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Synthesis and evaluation of new thienyl and bithienyl-bis-indolylmethanes as colorimetric sensors for anions

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The synthesis and full characterization of new bis-indolylmethanes containing thienyl and bithienyl moieties are reported. The sensor ability of the compounds in the presence of halide ions (F^-, Cl^-, Br^-, and I^-), NO_3^-, ClO_4^-, SO_4^{2-}, CN^-, and OH^- ions was investigated in acetonitrile. The experimental results indicate that they could act as selective chromogenic-sensing molecules for the most basic anions F^-, CN^-, and OH^-, as a well-defined color change from yellow to pink was observed. The interaction constants between compounds 1 and 2 in the presence of F^-, CN^-, and OH^- were calculated and increased in the order $OH^- > F^- > CN^-$. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: (bi)thiophene; bis-indolylmethanes; anion chemosensors; colorimetric sensors; heterocycles

INTRODUCTION

The design and synthesis of systems that are capable of sensing various biologically and chemically important anions are currently of major interest because anions play a fundamental role in chemical and biological processes.[1,7] Among various important anionic analytes, cyanide ions have biological and environmental relevance,[1,7] while the fluoride ion is one of the most significant due to its role in dental care[8,9] and treatment of osteoporosis.[10]

Colorimetric sensors have attracted much attention for allowing the so-called "naked-eye" detection in a straightforward and inexpensive manner, offering qualitative and quantitative information without using expensive equipments. A chemosensor usually consists of three parts, a recognition moiety, a spacer, and a signal reporter. Hydrogen-bond donors such as bis-pyrrolyl or bis-indolylmethanes, spyrrole/calixpyrrole, thiourea, guanidinium, azophenol, dipyrrolylquinoxalines, indolocarbazoles, diamino, amide and benzimidazole usually act as anion binding sites.[11–17]

Numerous bis-indolylmethanes and their derivates, a new kind of aza-heterocycles, have been isolated from various terrestrial and marine natural sources. These natural products have novel structures and exhibit important biological activities.[18] Therefore, there is a great interest in the synthesis of bis-indole compounds,[19–23] occurring naturally or not. In our research, it was found that bis-indolylmethanes containing an H atom in the *meso* position were unstable and easy to spontaneously oxidize to the corresponding conjugated products. It also led us to consider that the conjugated compound might display interesting anion binding and sensing characteristics. The choice of oxidized bis-indolylmethane as the chromogenic-sensing molecule was mainly based on the fact that the conjugated bis-indole skeleton could act not only as a color-reporting group but also as a binding affinity control group containing an acidic H-bond donor moiety and a basic H-bond acceptor moiety. The strong hydrogen bonding to, or deprotonation/protonation of, the indolyl moiety might modulate the internal charge transfer (ICT) state of oxidized bis-indolylmethane and give rise to large color changes.[24–29] Recently, several bis-pyrrolyl or bis-indolylmethane derivatives were reported as selective chemosensors for the fluoride ion,[30] and for cations of biological relevance.[31]

Donor–acceptor substituted thiophene derivatives have been used recently, by us, due to their optical and electronic properties, with various applications such as nonlinear optical chromophores,[32–35] organic-light emitting diodes[32,36], and sensors.[37–39]

Thienyl or bithienyl derivatives of bis-indolylmethanes which possess NH groups at the indole rings will be new candidates to investigate H-bond formation and proton transfer for the receptor–anion interactions, having in mind that, for these kind of sensors, the acidity of the NH proton of the imidazole ring can be tuned by changing the length of the π-conjugated bridge.

Therefore, we present the synthesis of new bis-indolylmethane sensors containing thienyl or bithienyl moieties. Moreover, the electron-excessive or electron-deficient nature of the heterocyclic ring systems may also play a major role in determining the overall electron-donating and accepting ability: electron-rich heterocycles (such as thiophene derivatives) act as auxiliary

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donors and electron-deficient heterocycles act as auxiliary acceptors.[35,40,41]

In this work, we propose a simple synthetic route to the bis-indolylmethane derivatives **1** and **2** in which indole and formyl-thiophene and bithiophene were used as precursors for the synthesis of new potential colorimetric sensors.

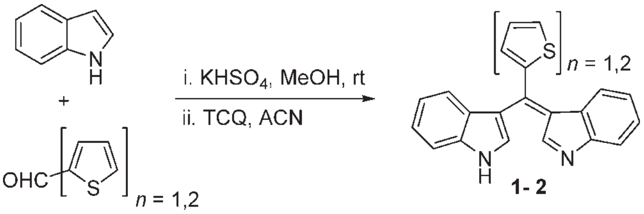
To the best of our knowledge, this is the first time that the synthesis and evaluation of the chemosensor properties of bis-indolylmethanes functionalized with (bi)thienyl moieties are reported in the literature. Our approach is original and different from other related reports,[30,31] due to the replacement of the aryl moiety by the heteroaromatic π-conjugated (bi)thiophene system, having in mind the modulation of the photophysical properties.

