Synthesis and solvatochromism studies of novel bis(indolyl)methanes bearing functionalized arylthiophene groups as new colored materials

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The demand for dyes with solvatochromic properties has increased in the last few years, mainly due to their wide range of applications in the analytical and industrial fields, such as in the textile industry. The phenomenon of solvatochromism is associated with the differential solvation of the ground and excited states of the solvatochromic compounds, leading to an important tool for the study of the nature of solute–solvent interactions. In this paper we report the synthesis of new bis(indolyl)methanederivatives bearing arylthiophene spacers (2a–d) functionalized with electron-donating and electron-withdrawing groups, and the photophysical studies in different solvents, such as ethanol, acetonitrile, dichloromethane, trichloromethane, dimethylsulfoxide, diethyl ether and 1,4-dioxane. Aiming to explore their solvatochromic behavior in the ground and excited states, all solvents employed have different hydrogen-bond donor abilities. The largest colour modifications were visualized for compound 2b, the solution colours of which are orange in DMSO, blue in trichloromethane, green in dichloromethane and purple in 1,4-dioxane. A negative solvatochromism was observed in 2b and positive one in 2a, 2c and 2d.

Introduction

Over the years, a large number of studies have been conducted in order to discover the influence of the solvent on the chemical and physical properties of the solute. The different solvations of the ground and first excited states are associated with the solvatochromism phenomenon, which is an important tool for the study of the nature of solvent–solute interactions. Dyes with solvatochromic properties have been widely applied to investigate the solvent properties of ionic liquids1,2 and/or solvent mixtures,3 and to detect low (below 50 ppm) concentrations of water in aprotic solvents.4 Studies with hemicyanine dyes are very relevant due to their application in the textile industry.5,6

The strong hydrogen-bond donor capability of the indolyl group NH in bis-(indolyl)methanes can lead to an internal charge transfer (ICT) state, which is responsible for a wide range of colour changes. Thus, the hydrogen bonding ability of the indolyl group can be modulated by the donor H-atom of the solvent and other guest species.7 As an example, Wang et al.8 reported a bis-(indolyl)methene which is a colorimetric sensor for aspartate and glutamate in water. The same authors9 published a simple tris-(indolyl)methene able to detect fluoride anions, also by naked eye detection of the colour change from yellow to pink, based on proton transfer stages. Also, they reported that the introduction of an electron withdrawing or donating group at the indole moiety modified the acidity of the hydrogen bond sites, resulting in a positive effect on the sensitivity and selectivity for anions. Following our research interest10 in photophysical and photochemical studies of new emissive and chromogenic materials, herein we report the synthesis and photophysical studies of four novel bis(indolyl)methane derivatives bearing arylthiophene spacers (2a–d) functionalized with electron-donating and electron-withdrawing groups (Scheme 1), in different solvents, such as ethanol, acetonitrile, dichloromethane, trichloromethane, dimethylsulfoxide, diethyl ether and 1,4-dioxane, all with different hydrogen bond donor (HBD) abilities, with the purpose of exploring their solvatochromic behaviour in the ground and excited states.

Experimental section

General synthesis

The reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck
Synthesis of bis-[indolyl]methanes 2a–d

KHSO₄ (1.20 mmol) was added to a mixture of indole (2.40 mmol) and formyl arylthiophene precursors 1a–d (1.20 mmol) in dry methanol (10 ml), and the reaction mixture was stirred at room temperature for 7 h. Then water (10 ml) was added to quench the reaction, and the aqueous phase was extracted with trichloromethane (3 × 20 ml). The organic phase was dried with anhydrous MgSO₄ and the crude compounds 2a–d were purified by recrystallization from trichloromethane.

