, F-2 and F-3 respectively

Sample	1H-NMR (ppm)	FTIR (cm-1)	UV (nm)	λ_{em} (nm)**
F-1	8.47, 8.25, 8.18, 7.23, 7.64 (m, 6H, aromatic protons) 3.3 (t, 1H, O<u>H</u>) 3.56 (m, 4H, -C<u>H</u>$_2$C<u>H</u>$_2$-) 2.87 (s, 3H, N-C<u>H</u>$_3$) 2.78 (s, 6H, N(C<u>H</u>$_3$)$_2$)	3428 (OH), 650-945 (aromatic ring), 1197 and 1315 (SO_2N)	330	440* 520
F-2	8.5, 8.25, 8.15, 7.6, 7.25 (m, 6H, aromatic protons) 5.6 and 6.1 (s, 2H, *cis* and *trans* C<u>H</u>$_2$=C(CH$_3$)-) 3.4 and 4.2 (m, 4H, -C<u>H</u>$_2$C<u>H</u>$_2$-) 2.75 (m, 9H, N-C<u>H</u>$_3$ and N(C<u>H</u>$_3$)$_2$) 1.89 (s, 3H, C<u>H</u>$_3$)	3408 (OCONH), 650-945 (aromatic ring), 1197 and 1315 (SO_2N)	330	430 510*
F-3	7.4 and 7.6: (d, 2H, C$_6$H$_4$C<u>H</u>=C<u>H</u>C$_6$H$_5$) 6.1 (d, 1H, C<u>H</u>=CH$_2$) 5.6 and 6.3 (s, 2H, *cis* and *trans* C<u>H</u>$_2$=CH) 8.65 (d, 1H, NH) 7.3 (m, 5H, Phe protons) 5.1 (s, 2H, COO-C<u>H</u>$_2$-C$_6$H$_4$-) 4.5 (s, 1H, NH-C<u>H</u>-COO) 3.0 (d, 2H, CH$_2$-Phe)	1651 (amide I) 1535 (amide II) 1627 and 899 (stilbene)	285 300 315* 330	360 390* 410 440

- *maximum
- ** λ_{ex}: 330 nm (F-1; F-2) and 334 nm (F-3)

As it was aforementioned, the fluorescence spectral properties of synthesized derivatives can be influenced by the nature of various agents immersed in fluoroprobe solutions. For this reason, the dansyl probes are particularly useful for the study of microscopic interactions, as their fluorescence emission maximum is dependent upon their physicochemical microenvironment.[21] To get a better understanding of this interference, the fluorescence studies of dansylated derivatives were performed at the same excitation wavelength characteristic for the fluorophore moiety, 330 nm respectively.

If in case of 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (F-1) in DMF solution the fluorescence spectra revealed the presence of a maximum at 440 nm (short wave emission band, SE) and a small shoulder at 520 nm, which is typical for dansyl fluorophore, for 5-dimethylamino-1-(β-methacryloyloxyethylcarbamoyloxyethyl)-N-methylsulfonamidonaphthalene (F-2) the strong emission is detected at 520 nm (long wave emission band, LE) and is accompanied of a supplementary shoulder located at 433 nm which may prove the dual fluorescence.

As we already discussed, the strong emission from 440 nm is indebted to the dimethylamino group capable to adopt a coplanar conformation with the naphtyl group into a hydrophobic microenvironment. [20] It is obvious that the red shift appeared in the spectrum of F-2 could be an indication of the existence of a charge transfer structure in the excited state which involves the transfer of a lone pair electron of dimethylamino into a π-π* antibonding orbital of the naphthalene ring.

With the purpose of proving the dual emission of both dansylated derivatives, there were performed two experiments, the first one consisting in registration of the fluorescence spectra using solvents with different polarities and the latter, the effect of temperature on the location of fluorescence bands of the solution. Thus, in case of F-2 in a polar solvent (DMF) there were observed two emission bands as mentioned earlier (520 nm and 433 nm), while for low polarity solvents (THF, chloroform, ethyl acetate), a single emission band at about 490 nm was visualized (Figure 2a). Also, it was found that fluorescence emission varies with solvent polarity as measured for F-1(not shown), demonstrating thus the dual fluorescence.

