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New Compounds Measured by Fluorescence Spectroscopy. Amino-Fluorene-Thiophene Derivatives to Be Proposed as Polarity Indicators.

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Abstract

The solvatochromic effect is high in conjugate compounds and easy to observe by the colour change emitted when the solutions are exposed to UV light. It was found in a series of aminofluorene thiophene derivatives, previously synthesized, that irradiating at different wavelengths, the same pattern is obtained, *i.e*. a dual behaviour in the solvatochromism of the studied compounds. For each one, a bathochromic and hypsochromic effect exists, in polar and nonpolar solvents, respectively. Wavelength *vs*. polarity index plots clearly showed the abovementioned dual behaviour as well as the improved linearity in its plots. Amidst the wavelengths at which each compound is excited in each solvent, 280 nm was selected as the fixed wavelength for the measurements; (E)-9,9-diethyl-N-hexyl-N-phenyl-7-(2-(thiofen-2-yl) vinyl)-9H-fluoren-2-amine (M6-6) exhibits better linearity as compared to the other studied compounds, being the best to be proposed as polarity sensor or indicator.

Keywords: solvatochromism, polarity indicator, aminofluorene thiophene derivatives, fluorometry.

1.Introduction

In the last few years the interest to generate new compounds that allow determining properties or changes in the matter, without needing time-consuming approaches, has become a necessity. To make this possible, multiplecompounds that are sensitive to variations in solution have been synthesized; among them, compounds exist that can detect some change of property or characteristic and display it as a change in the sensor (transducer), as discussed elsewhere [1-7]. Within the multiple possible responses to be delivered, fluorescence is one of the most common. Numerous papers have been published where the detection of certain agents in solution were carried out using fluorescence, *e.g.* detection of ions [8,9], of specific sites in proteins [10], of pH [11], some small molecules and temperature changes [11-14]. Among the molecules intended to become sensors, a group of special interest exists: polarity sensors, specifically the molecules that undergo a change in their emission or fluorescence patterns, which allows correlating polarity changes in a solvent with the changes by solvatochromism [15,16]. The current research consists in studying electron donor molecules derived from fluorene and thiophene (Fig. 1). The nomenclature used is signalled in table 1. These molecules are part of the donor-□□acceptor (D-□-A) synthetic route of compounds, which undergo important changes by solvatochromism, however, the molecules shown here exhibit a linear behavior [17,18].

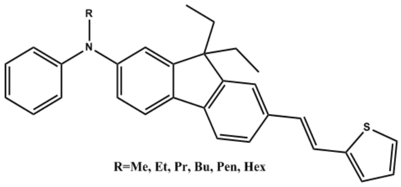

Figure 1. Molecular structure of the synthesized dyes: M6-1(Me), M6-2(Et), M6-3(Pr), M6-4(Bu), M6-5(Pen) and M6-6(Hex).

Table 1. nomenclature of the studied compounds

2.

Code name	IUPAC name
M6-1	(E)-9,9-diethyl-N-methyl-N-phenyl-7-(2-(thiophen-2-yl)vinyl)-9H-fluoren-2-amine
M6-2	(E)-N,9,9-triethyl-N-phenyl-7-(2-(thiophen-2-yl)vinyl)-9H-fluoren-2-amine
M6-3	(E)-9,9-diethyl-N-phenyl-N-propyl-7-(2-(thiophen-2-yl)vinyl)-9H-fluoren-2-amine
M6-4	(E)-N-butyl-9,9-diethyl-N-phenyl-7-(2-(thiophen-2-yl)vinyl)-9H-fluoren-2-amine
M6-5	(E)-9,9-diethyl-N-pentyl-N-phenyl-7-(2-(thiophen-2-yl)vinyl)-9H-fluoren-2-amine
M6-6	(E)-9,9-diethyl-N-hexyl-N-phenyl-7-(2-(thiophen-2-yl)vinyl)-9H-fluoren-2-amine

Experimental

All solvents used, both in synthesis and measurements, must be dry (Supp. Info. Methods). The synthesis of the products was reported elsewhere [17,18]. All UV-Vis measurements were run on an Agilent UV-Vis spectrophotometer. Spectrofluorometric measurements were conducted on a HORIBA Scientific Fluoromax-4 spectrofluorometer. The measurements were accomplished by using solutions between 2 and 3 μmol·L^{-1} of each dye in the assayed solvents (were the compounds are soluble): dichloromethane (DCM), tetrahydrofurane (THF), ethyl acetate (ETA), dioxane (DIO), acetone (ACT), acetonitrile (ACN), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

3. Results and discussion

The compounds under survey exhibit a noticeable color shift when exposed to wavelengths close to their maximum absorption (Fig. 2). Fluorometric measurements for these compounds showed various patterns due to solvent effect, however, this change does not present a unique clear trend.