3,3′-[(5′-Phenyl-2′-yl)imidoyl]bis[1H-indole] (2a). Pink solid (87%). Mp: 220.8–222.0 °C. UV (acetone): λ max (log ε) 292.0 (4.60). IR (Nujol) ν = 3383 (NH), 2920, 2953, 1548, 1493, 1415, 1329, 1214, 1158, 1119, 1091, 1033, 1006, 822, 793, 761 cm⁻¹. ¹H NMR (DMSO-d₆) δ = 6.13 (s, 1H, CH), 6.86–6.91 (m, 3H, 2× H-5 and H-3'), 7.01–7.08 (m, 4H, 2× H-6 and 2× H-2'), 7.21 (t, 1H, J= 7.5 Hz, H-4'), 7.30–7.36 (m, 5H, H-5', H-3', H-2', H-6' and H-4'), 7.42 (d, 2H, J = 7.5 Hz, 2× H-7'), 7.53 (d, 2H, J = 8.4 Hz, 2× H-4'), 10.89 (s, 2H, 2× NH). ¹³C NMR (DMSO-d₆) δ = 135.13 (CH), 111.52 (C₅' and C₆'), 117.66 (2× C₃), 118.32 (2× C₅), 119.07 (2× C₇), 120.97 (2× C₆), 122.84 (C₄'), 123.35 (2× C₂), 124.83 (2× C₄), 125.92 (C₃'), 126.28 (2× C₃a), 127.08 (C₄'), 128.97 (C₃' and C₅'), 134.04 (C₁'), 136.47 (2× C₇a), 140.92 (C₅'), 149.53 (C₂'). MS (EI) m/z (%): 404 (M⁺), 100, 403 (36), 286 (42), 243 (27), 117 (21), 89 (10). HRMS: (EI) m/z (%) for C₂₇H₂₄N₄S: calcd 447.1376; found 447.1371.

UV/Vis absorption spectra were recorded on a Perkin Elmer lambda 45 spectrophotometer and fluorescence on a Perkin Elmer L55. The linearity of the fluorescence emission vs. the concentration was checked in the concentrations used (10⁻⁴–10⁻⁶ M). A correction for the absorbed light was performed when necessary. The photophysical characterization was performed by a stock solution of compounds 2a–2d (ca. 10⁻³ M) dissolving an appropriate amount of the compound in a 10 ml volumetric flask and diluting it to the mark with absolute ethanol, acetone, dichloromethane, trichloromethane, dimethylsulfoxide, 1,4-dioxane and diethyl ether. The stock solutions were then diluted till 10⁻⁵–10⁻⁶ M. All the measurements were performed at 298 K. Luminescence quantum yields were measured using a solution of quinine sulphate in sulphuric acid (0.1 M) as the standard [Φₚ = 0.54].

All solvents used were of the highest purity and were from Merck. The spectroscopic polarity parameters, physical
properties and polarity functions of the solvent used are presented in Table 1.

Results and discussion

In order to compare the effect of the electronic nature of the substituent at position 4 of the aryl moiety on the solvatochromic properties of chromophores 2a–d, formyl-derivatives containing electron-donor or electron-withdrawing groups (R = H, MeO, NMe2, NO2) at the arylthienyl moiety were used as precursors. Indole and 5-phenylthiophene-2-carbaldehyde 1a were commercially available and the synthesis of 5-(4-methoxyphenyl)thiophene-2-carbaldehyde, 5-(4-(N,N-dimethylamino)phenyl)thiophene-2-carbaldehyde and 5-(4-nitrophenyl)thiophene-2-carbaldehyde 1b–d has been reported by us recently.11c,b

Thus, heterocyclic probes 2a–d with the arylthienyl moiety (bearing donor or electron-withdrawing groups) linked to the bis-(indolyl)methane system were synthesized in moderate to excellent yields (42–90%) in methanol at room temperature for 7 h, catalysed by potassium hydrogen sulphate (Scheme 1).11c

In the 1H NMR spectra of bis-(indolyl)methanes 2a–d, a broad singlet at about 10.17–10.89 ppm was attributed to the two NH groups in the bis-indolyl moiety. The NH was also identified by IR spectroscopy as a sharp band within the spectral region of 3383–3409 cm⁻¹.

Many chromophores show shifts in the absorption and emission bands in different solvents, which could be due to differences in the solvent properties such as polarity, relative permittivity and the solvent’s polarization. Looking at the photophysical properties of the solute, such as the dipole moment and polarization changes of the molecule in the ground and excited states, the solvent effect can offer relevant information. The dipole moment changes in the molecule in the excited state, with respect to the ground state, can be achieved by different methods based on solvatochromism (internal electric field effect).12,13 When the absorption and/or emission bands of a compound change with the solvent polarity, they are called solvatochromic. It can be either positive or negative, depending on whether a red or a blue shift is observed with the increase of the solvent polarity, respectively.14