The second experiment implied the monitoring of the emission band characteristic for dansylated derivatives with the temperature. With increasing temperature of the DMF solution, this significantly affects the intensities of dual fluorescence causing a decrease of SE and LE bands with 36% and 8% respectively. Moreover, this variation is accompanied by a hypsochromicaly shift of about 6 nm as the temperature increased from 27 at 50 °C (Figure 2b). From the above observations, we conclude that the twisted intramolecular charge transfer (TICT) achieved in the excitated state of the dansyl molecule from both dansylated derivatives play a significant role in TICT formation by the solvent polarity and temperature.

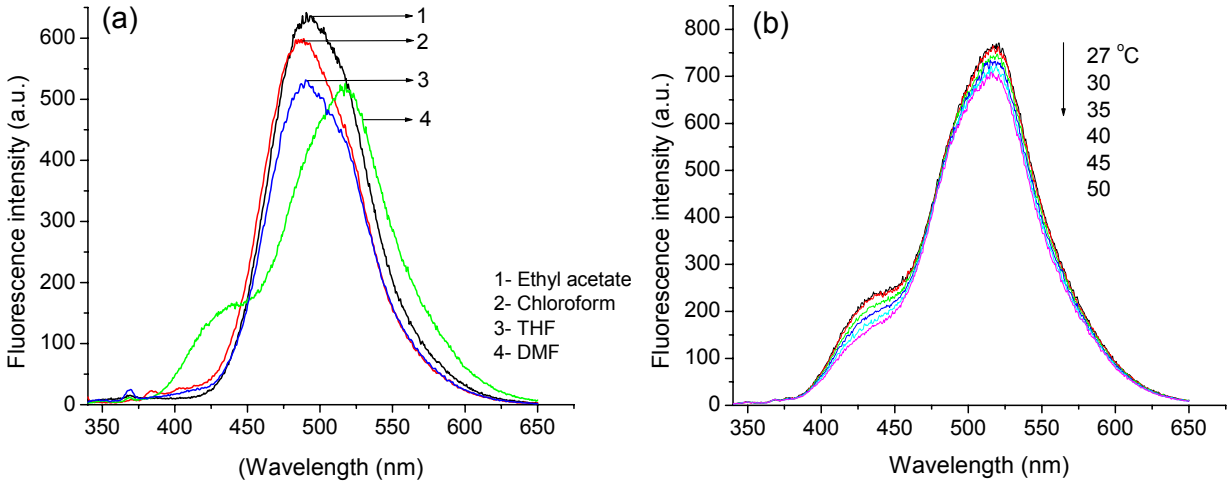

Fig. 2 – Fluorescence behavior of F-2 in polar/nonpolar solvents (a) and after increasing the temperature in DMF (b).

In order to obtain information about mechanism that could produce the fluorescence enhancement required of "turn-on" chemosensors, the acid sensing ability of dansylated fluoroprobes (F-1, F-2) in DMF solution was evaluated by fluorescence titration against increasing concentration of HCl and p-toluenesulphonic acid (APTS). Thus, Figure 3a displays the emission spectra of F-1 in the presence of different concentrations of HCl, where it can be observed that the fluorescence intensity increases proportionally with concentration of HCl, hereby the detection limit is 0.6 x 10^{-4} mol/L acid. Further, by adding higher concentration, respectively 11.3 x 10^{-4} mol/L HCl the fluorescence intensity is enhanced with about 29 %, whereas at 12.8 x 10^{-4} mol/L APTS it was remarked an increase of the emission maximum with 38 %, the minimal detected concentration being of 2.8 x 10^{-4} mol/L (Figure 3b). The graphical representation of the fluorescence emission in DMF solution of F-2 before and after adding 2.4 x 10^{-3} mol/L HCl illustrates an increase of fluorescence intensity with about 20% (Figure 4a). Consequently, the minimal detected concentration was 0.6 x 10^{-3} mol/L HCl suggesting a lower sensitivity for F-2 comparatively with that found in the case of F-1. Considering the APTS effect on the fluorescence intensity of F-2, the obtained results evidenced that a concentration of 18.5 x 10^{-3} mol/L generates an emission enhanced with about 32%, the detection limit being of 4.7 x 10^{-3} mol/L (Figure 4b). The response profile for F-1, F-2 might arise from the fact that the dansyl probe reacts with strong protic acids, but in contrast with those expected, the site of attack is not to the dimethylamino nitrogen. However, the reaction of the electrophilic reagents with both dansyl derivatives led to chemically modified species that are highly fluorescent and no to a decay of the fluorescence. The origin of fluorescence enhancement could be interpreted via the formation of emissive adduct between the N-substituted sulfonamide group and acid, implying thus a suppression of intramolecular photoinduced electron transfer (PET) from the nitrogen lone pairs to aromatic ring (naphthalene). Moreover, the rate of one or more vibrational relaxation processes from the excited state (radiative decay, internal conversion or intersystem crossing) is altered. Additionally, the existence of complexation-induced conformational restriction that would reduce the rate of vibrationally coupled internal conversion seems reasonable.

