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(PHENOTHIAZINYL)VINYL-INDOLIUM CATIONIC DYES

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ABSTRACT. New 2-(2-(10*H*-phenothiazin-3yl)vinyl)-3*H*-indolium cationic dyes were successfully prepared by Knoevenagel condensation of 1,2,3,3-tetramethyl-3*H*-indolium iodide with 10-methyl-10*H*-phenothiazine-3-carbaldehyde and 10*H*-phenothiazine-3-carbaldehyde respectively. Their optical properties were emphasized by UV-Vis absorption spectroscopy. The position of their characteristic intramolecular charge transfer absorption maxima is situated in the visible range (550-630 nm), exhibiting solvatochromism induced by solvent polarity. Experimental evidences of linear optical properties were completed by a theoretical DFT computational study.

Key words: *10H-phenothiazine, indolium salts, cyanine dyes*

INTRODUCTION

The tuneable optical properties of cyanine dyes supported the development of new organic functional dyes. The phenothiazine was selected in the design of several Donor–π–Acceptor type molecular structures characterized by intense optical absorption and emission properties, taking benefit of its electron rich heterocyclic core which recommends it as an excellent electron donor and its butterfly conformation which may hinder the molecular aggregation.

The Knoevenagel condensation of N-alkyl quaternary ammonium salts, described as a convenient reaction path for the preparation of dimethine cyanine dyes [1] was successfully applied in the preparation of cyanine dyes

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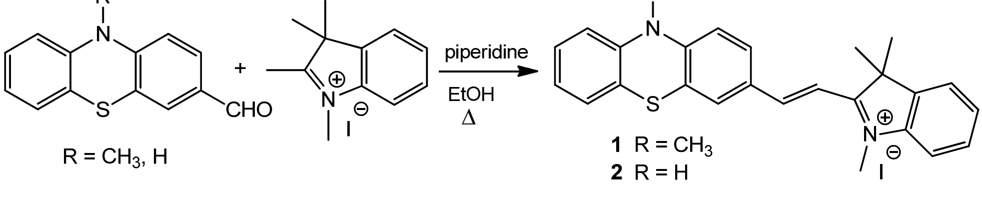
containing phenothiazine as electron donor moiety and indolium quaternary salts as acceptors. Condensation of 10-alkyl-10*H*phenothiazine-3-carbaldehyde derivatives with different 2, 3, 3-trimethyl-indolium quaternized salts such as: 5-carboxy-1-hexyl-2, 3, 3-trimethyl-indolium [2], 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium [3] and 1-ethyl-2,3,3-trimethyindolenium respectively, [4] gave cyanine dyes characterized by intense intramolecular charge transfer (ICT) absorption bands situated in the visible region of the electromagnetic spectrum. Their linear optical properties appear modulated by solvatochromism and substitution of the heterocyclic units with auxochromic groups recommending them for potential applications in materials science.

Our previous results in the preparation and assessment of the optical properties of cationic dyes containing electron donor 10*H*-phenothiazine units and electron acceptor pyridinium units connected through a vinylene bridge [5] stimulated our interest in the field of cyanine dyes. In this work we describe the syntesis of new 2-((phenothiazin-3yl)vinyl)-indolium cationic dyes designed to enrich the series of dimethine cyanine dyes reported in the literature with the purpose of gathering more systematic information on their structure-optical properties relationship.