One method used for quantitatively characterizing solute–solvent interactions is the Kamlet–Taft equation, in which the absorption and emission energies are correlated with different solvent parameters by the following eqn (1):

\[ \delta \Pi^\alpha = 10 \left( \frac{\nu_\alpha}{\nu} \right) \beta + \delta \Pi^* + \delta \Pi^{**} \]

where \( \nu_\alpha \) is the value of absorption and/or emission in a reference solvent; \( \alpha \): the solvent’s hydrogen bond donor (HBD) acidity; \( \beta \): the solvent’s hydrogen bond acceptor (HBA) basicity; \( \Pi^\alpha \): the solvent’s dipolarity/polarizability; and the parameters \( a, b \) and \( p \) (corresponding to the responses of the solute property to the solvent property) can be obtained through a multiparametric fitting.

In order to estimate the dipole moments, the absorption and fluorescence emission spectra of compounds 2a–d were obtained in different solvents such as absolute ethanol, acetonitrile, dichloromethane, trichloromethane, dimethylsulfoxide, 1,4-dioxane and diethylether. These solvents present a dielectric constant (\( \varepsilon \)) varying from 2.2 to 47.2 (see Table 1). In Table 1, the \( \alpha, \beta \) and \( \Pi^* \) parameters of all solvents tested16 are summarized.

The photophysical data, such as the maximum wavelength of absorption and emission bands, as well as the charge transfer bands of compounds 2a–d in the studied solvents, are presented in Table 2.

Concerning the same solvent, the insertion of electron-donating (OMe, NMe2) and electron-withdrawing (NO2) groups in compounds 2b, 2c and 2d, respectively, induced changes in the ground and excited states14 when compared to compound 2a. Fig. 1 shows the UV/Vis absorption and emission bands of all compounds studied in acetonitrile, where a red shift is observed. In the absorption band, a value of 292 nm (2a) < 300 nm (2b) < 325 nm (2c) < 370 nm (2d) is presented (see Table 2 and Fig. 1), with the largest band shifts being observed for compound 2d (\( \Delta \lambda = 78 \) nm) with an electron-withdrawing group (NO2). However, in the emission band, a value of 420 nm (2a) < 365 nm (2b) < 400 nm (2c) < 450 nm (2d) is detected (see Table 2 and Fig. 1), with the longest shift being observed for compound 2d (\( \Delta \lambda = 30 \) nm) with an electron-withdrawing group (NO2). The presence of lone pairs of electrons at the oxygen and nitrogen atoms does not change the \( \pi-\pi^* \) nature of the transition, but affects the energy levels of the n–\( \pi^* \) transitions.14 The relative fluorescence quantum
yield of compounds 2a–2d was measured in all solvents studied using a solution of quinine sulphate in sulphuric acid as a reference.

Fluorescence quantum yields were found to be ca. \( \phi = 0.01-0.06 \) for 2a, ca. \( \phi = 0.01-0.07 \) for 2b, ca. \( \phi = 0.03-0.30 \) for 2c and ca. \( \phi < 1 \times 10^{-3} \) for 2d. As can be seen, the highest values of fluorescence quantum yield were obtained for compound 2c with a dimethylamino group and the lowest for 2d with a nitro group.

Compounds containing electron-withdrawing groups, such as 2d, have a low-lying \( n-\pi^* \) excited state and thus exhibit low fluorescence quantum yields, due to a non-radiative process. In compound 2c, the transitions corresponding to the promotion of an electron from an \( n \) orbital to a \( \pi^* \) orbital are more intense than the \( n-\pi^* \) transitions involving the lone pairs at the nitro group, which justifies the highest fluorescence quantum yield observed.

Concerning the different solvents, compound 2a shows an absorption band at ca. 292 nm and in apolar solvents such as trichloromethane and 1,4-dioxane a charge transfer (CT) band at 450 nm and 440 nm is observed, respectively. A colour change from colourless to yellow (1,4-dioxane) and/or orange (trichloromethane) is also identified (Fig. 2). In relation to the emission, a change in the maximum band from 365 nm (trichloromethane) to 455 nm (dimethylsulfoxide) could be seen (Fig. 3A and Table 2).

Compound 2a in the most apolar solvents has an emission band at ca. 365 nm, and with the solvent polarity increase, a red shift in the emission band to 390 nm, 450 nm and 455 nm for ethanol, acetonitrile and DMSO, respectively, is detected. In this case a positive solvatochromism is observed (Fig. 3A).