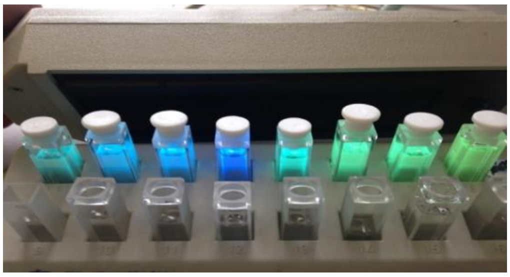

Figure 2. UV irradiated M6-1 solutions in different solvents. Solvents sorted by polarity, from left to right: DCM-THF-ETA-DIO-ACT-ACN-DMF-DMSO, *vs.* the pure solvent (without compound within).

Comparing the recorded fluorescence spectra for the six studied compounds, some important characteristics can be inferred for each one. In addition, some trends in the shift of the maximum emission peak can also be assessed. Two excitation wavelengths are selected, the first at about 380 nm (depending on the dye measured), corresponding to the maximum absorption, and the second 100 nm less than the former in order to observe which effect occurs close to wavelengths commonly emitted by UV lamps.

3.1 Behaviour of compounds in solution

When these compounds are exposed at two different wavelengths, in general, they show several emission patterns (Figs. 3 and Supp. Info. Figs. S1 to 5). Some molecules show a two maxima spectra that changes to one maxima, just changing the wavelength of excitation, this is the case of M6-2 and 4. M6-3 has a different behaviour, two maxima spectra to one in nonpolar solvent and one-to-one maxima in polar solvents. Products as M6-1, M8-5 and M8-6, show just one-to-one maxima pattern.

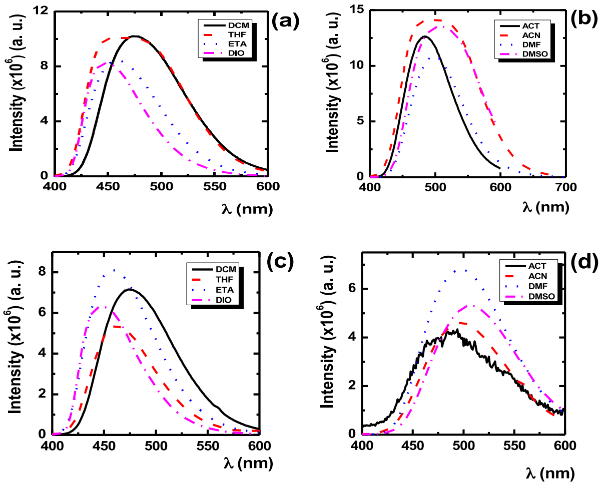

Figure 3.M6-1 emission in the assayed solvents, exciting at □ $_{max}$ in (a) nonpolar solvents; (b) polar solvents. At □ ≠ □ $_{max}$ in (c) nonpolar solvents; (d) polar solvents.

According on the maxima values of each spectra (Table 2 and Supp. Info. Table S1 to S5), a different change in the values is clearly noticed, showing two contrasting influences from the solvents. The results between non-polar solvents (DCM to DIO) and polar solvents (ACT to DMSO), indicate different electronic transitions. These transitions become more and more energetic when the polarity increases from DCM to DIO and the opposite happens when the polarity increases from ACT to DMSO, which may be ascribed to a change of character of the molecule main transition [19-25]. In addition, the above agrees with the idea that in nonpolar solvents the hypsochromic shift [26] would show the n-□* type transition that takes place from the nitrogen non-binding pair towards the conjugate chain. On the other hand, in polar solvents a bathochromic displacement [27] of the □□□* type transition, belonging only to the conjugate chain, occurs.

Table 2. M6-1 maximum emission in solvents of different polarity, excited at different □.

Solvent	Solvent polarity index	λmax excitation (nm)	λmax emission (nm)	λexcitation ≈ λlamp (nm)	λmax emission (nm)
DCM	3.1	377	475	280	474
THF	4.0	380	470		462
ADE	4.4	380	458		458
DIO	4.8	368	449		449
ACT	5.1	380	484		494
ACN	5.8	378	498		498
DMF	6.4	378	499		497
DMSO	7.2	387	511		507

3.2 Graph analysis, maximum emission-to-polarity ratio

In order to determine the relationship between maximum emission and solvent polarity changes, calibration curves were constructed to analyse their correlation. Different curves were obtained (Figs. 4 and Supp. Info. Figs. S6 to S10), that show the different patterns for each of the studied compounds in the employed solvents. This is the result of different types of excited states that decay towards fluorescence. In the current case, a transition from the electron donating nitrogen prevails in nonpolar solvents, while in polar solvents □ chain-dependent transition and its charge transfer predominate [31].