RESULTS AND DISCUSSION

Synthesis

Commercially available 2-formylthiophene, 5-formyl-2,2′-bithiophene and indole were used as precursors in the synthesis of bis-indolylmethanes **1** and **2** in order to evaluate the effect of the length of the π-conjugated bridge and also the electron donating strength of these heterocycles on the sensor properties of chromophores **1** and **2**.

The bis-indolylmethanes **1** and **2** with thienyl or bithienyl systems were synthesized by reaction of indole with the formyl derivatives, in methanol at room temperature[20] for 7 h, followed by reaction with tetrachloro-1,4-benzoquinone (TCQ) in acetonitrile, during 4 h at room temperature. Compounds **1** and **2** were obtained in moderate to good overall yields (40–76%) (Scheme 1, Table 1). The stronger electrophilic nature of 5-formyl-2,2′-bithiophene, due to the extended conjugation when compared to 2-formylthiophene, facilitates the nucleophilic attack of the indole to the carbonyl group and thus, could be responsible for the marked difference on the yields obtained.



Scheme 1. Synthesis of thienyl and bithienyl-bis-indolylmethanes **1** and **2**

Spectrophotometric titrations and metal sensing effect of compounds 1 and 2

The anion sensing and chelating properties of compounds **1** and **2** were studied by UV–Vis spectroscopy in acetonitrile solution. The electronic absorption spectra of compounds **1** and **2** in acetonitrile were obtained (Table 1). The position of the absorption bands was influenced by the structure of the compounds, for example, by the length of the π-conjugated oligothiophenic system: the longest wavelength transition was shifted from 432 nm for **1** to 445 nm for **2** due to more extensive electron delocalization. The longest wavelength transition bands centered at 432 nm (**1**) and 445 nm (**2**) could be assigned to the ICT band of the conjugated chromophores. A shoulder peak was observed at 492 nm (**1**) and 502 nm (**2**) which could be assigned with the hydrogen bonding interactions observed in this kind of compounds.[30,31]

Interaction with the halide ions (F^-, Cl^-, Br^-, and I^-), NO_3^-, ClO_4^-, SO_4^{2-}, CN^-, and OH^- ions were studied by anion titration experiments. In the presence of F^-, CN^-, and OH^-, a new absorption band centered at 533 nm (**1**) and 525 nm (**2**) was observed. The color of the solution immediately changed from yellow to pink (Figs. 1 and 2). This new band could be attributed to the deprotonated form of the compounds **1** and **2**,[30,31] and reached a plateau with the addition of 10 equivalents of OH^-, 12 equivalents of F^-, and 25 equivalents of CN^- for compound **1**, and 9 equivalents of OH^-, 11 equivalents of F^-, and 20 equivalents of CN^- for compound **2**. Simultaneously, a well-defined isosbestic point was observed for each titration at 474 nm, which indicated that a clear interconversion between the acid and basic forms occurred.

For the other anions studied, no change in color or in the spectra of compounds **1** and **2** was observed, even in the presence of 100 equivalents of Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, and ClO_4^-. In the case of SO_4^{2-} and ClO_4^-, it was visible an increase in the absorption at around 320 nm due to its ionic absorption (Fig. 3).[42] Stability constants for the interaction of compounds **1** and **2** in the presence of OH^-, F^-, and CN^- ions were calculated using the SPECFIT/32 software[43] and are summarized in Table 2. For both compounds, the stronger interaction was observed with OH^- and F^- ions, with similar stability constants. The weaker interaction was always observed for the cyanide ion. There is a relationship between the calculated stability constants and the chemical shift in the ^{1}H NMR spectra of the NH proton in indole

Table 1. Yields and IR, ^{1}H NMR and UV–Vis data for bis-indolylmethanes **1** and **2**

		δ_H (ppm)^a		IR	UV–Vis
Product	Yield (%)	N=CH	NH	v (cm^{-1})^b	λ_{max} (nm)^c (log ε)
1	40	8.63	13.97	3442 (NH)	432 (4.04)
2	76	8.69	13.89	3427 (NH)	445 (4.15)

[a] in DMSO-d_6.
[b] in KBr discs.
[c] in acetonitrile.