A hypsochromic shift (blue shift) of the CT absorption bands in compound 2b with the solvent polarity increase is observed, whereas the CT maximum absorption band appears...
Compound 2c is practically not affected in the ground state with the polarity of the solvent, presenting an absorption band centered at ca. 325–330 nm, with the exception of trichloromethane in which a CT band at 415 nm and a red color is observed (Fig. 2). In the emission spectra a bathochromic shift is detected with the solvent’s polarity increase, being the maximum of the emission band centered at ca. 386 nm (diethyl ether, 1,4-dioxane) < 390 nm (ethanol) < 395 nm (dichloromethane) < 400 nm (trichloromethane, acetonitrile) < 405 nm (DMSO) (Fig. 3C). Furthermore, compound 2d, in a similar manner to compound 2c, is practically not affected in the ground state, presenting an absorption band around 365–374 nm, as well as in the emission spectra where a weak emission is observed centered at ca. 450 nm in all solvents. On the other hand, in the most apolar solvent, 1,4-dioxane, it presents a CT band at ca. 510 nm, giving a red color in this solvent (Table 2 and Fig. 2).

Overall, regarding the solvatochromic effect in the excited state (see Fig. 3), the most pronounced was observed for compounds 2a, 2b and 2c where a red shift in the emission was obtained for 2a and 2c, and a blue shift in the absorption for 2b, with the solvent polarity increase. Considering these results, the multiparametric fitting of the Kamlet–Taft eqn (1) was carried out using the solvent parameters listed in Table 1 for all solvents. Based on this fitting a linear plot of \( \nu_{\text{exp}} \) versus \( \nu_{\text{calc}} \) was determined for compounds 2a–2c; the fitted parameters are presented in Table 3.

The \( p \) values in Table 3 show that the contribution of dipolarity/polarizability decreases the stabilization of the excited state of the compounds from 2c, 2a to 2b, where 2b is the most unstable and 2c the most stable in the excited state. Looking at coefficient \( a \), compounds 2a and 2c are less negative than 2b, suggesting stabilization of excited states for 2a and 2c.

The dipole moments in the ground and excited states were estimated taking into account the theory of Kawski et al.\(^{18}\) which can be defined by: \( \nu_{\text{g}} = \nu_{\text{e}} = m_{1} f(\epsilon, n) + \text{constant} \) and \( \nu_{\text{g}} + \nu_{\text{e}} = m_{2} [f(\epsilon, n) + 2 g(n)] + \text{constant} \), whereas \( \nu_{\text{g}} \) and \( \nu_{\text{e}} \) are the band absorption and emission frequencies (cm\(^{-1}\));

\[
f_{0}\epsilon_{n} \mu_{\text{p}} \delta_{n}^{\mu_{\text{p}}^{2}} \frac{2n^{2} \mu_{\text{p}}^{2} \mu_{\text{p}}^{2}}{n^{2} - 1}
\]

is the solvent polarity parameter and

\[
g_{\delta n} \mu_{\text{p}}^{2} \delta_{n}^{\mu_{\text{p}}^{2}} = \frac{m_{1}^{1/4} \mu_{\text{p}}^{2} - \mu_{\text{p}}^{2}}{\hbar c a^{2}}
\]

where \( \mu_{\text{p}}^{2} \) is Planck’s constant, \( c \) the velocity of light in vacuum, \( \epsilon \) the permittivity and \( n \) the refraction index, \( \mu_{\text{p}} \) and \( \mu_{\text{g}} \) the dipole moments in the ground and excited states. If the

Table 3 \( \nu_{0}, a, b \) and \( p \) values, in cm\(^{-1}\), slope and correlation coefficients obtained from the Kamlet–Taft multiparametric fitting of the absorption (2b) and emission data (2a, 2c)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu_{0} ) (cm(^{-1}))</th>
<th>( a ) (cm(^{-1}))</th>
<th>( b ) (cm(^{-1}))</th>
<th>( p ) (cm(^{-1}))</th>
<th>Slope</th>
<th>( r^{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>25642</td>
<td>-4221</td>
<td>11307</td>
<td>-9573</td>
<td>1</td>
<td>0.73</td>
</tr>
<tr>
<td>2b</td>
<td>33149</td>
<td>-6436</td>
<td>1241</td>
<td>-12381</td>
<td>1</td>
<td>0.87</td>
</tr>
<tr>
<td>2c</td>
<td>27073</td>
<td>-3613</td>
<td>-1914</td>
<td>-985</td>
<td>1</td>
<td>0.99</td>
</tr>
</tbody>
</table>
ground and excited states are parallel,\textsuperscript{19} the dipole moment of molecules in the ground and excited states can be determined by the equations