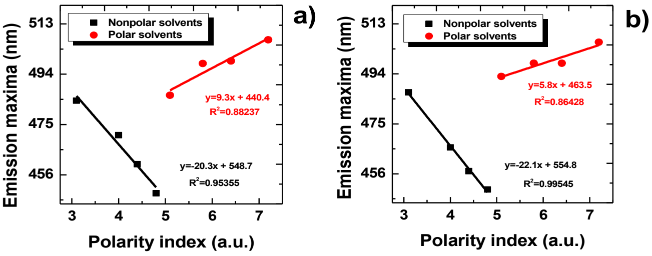

Figure 4. M6-6 polarity index *vs*. emission □$_{max}$: (a) exciting at □ $_{max}$; (b) exciting at □ ≠ □ $_{max}$.

Finally, a comparison of the squared correlation coefficients (Table 3), enables determining which compound is the best as sensor in the solvents and wavelength studied. Comparing each compounds values excited at the maximum absorption wavelength, it is observed that in nonpolar solvents M6-6 displays the highest relationship between the variables. On the other hand, in polar solvents, M6-1 exhibits the highest ratio, however, it is not possible to find any relationship between chain length and excitation maxima.

Table 3. Pearson's squared correlation coefficients for each line and for each studied compound (highest and lowest values are highlighted in blue and red, respectively)

	Excitation = □max		**Excitation □≠ □max**		**excitation average = □max**	**excitation average ≠ □max**	**Average of both excitations**
Compound/ solvent polarity	**nonpolar**	**polar**	**nonpolar**	**polar**			
M6-1	0.815	0.904**	0.972	0.718	0.859	0.845	0.852
M6-2	0.909	0.272*	0.959	0.792	0.591	0.875	0.733
M6-3	0.872	0.499	0.952*	0.713*	0.685	0.833*	0.759
M6-4	0.174*	0.690	0.964	0.808	0.432*	0.886	0.659*
M6-5	0.950	0.651	0.975	0.812	0.800	0.893	0.847
M6-6	0.953**	0.882	0.995**	0.864**	0.918**	0.930**	0.924**
Average of each type of solvent	0.779	0.650	0.969	0.785	-	-	-

***Hower value. **Higher value.**

When it is excited at other wavelength, M6-6 exhibits the highest variables ratio, in both polar and nonpolar solvents, and M6-3 the lowest of all. Also, in the above case, it was not possible to find a relationship with substituent length. Finally, averages comparisons show which wavelength and which compound is the best to sense polarity, in that case it is M6-6. As for wavelengths, exciting at 280 nm usually afforded the best results. On the other hand, the compounds are most efficient when measuring in nonpolar solvents. Comparing the compounds, the relationship between the M6-6 variables behaves more linear than the rest, M6-4 being the worst of them. Table 4 shows the coefficient values for each of the registered lines, showing they do not differ much each other (separating non-polar and polar solvents), but it exists a change in the signal (positive-to-negative), of the slope, where the correlation coefficients tend to be low (table 3).

Table 4. Coefficients of calibration curves (Figs. 4 and Supp. Info. Figs. S6 to S10), for each studied compound (y = mx+ b, where y = I; x = solvent polarity index; m = slope and b = y axis intercept). R values in the inset of any graphic.

Compound/ □□excitation	**□max**				**□□≠□□max**			
Solvent polarity	**Nonpolar**		**Polar**		**Nonpolar**		**Polar**	
Coefficient	**m**	**b**	**m**	**b**	**m**	**b**	**m**	**b**
M6-1	-15.1	524.6	12.0	424.6	-14.1	518.3	5.7	464.4
M6-2	-29.5	573.0	19.4	383.5	-17.3	531.4	10.5	431.9
M6-3	-21.0	579.3	0.30	490.9	-18.4	536.3	10.9	428.3
M6-4	-14.9	517.4	20,2	368.7	-15.2	525.1	10.4	432.7
M6-5	-16.7	533.2	8.5	446.6	-17.5	536.0	11.5	426.0
M6-6	-20.3	548.7	9.3	440.4	-22.1	554.8	5.8	463.5

Conclusions

Six compounds evidencing solvatochromic effect when exposed to UV radiation have been synthesized and assayed as polarity sensors or indicators. The emission spectra, excited at different wavelengths, were determined at both the maximum absorption and another fairly close maximum. A dual behavior of the maxima was determined owing to solvent effect: in polar solvents a bathochromic change occurs and in nonpolar solvents a hypsochromic change takes place. This behavior is related to different excited states that are stabilized and then decay in fluorescence, all due to solvent effect. Wavelength *vs*. polarity index plots clearly showed this dual behavior. The optimum wavelength to conduct measurements is 280 nm, and the compounds are most efficient when measuring in nonpolar solvents, being M6-6 which presents better linearity in its plots, as compared to the other studied compounds. So, M6-6 is the best to be proposed as polarity sensor or indicator.

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Supplementary Material

In this section it is shown the drying methods of the solvents used in this work, e.g. DMSO. Moreover, we show the emission patterns of M6-2, 3, 4, 5 and 6 with the respective emission maxima tables, discussed in the results and discussion section.