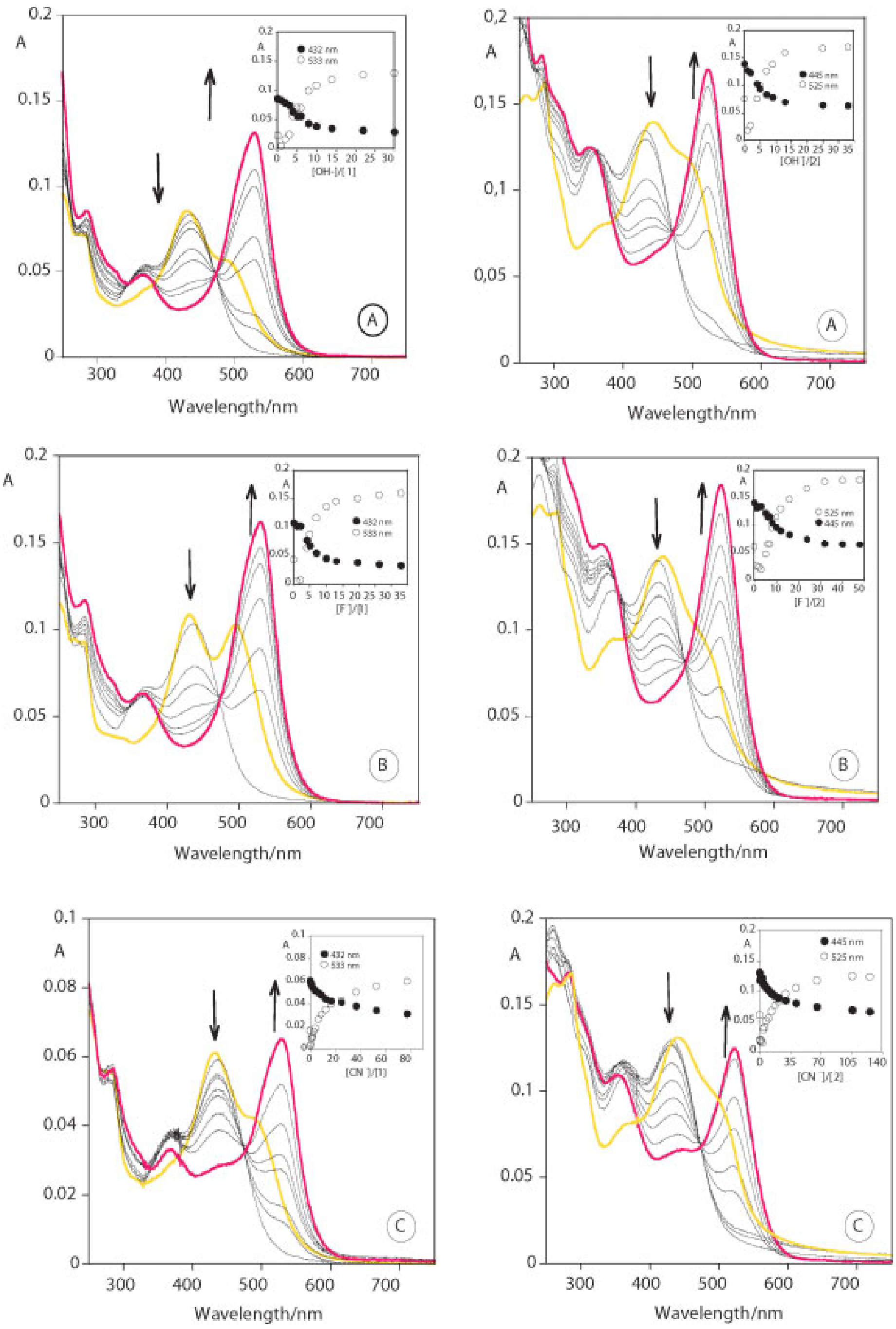


Figure 1. UV–Vis spectral changes of compounds **1** and **2** in acetonitrile solution (1.00×10^{-5} M) with the addition of increasing amount of OH^- (A), F^- (B), and CN^- (C) solutions. The yellow spectrum represents the free ligands and the red spectrum show the deprotonated form **1** and **2**. Insets: absorption at 432 and 533 nm for **1**, and 445 and 525 nm for **2**

moiety, which is a indicator of the acidity of the NH. Thus, compound **1** which exhibits the higher chemical shift, gives rise to the higher stability constants for all the anions studied.