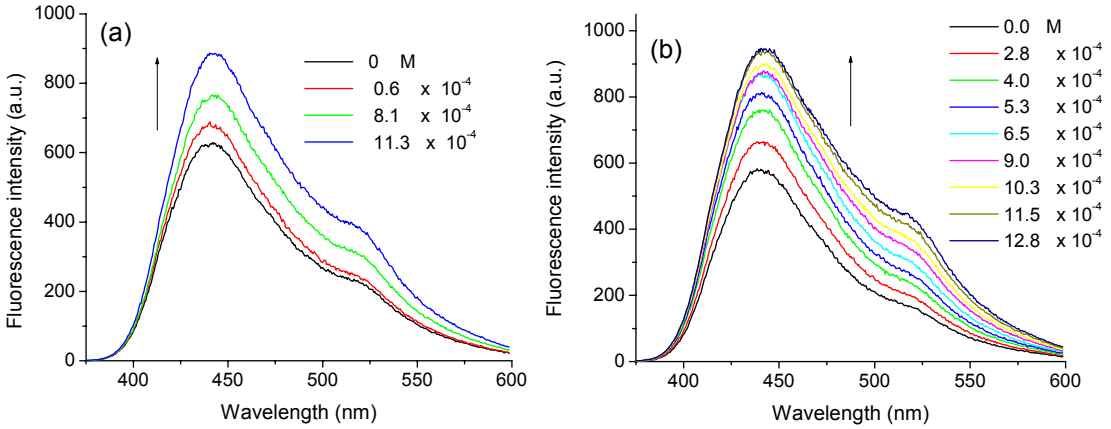

Fig. 3 – Emission fluorescence spectra of F-1 in DMF titrated with HCl (a) and APTS (b) (λ_{ex}=330 nm).

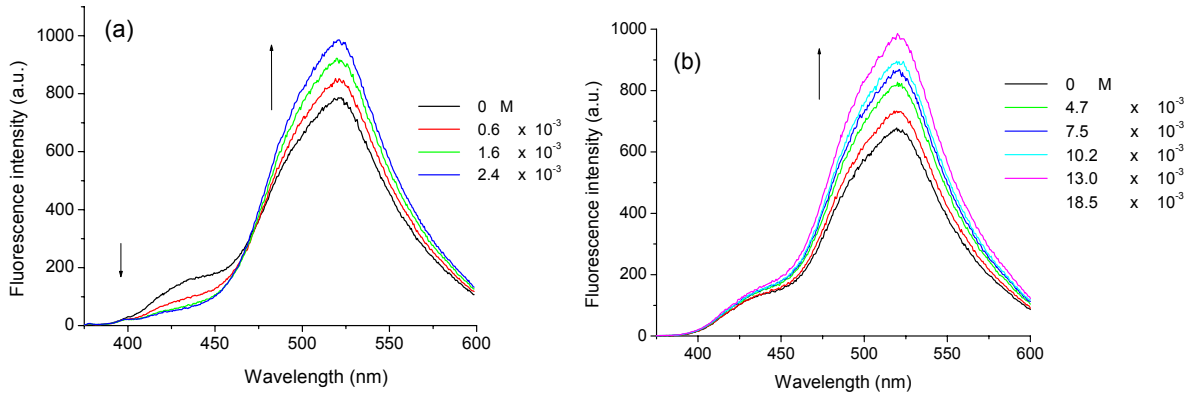

Fig. 4 – Emission fluorescence spectra of F-2 in DMF titrated with HCl (a) and APTS (b) (λ_{ex}=330 nm).