RESULTS AND DISCUSSIONS

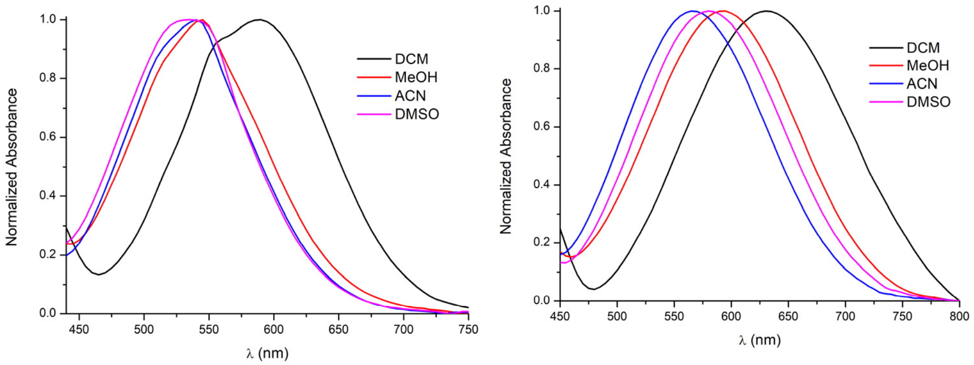
Two new 2-(2-(10*H*-phenothiazin-3yl)vinyl)-3*H*-indolium (PVI) cationic dyes were successfully prepared by Knoevenagel condensation of 1,2,3,3-tetramethyl-3*H*-indolium iodide with 10-methyl-10*H*-phenothiazine-3-carbaldehyde (PVI **1**) and 10*H*-phenothiazine-3-carbaldehyde respectively (PVI **2**), as shown in scheme 1.



Scheme 1

The structural assignments of PVI **1** and **2** were based on spectroscopic data. MS spectra confirmed the molecular weight of the cationic dyes. In the ^{1}H-NMR spectra the key signals generated by the protons belonging to the vinyl bridge appeared split in doublet with vicinal coupling constants of 16.2 Hz, thus suggesting the formation of the geometrical *trans*- isomer.

The optical properties of PVI **1** and **2** were emphasized by UV-Vis absorption spectroscopy. The position of their characteristic intramolecular charge transfer (ICT) π→ π* absorption maxima are situated in the visible range (550-630 nm), exhibiting solvatochromism induced by solvent polarity as depicted in figure 1. This behaviour was also observed in the case of similar cyanine dyes and explained by a better stabilization of the polar ground state upon increasing solvent polarity [4].



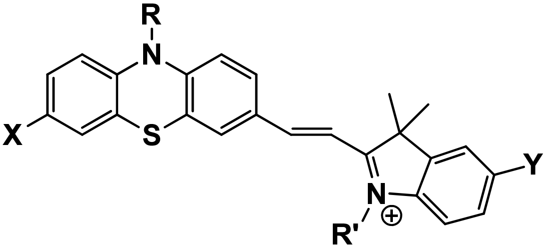
a **b**

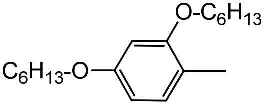
Figure 1. Electronic absorption spectra in different solvents for: a) PVI **1**, b) PVI **2**

A large batochromic shift can be observed in each case when dichloromethane (DCM) was used as a solvent. The position of the recorded absorption maxima shows an important red shift in the case of PVI **2** (λ_{max} 630 nm) as compared to PVI **1** (λ_{max} 585 nm) suggesting a superior electron donating ability of the unsubstituted phenothiazine unit.

In table 1 the electronic properties of PVI **1** and **2** were depicted together with those of previously reported similar cyanine dyes. The highest bathochromic shift was observed for the cyanine dye containing two auxochromic groups: one electron donor dialcoxiaryl substituent coupled to the phenothiazine unit and one electron withdrawing substituent (-COOH) attached to the indolium moiety (table 1). The length of the alkyl chain attached to the heterocyclic N atom slightly influenced the position of the absorption maxima.