CONCLUSIONS

In summary, we have synthesized new bis-indolylmethanes containing thienyl and bithienyl moieties **1** and **2** from thiophene and 2,2′-bithiophene aldehydes in moderate to good yields. Both compounds could be used as selective sensors for the most basic anions OH^-, F^-, and CN^- in aprotic solvent (CH_3CN). Well-defined color changes from yellow to pink were observed upon addition of these anions, acting as efficient chromogenic-sensing molecules. The stability constants indicated that the interaction was stronger with OH^-. This fact might be rationalized by the modulation of the ICT state due to the deprotonation of the H-bond acceptor moiety.

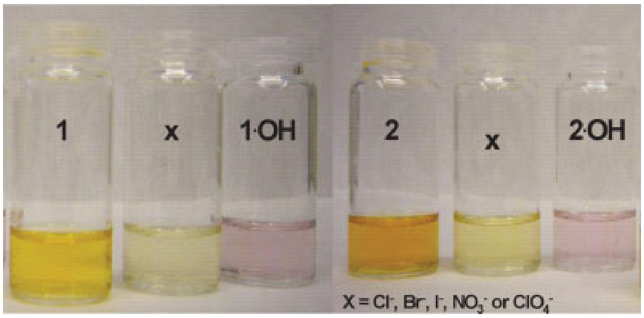


Figure 2. Color change of acetonitrile solutions of **1** and **2** in the presence of 10 equivalents of OH^- (similar color changes were observed with F^- and CN^-) and 100 equivalents of the other anions tested (Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-)

Table 2. Calculated stability constants for the interaction of bis-indolylmethanes **1** and **2** with OH^-, F^-, and CN^- ions in acetonitrile

Compound	Anion interaction	Log *K*
1	OH^-	$7.26 \pm 9.25 \times 10^{-2}$
	F^-	7.15 ± 0.10
	CN^-	$6.06 \pm 8.68 \times 10^{-2}$
2	OH^-	7.19 ± 0.11
	F^-	$6.59 \pm 7.10 \times 10^{-2}$
	CN^-	$6.08 \pm 8.56 \times 10^{-2}$

EXPERIMENTAL

Synthesis general

Reaction progress was monitored by thin layer chromatography (0.25-mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F254), while purification was effected by silica gel column chromatography (Merck Kieselgel 60; 230–400 mesh). NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^1H and 75.4 MHz for ^{13}C or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^1H and 100.6 MHz for ^{13}C using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS and given in ppm). Mps were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. Mass spectrometry analyses were performed at the "C.A.C.T.I. Unidad de Espectrometria de Masas" at the University of Vigo, Spain. Indole, 2-formyl-thiophene and 5-formyl-2,2′-bithiophene were commercially available.

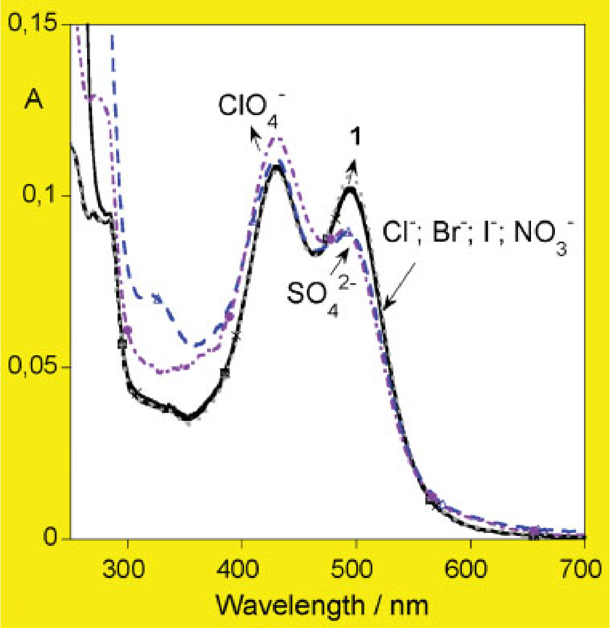


Figure 3. UV–Vis spectral changes of compound **1** in acetonitrile solution (1.00×10^{-5} M) with the addition of 100 equivalents of Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, or ClO_4^-. This figure is available in color online at www.interscience.wiley.com/journal/poc

General procedure for the synthesis of bis-indolylmethanes 1 and 2

$KHSO_4$ (1.20 mmol) was added to a mixture of indole (2.40 mmol) and the corresponding aldehyde (1.20 mmol) in dry methanol (10 mL), and the reaction 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 $CHCl_3$ (3×20 mL). The organic phase was dried with anhydrous $MgSO_4$. Evaporation of the solvent gave the crude indolyl products which were used in the next step without further purification. Indolyl compounds (0.4 mmol) were dissolved in acetonitrile (5 mL). TCQ (0.2 mmol) solution in acetonitrile was added dropwise to the mixture. This reaction was stirred at room temperature for 4 h and gave a dark red precipitate, which was filtered, washed with acetonitrile, and recrystallized from $CHCl_3$ to give the pure title compounds **1** and **2**.