Analyzing the vibronic fluorescence spectrum of (S)-N-acryloylphenylalanine-4-styrybenzyl ester (F-3) it was noticed the presence of both monomer (360, 390 nm) and excimer emission (410, 440 nm), the latter indicating the possibility of a singlet state fluorophore to interact with another in the ground state to form a fluorescent an excimer (dimer) or aggregate complex. For the situation involving excimer formation in F-3, the observed fluorescence at increasing concentration of fluorophore from 1 x 10^{-5} mol/L to 5 x 10^{-5} mol/L (Figure 5) evidenced that the monomer fluorescence (360, 390 nm) decreases concomitantly with the intensity of the excimer fluorescence (410, 440 nm). The observation of a high ratio between the excimer intensity (410 and 440 nm) and that of the monomer (360 and 390 nm) provides support for the formation of excimer or aggregate in organic solvent.

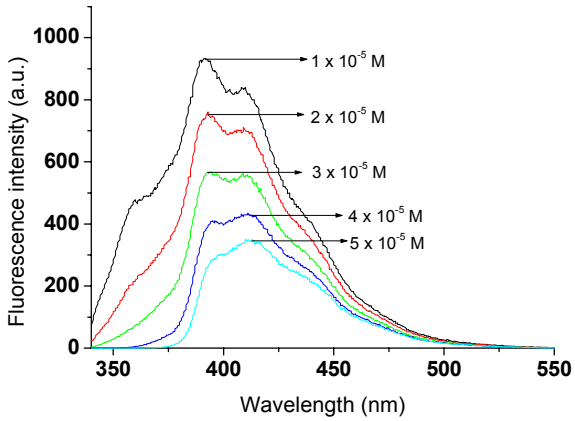

Fig. 5 – Emission fluorescence spectra at different concentration of F-3 in DMF solution.

We report here that the fluorescence characteristics of stilbene probe excited at 334 nm can be profoundly modified by adding different types of nucleobases. Thus, upon addition of 2.5 x 10^{-3} mol/L adenine, a 19% enhance of fluorescence emission intensity is determined, while the minimal detected concentration was about 0.5 x 10^{-3} mol/L (Figure 6a). An analogous plot of fluorescence intensity as a function of added cytosine is shown in Figure 6b, when the added pyrimidinic base produces a 44% increase in fluorescence emission intensity. Within this context, the intensity maximum is achieved at 22.7 x 10^{-3} mol/L, and the detection limit is 0.7 x 10^{-3} mol/L. Under similar experimental conditions but changing the added reactant, respectively, 0.89 x 10^{-3} mol/L thymine, the fluorescence emission intensity of stilbene molecule is reflected by a slight (11%) increase of the fluorescence, the minimal detected concentration being 0.2 x 10^{-3} mol/L (not shown). Therefore, for the same concentration of purinic or pyrimidinic bases (0.89 x 10^{-3} mol/L), it can be concluded that the most efficient agent which generates an increase of the fluorescence emission is thymine, followed by adenine and cytosine.

Interestingly, exciting at 267 nm, a fluorescence decay of the above stilbene derivative was observed.[17]

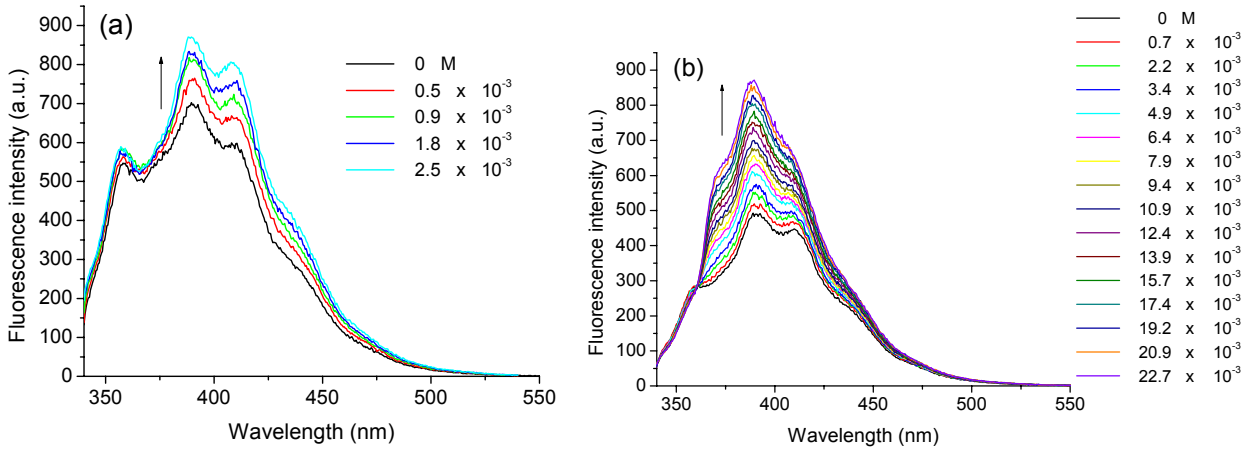

Fig. 6 – Emission fluorescence spectra of F-3 in DMF titrated with adenine (a) and cytosine (b) (λ_{ex}=334 nm).