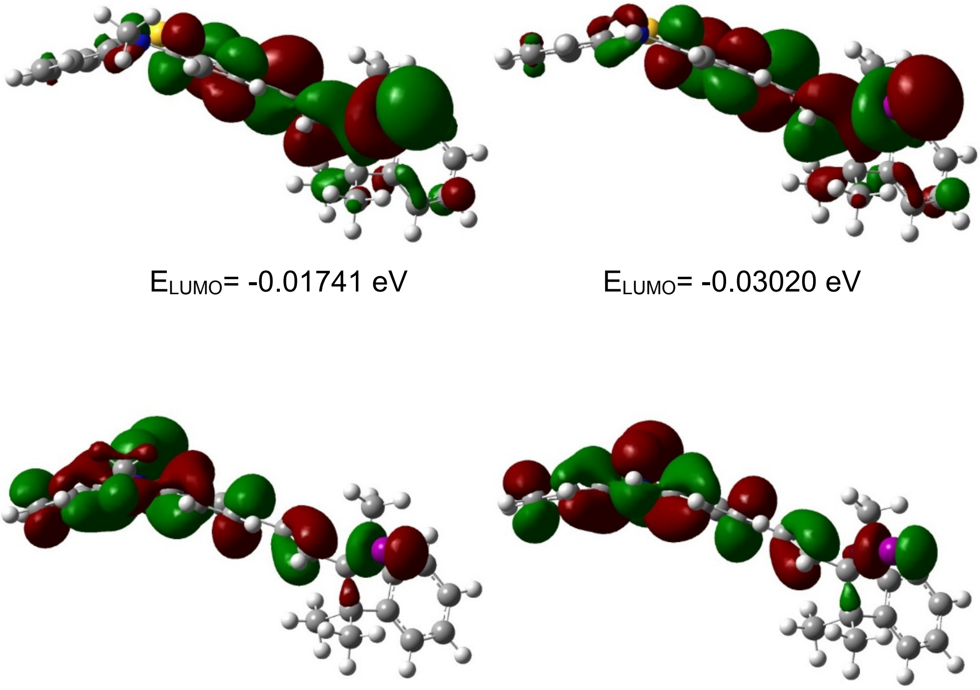
Table 1. Position of the characteristic intramolecular charge transfer π→π* absorption maxima for 2-((*N*-alkyl-10*H*-phenothiazin-3yl)vinyl)-3,3-dimethyl-1-alkyl-3*H*-indolium dyes in dichloromethane solvent.



R	R'	X	Y	λ_{abs}	Ref.
n-C_8H_{17}	C_2H_5	H	H	591 nm	[4]
n-C_6H_{13}	n-C_8H_{17}		-COOH	679 nm	[2]
CH_3	CH_3	H	H	585 nm	PVI **1**
H	CH_3	H	H	630 nm	PVI **2**

The steric effect induced by a bulky alkyl substituent attached to the phenothiazine N atom may render less effective the participation of the lone pair of electrons to the extended conjugated system. The optimized geometries of PVI **1** and **2** suggested an equatorial position of the substituent attached to the phenothiazine N atom, thus enabling the participation of the lone pair of electrons to the extended conjugated system.

An inspection of the electron distribution in the molecular orbitals of each PVI **1** and **2** indicated that the frontier filled orbitals HOMO appear located predominantly on the electron donor phenothiazine unit, whereas the unoccupied molecular obitals LUMO are located predominantly on the indolium core. In figure 2 plots of the frontier molecular orbitals are depicted together with the computed energies resulted by DFT geometry optimizations on PVI **1** and **2**. The separation of computed energy levels of the frontier molecular orbitals appeared slightly larger for PVI **1**.



E_{LUMO}= -0.01741 eV E_{LUMO}= -0.03020 eV

E_{HOMO}= -7.60449 eV E_{HOMO}= -7.59089 eV

PVI **1** PVI **2**

Figure 2. Plots of frontier molecular orbitals of PVI **1** and **2** and their corresponding values of computed energies resulted by DFT geometry optimizations and computation at B3LYP/6-31(d,p) level using the Gaussian 09W program package.

CONCLUSIONS

The new 2-(2-(10*H*-phenothiazin-3yl)vinyl)-3*H*-indolium cationic dyes described in this work broadened the series of cyanine dyes containing phenothiazine as electron donor and indolium quaternary salts as electron withdrawing unit. Their optical properties experimentally observed by UV-Vis absorption spectroscopy indicate a superior electron donating ability of the unsubstituted phenothiazine unit, in comparison to the N-alkyl derivatives.

EXPERIMENTAL SECTION

HRMS spectra were recorded using Thermo LTQ *Orbitrap XL* mass spectrometer.