3-[(1H-indol-3-yl)(thien-2-yl)methylene]-3H-indole (**1**) was obtained as a red solid (40%) mp > 320 °C. UV (acetonitrile): λ_{max} nm (log ε) 284 (3.88), 432 (4.04), 492 (sh) (3.96). IR (KBr): υ (cm^{-1}) 3442 (NH), 3072, 2847, 1614, 1515, 1481, 1410, 1336, 1201, 1121, 1044, 1015, 862, 809, 749, 569. ^1H NMR (DMSO-d_6) δ 6.84 (br d, $J = 7.8$ Hz, 2H, 2x H-7), 7.13 (t, $J = 7.8$ Hz, 2H, 2x H-5), 7.37–7.42 (m, 3H, 2x H-6 and H-3′), 7.64 (t, $J = 4.5$ Hz, 1H, H-4′), 7.72 (d, $J = 8.1$ Hz, 2H, 2x H-4), 8.00 (d, $J = 3.9$ Hz, 1H, H-5′), 8.63 (s, 2H, 2x H-2), 13.97 (br s, 1H, N*H*) ppm. ^{13}C NMR (DMSO-d_6) δ 114.37, 120.36, 121.46, 124.06, 125.74, 128.25, 130.94, 131.13, 139.21, 139.87, 146.19 ppm. MS (EI): *m/z* (%) 326 (M^+, 70), 325 (100), 297 (10), 293 (11), 243 (12), 210 (13). HRMS (EI): *m/z* (%) for $C_{21}H_{14}N_2S$; calcd 326.0878; found 326.0876.

3-[(1H-indol-3-yl)(bithien-5-yl)methylene]-3H-indole (**2**) was obtained as a dark red solid (76%), mp > 320 °C. UV (acetonitrile): λ_{max} nm (log ε) 287 (4.21), 445 (4.15), 502 (sh) (4.05). IR (KBr): υ (cm^{-1}) 3427 (NH), 3069, 1611, 1484, 1414, 1307, 1190, 1124, 1044, 845, 809, 749, 618. ^1H NMR (DMSO-d_6) δ 6.87 (br s, 2H, 2x H-7), 7.10–7.13 (m, 2H, 2x H-5), 7.23–7.25 (m, 1H, H-4‴;), 7.36–7.39 (m, 2H, 2x H-6), 7.72 (d, $J = 7.8$ Hz, 2H, 2x H-4), 7.77 (d, $J = 3.6$ Hz, 1H, H-3‴;), 7.82 (d, $J = 4.8$ Hz, 1H, H-5‴;), 7.92 (d, $J = 4.4$ Hz, 1H, H-3′), 8.13 (d, $J = 4.4$ Hz, 1H, H-4′), 8.69 (br s, 2H, 2x H-2), 13.89 (s, 1H, N*H*) ppm. ^{13}C NMR (DMSO-d_6) δ 114.27, 119.75, 121.45, 123.88, 125.57, 125.66, 127.92, 128.38, 128.60, 129.33, 129.74, 135.13, 139.07, 142.05, 143.74, 145.21, 152.31, 156.67 ppm. MS (FAB): *m/z* (%) 409

([M + H]$^+$, 100), 408 (M$^+$, 10), 307 (31), 289 (16), 232 (25), 155 (28), 154 (92). HRMS (FAB): *m/z* (%) for $C_{25}H_{17}N_2S_2$; calcd 409.0833; found 409.0838.

Spectrophotometric measurements

Absorption spectra were recorded on a Perkin Elmer lambda 35 spectrophotometer. The linearity of the absorption *versus* concentration was checked in the concentration range used (1.0×10^{-4}–1.0×10^{-6} M). All spectrophotometric titrations were performed as follows: stock solutions of compounds **1** and **2** (*ca.* 1.0×10^{-3} M) were prepared by dissolving an appropriate amount of the compound in a 50 mL volumetric flask and diluting to the mark with freshly dried CH_3CN UVA-sol grade. All measurements were performed at 298 K. The titration solutions ($[1] = [2] = 1.0 \times 10^{-5}$ M) were prepared by appropriate dilution of the stock solutions. Titrations of the compounds were carried out by addition of microliter amounts of standard solutions of the anions in acetonitrile. All anions were used as their tetrabutylammonium salts. A correction for the absorbed light was performed when necessary.

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