In order to explain the reason that gives such a fluorescence response we may take in consideration that the natural nucleobases found in DNA, exhibit a weak fluorescence when these are excited with 334 nm. Therefore, cytosine shows two distinct fluorescence bands (366 nm and 381 nm), while adenine and thymine display three emission bands located at 358 nm, 375 nm and 410 nm, and respectively, at 360 nm, 375 nm and 400 nm (not shown). Thus, for every analyzed system which contains F-3 and adenine, cytosine or thymine, the enhanced fluorescence observed may be an effect of overlapping the characteristic emission of every constituent.

EXPERIMENTAL

Materials: All the reagents and solvents were purchased from Aldrich and used without any further purification. Details of the general procedures, synthesis and instrumentation have been described in our prior publications.[17, 20]

Characterization: ^{1}H-NMR and FTIR spectra were measured on a Bruker 400 MHz spectrophotometer in DMSO-d_6 at room temperature with TMS as an internal standard and a Specord M80 spectrophotometer respectively. The UV absorption spectra were recorded with a SPECORD M42 spectrophotometer in DMF solution. The steady state fluorescence emission spectra of the fluoroprobes were recorded in the range of 375-600 nm (dansylated derivatives) and 340-550 nm (stilbene derivative), the measurements being performed using a Perkin Elmer LS 55 spectrophotometer in DMF solution, with an excitation wavelength of 330 nm and 334 nm respectively at variable temperatures.

Synthesis of 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (F-1)

Dns-1 was synthesized as earlier reported.[20] Shortly, 5-(dimethylamino)naphthalene-1-sulfonyl chloride (2 g, 7.42 mmol) solved in dichloromethane was gradually added to a solution of 2-methylamino)ethanol (1.1 mL, 14.8 mmol) at 0 ^{o}C. After 30 minutes of stirring at this temperature the reaction continued at room temperature for other 24 hours, the resulting product being filtered and concentrated under reduced pressure. For further purification Dns-1 was solved in chloroform and eluted on silica gel column.

Synthesis of 5-dimethylamino-1-(β-methacryloyloxyethylcarbamoyloxyethyl)-N-methylsulfonamidonaphthalene (F-2)

2-isocyanatoethylmethacrylate (0.88 mL, 6.16 mmol) was drop wise added to a solution of 5-dimethylamino-1(β-hydroxyethyl)-N-methylsulfonamidonapthalene (1.9 g, 6.46

mmol) in 25 mL dioxane, using dibutyltindilaureate as catalyst. The mixture was stirred for 24 hours under nitrogen atmosphere at 45°C and then concentrated under reduced pressure. The resulting product (Dns-1) was eluted on silica gel column using chloroform as solvent.

Synthesis of (S)-N-acryloylphenylalanine-4-styrybenzyl ester (F-3)

The esterification of (S)-N-acryloylphenylalanine (2 g, 9.1 mmol) was performed by dissolving the monomer in tetrahydrofuran (THF) followed by the addition of 1.1′-carbonyldiimidazole (1.47 g, 9.1 mmol) as activation agent. The mixture was stirred at room temperature for one hour and then 1.91 g (9.1 mmol) stilbene methanol solved in THF was added continuing the stirring at room temperature for 3 days. The crude product was precipitated in water and collected by filtration. Yield 1.8 g (61.43%).

CONCLUSIONS

In summary, there were revealed new information about fluorescence behavior of three new fluoroprobes containing dansyl or stilbene molecule. Particularly, the dansyl derivatives show a considerably fluorescent enhancement as well as improved selectivity toward HCl and APTS, while the stilbene derivative, proved the same performance in the presence of some purinic and pyrimidinic bases. Thus, the highly efficient fluorescence "turn-on" sensing for this kind of analytes, will propose our compounds to find further applications in the development of chemosensors for biological molecules.

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