$$m_2-m_1 \frac{1}{2} \frac{h c a^{-1} i=2}{2m_1} \delta \mu$$

and

$$m_3 \cdot \mu m_2 \frac{1}{2} \frac{h c a^{-1} i=2}{2m_2} \delta \mu$$

The ground and excited state dipole moments for compounds 2a and 2c were determined through the linear curve fitting of $\nu_4 - \nu_1$ and $\nu_6 + \nu_1$ as a function of $f(\epsilon, n)$ and $f(\epsilon, n) + 2 g(n)$. The data were fitted to a straight line and the resulting slopes lead to the $m_1$ and $m_2$ values. The dipole moments were then calculated considering the above equations and are summarized in Table 4. According to Table 4 the values of $\mu_{2a} = 1.78$ D, $\mu_{2a} = 6.82$ D ($\Delta \mu = 5.04$ D), $\mu_{2c} = 3.60$ D, and $\mu_{2c} = 5.48$ D ($\Delta \mu = 1.88$ D) were obtained. The values obtained indicate that compounds 2a and 2c have excited state dipole moments ($\mu_2$) higher than those in the ground state ($\mu_1$). This fact means that compounds 2a and 2c are more polar in the excited states when compared to the ground states. The higher dipole moments in the excited state could suggest the appearance of a relaxed intramolecular charge transfer (ICT) state. Such a solvent relaxation explains the increase in the red shift of the fluorescence spectrum with the solvent polarity increase.\textsuperscript{14}

Since compound 2b presented a strong negative solvatochromism whereas the transfer of charge in the CT excited state is antiparallel to the ground state (the excited state has a lower dipole moment than the ground state), the dipole moments were calculated according to the Lippert–Mataga Eqn (4).\textsuperscript{14}

$$\begin{align*}
\frac{2}{3} \nu_4 - \nu_1 \frac{1}{h c} \frac{\mu_4 - \mu_1}{3} \mathrm{~A}^{-1} \Delta \mu \quad \text{constant} \\
\nu_6 + \nu_1 \frac{1}{h c} \frac{\mu_6 - \mu_1}{3} \mathrm{~A}^{-1} \Delta \mu \quad \text{constant} \\
\frac{1}{h c} \frac{\mu_6 - \mu_4}{3} \mathrm{~A}^{-1} \Delta \mu \quad \text{constant}
\end{align*}$$

The slope from the linear regression of $\nu_4 - \nu_1$, $\nu_6 + \nu_1$ or $\nu_4$ as a function of $\Delta \mu$ gives us the dipole moment of compound 2b in the ground ($\mu_1$) and excited ($\mu_2$) states and is presented in Table 4. Looking at Table 4, values of 14.5 D and 1.30 D for $\mu_2$ and $\mu_1$ ($\Delta \mu = 13.2$ D), respectively, were obtained for 2b. As expected, the ground state dipole moment value is really higher compared with the excited state, and with the other compounds, which justifies the larger negative solvatochromism shown by compound 2b, as well as the strong colour changes in the different solvents studied.

### Conclusions

Novel bis-iodolylmethanes 2a–d bearing functionalized arylthiophene spacers were synthesized in moderate to excellent yields through a simple synthetic procedure and a simple purification methodology and completely characterised.

The solvatochromic studies showed that the largest colour modifications were visualized for compound 2b, whereas colours of orange for DMSO, blue for trichloromethane, green in dichloromethane and purple for 1,4-dioxane were observed. Apart from compound 2b, all other compounds showed a positive solvatochromism. The strong colour changes and a large negative solvatochromism in 2b are in agreement with the dipole moment in the ground and excited states, whereas a value of 14.5 D and 1.30 D for $\mu_2$ and $\mu_1$ ($\Delta \mu = 13.2$ D) was obtained. Thus, as expected, the ground state dipole moment value is really higher when compared with the excited state, and with the other compounds.

### Notes and references


8. L. Wang, X. He, Y. Guo, J. Xu and S. Shao, pH-Responsive chromogenic-sensing molecule based on bis(indolyl)-