NMR spectra were recorded at room temperature on 600 MHz Bruker Avance instrument. Chemical shifts are expressed in δ (ppm) relative to standard tetramethylsilane (TMS).

UV-Vis absorption spectra were recorded in various solvents with a Perkin Elmer Lambda 35 spectrometer DFT calculations:

Geometries constructed with Gaussview [6] have been optimized with the Gaussian software package [7] using the 6-31G(d,p) basis set. Frequency analysis has been performed in order to ensure that the optimized geometries are genuine minima.

Phenothiazine carbaldehydes were prepared according to our previously reported procedures. [8]

1,2,3,3-Tetramethyindolium iodide was prepared according to literature reported procedure [1].

General procedure for the synthesis of 2-(2-(10H-phenothiazin-3yl)vinyl)-3H-indolium cationic dyes

1,2,3,3-tetramethyindolium iodide (1.5g, 5.0 mmol), phenothiazin-3-yl carbaldehyde (4.5 mmol) and piperidine (1.0 ml) were added to 50 ml ethanol. The reaction mixture was stirred for 12 h under reflux. The precipitate was filtered and the solvent was evaporated to dryness. The solid was purified by column chromatography on silica gel solid support using dichloromethane as mobile phase.

2-(2-(10-methyl-10H-phenothiazin-3yl)vinyl)-3H-indolium iodide 1.

Purification by column chromatography, gave 0.6 g, yield 35%, dark purple powder.

HRMS: found 397.17410, $C_{26}H_{25}N_2S^+$ requires 397.17330

^{1}H RMN (600 MHz, DMSO) , δ(ppm)= 1.78 (s, 6H); 3.45 (s, 3H); 4.11 (s, 3H); 7.06 (m, 2H); 7.13 (d, 1H, ^{3}J= 8.4 Hz); 7.22 (dd, 1H, ^{3}J=7.8 Hz, ^{4}J= 1.8 Hz); 7.28 (td, 1H, ^{3}J=7.8 Hz, ^{4}J= 1.2 Hz); 7.54 (d, 1H, 16.2 Hz); 7.61 (m, 2H); 7.85 (d, 1H, ^{3}J=7.8 Hz); 8.08 (dd, 1H, ^{3}J=9.0 Hz, ^{4}J= 1.8 Hz); 8.12 (d, 1H, ^{4}J= 1.2 Hz); 8.32 (d, 1H, 16.2 Hz)

^{13}C RMN (150 MHz, DMSO), δ(ppm)= 152.4; 150.1; 143.8; 142.3; 133.0; 129.4; 129.3; 128.6; 128.2; 127.4; 124.2; 123.2; 123.0; 121.4; 116.1; 115.3; 115.2; 110.8; 55.4; 52.2; 44.1; 36.3; 34.6; 26.0; 22.6;

2-(2-(10H-phenothiazin-3yl)vinyl)-3H-indolium iodide 2.
Purification by column chromatography, gave 0.1g, 25% as dark powder. HRMS: found 383.15877, $C_{25}H_{23}N_2S^+$ requires 383.15765.

^{1}H RMN (600 MHz, DMSO), δ(ppm)= 1.75 (s, 6H); 4.05 (s, 3H); 6.63 (dd, 1H, ^{3}J= 7.8 Hz), 6.72 (m, 2H); 6.84 (t, 1H); 6.95 (d, 1H, ^{3}J=7.0); 7.03 (t, 1H, ^{3}J= 7.8 Hz); 7.37 (d, 1H, ^{3}J=16.2 Hz); 7.58 (m, 2H); 7.83 (m, 4H); 8.18 (d, 1H, ^{3}J= 16.2 Hz)
^{13}C RMN (150 MHz, DMSO), δ(ppm)= 152.4; 146.7; 143.5; 142.3; 139.0; 129.3; 129.2; 128.9; 128.8; 128.7; 128.4; 126.7; 123.9; 123.5; 123.2; 117.6; 116.3; 115.9; 114.8; 114.7; 109.1; 34.2; 26.2; 22.6; 22.0

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