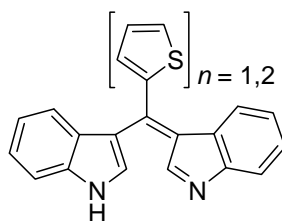# Table of contents

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

Rosa M. F. Batista, Elisabete Oliveira, Cristina Nuñez, Susana P. G. Costa, Carlos Lodeiro, M. Manuela M. Raposo

The synthesis of new *bis*-indolylmethanes containing thienyl and bithienyl moieties is reported. The title compounds could be used as efficient chromogenic-sensing molecules for basic anions $OH^-$, $F^-$ and $CN^-$ in an aprotic solvent ($CH_3CN$), as they displayed marked color changes from yellow to pink upon addition of these anions.

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

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**Abstract:** 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 $OH^- > F^- > CN^-$.

**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] Among various important anionic analytes, cyanide ions have biological and environmental relevance,[1] while the fluoride ion is one of the most significant due to its role in dental care[2] and treatment of osteoporosis.[3]

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, (thio)urea, guanidinium, azophenol, dipyrrolylquinoxalines, indolocarbazoles, (di)amino, amide and (benz)imidazole usually act as anion binding sites.[4-7]

Numerous *bis*-(indolyl)methanes 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.[8] Therefore, there is a great interest in the synthesis of *bis*-indole compounds,[9] occuring naturally or not. In our research, it was found that *bis*-(indolyl)methanes 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*-(indolyl)methane as the chomogenic-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*-(indolyl)methane and give rise to large color changes.[10] Recently, several *bis*-pyrrolyl or *bis*-indolylmethane derivatives were reported as selective chemosensors for the fluoride ion,[11a] and for cations of biological relevance.[11b]

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,[12a-d,i] organic-light emitting diodes[12a,e] and sensors.[12f-g]

Thienyl or bithienyl derivatives of *bis*-(indolyl)methanes 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*-(indolyl)methane 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 donors and electron-deficient heterocycles act as auxiliary acceptors.[12f-h,13]

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

To our knowledge, this is the first time that the synthesis and evaluation of the chemosensor properties of *bis*-(indolyl)methanes functionalized with (bi)thienyl moieties are reported in the literature. Our approach is original and different from other related reports,[11] 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 and 5-formyl-2,2'-bithiophene and indole were used as precursors in the synthesis of *bis*-(indolyl)methanes **1**-**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**-**2**.

The *bis*-(indolyl)methanes **1**-**2** with thienyl or bithienyl systems were synthesised by reaction of indole with the formyl derivatives, in methanol at room temperature[9b] for 7 h, followed by reaction with tetrachloro-1,4-benzoquinone (TCQ) in acetonitrile, during 4 h at room temperature. Compounds **1**-**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 >

< Table 1 >

**Spectrophotometric titrations and metal sensing effect of compounds 1-2**

The anion sensing and chelating properties of compounds **1** and **2** were studied by UV/visible spectroscopy in acetonitrile solution. The electronic absorption spectra of compounds **1-2** in acetonitrile were obtained (Table 1). The position of the absorption bands was influenced by the structure of the compounds, e.g. by the length of the $\pi$-conjugated (oligo)thiophenic 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 (Internal Charge Transfer) 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.[11]

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 (Figure 1 and 2). This new band could be attributed to the deprotonated form of the compound **1** and **2**,[11] 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 occured.

**< Figure 1 >**

**< Figure 2 >**

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 (Figure 3).[14] 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[15] 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 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.

< **Figure 3** >

< **Table 2** >

**Conclusions**

In summary, we have synthesized new *bis*-(indolyl)methanes containing thienyl and bithienyl moieties **1-2** from thiophene and 2,2'-bithiophene aldehydes in moderate to good yields. Both compounds could be used as a selective sensors for the most basic anions OH⁻, F⁻ and CN⁻ in aprotic solvent (CH$_3$CN). 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 internal charge transfer state due to the deprotonation of the H-bond acceptor moiety.

**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 ¹³C or a Bruker Avance III 400 at an operating frequency of 400 MHz for ¹H and 100 MHz for ¹³C 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.

**General procedure for the synthesis of *bis*-(indolyl)methanes 1-2**

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 7h. 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 (5mL). Tetrachloro-1,4-benzoquinone (0.2 mmol) solution in acetonitrile was added dropwise to the mixture. This reaction was stirred at room temperature for 4h and gave a dark red precipitate, which was filtered, washed with acetonitrile, and recrystallized from CHCl$_3$ to give the pure title compounds **1-2**.

*3-((1H-indol-3-yl)(thien-2-yl)methylene)-3H-indole* (**1**) was obtained as a red solid (40%) mp > 320 ºC. UV (acetonitrile): $\lambda_{max}$ 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. $^1$H NMR (DMSO-$d_6$) δ 6.84 (br d, $J$ = 7.8 Hz, 2H, 2 x H-7), 7.13 (t, $J$ = 7.8 Hz, 2H, 2 x H-5), 7.37-7.42 (m, 3H, 2 x H-6 and H-3'), 7.64 (t, $J$ = 4.5 Hz, 1H, H-4'), 7.72 (d, $J$ = 8.1 Hz, 2H, 2 x H-4), 8.00 (d, $J$ = 3.9 Hz, 1H, H-5'), 8.63 (s, 2H, 2 x 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$_2$S; 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 ºC. UV (acetonitrile): $\lambda_{max}$ 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. $^1$H NMR (DMSO-$d_6$) δ 6.87 (br s, 2H, 2 x H-7), 7.10-7.13 (m, 2H, 2 x H-5), 7.23-7.25 (m, 1H, H-4''), 7.36-7.39 (m, 2H, 2 x H-6), 7.72 (d, $J$ = 7.8 Hz, 2H, 2 x 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, 2 x 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 *vs.* concentration was checked in the concentration range used ($1.0 \times 10^{-4}$ - $1.0 \times 10^{-6}$ M). All spectrophotometric titrations were performed as follows: stock solutions of compound **1** and **2** (*ca.* $1.0 \times 10^{-3}$ 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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[15] SPECFIT/32 Global Analysis System, v. 3.0, Spectrum Software Associates, Malborough, MA, USA.

**Captions**

**Scheme 1.** Synthesis of thienyl and bithienyl-*bis*-(indolyl)methanes **1** and **2**.

**Table 1.** Yields and IR, $^1$H NMR and UV-vis data for *bis*-(indolyl)methanes **1** and **2**.

$^a$ in DMSO-$d_6$.

$^b$ in KBr discs.

$^c$ in acetonitrile.

**Table 2.** Calculated stability constants for the interaction of *bis*-(indolyl)methanes **1** and **2** with OH$^-$, F$^-$ and CN$^-$ ions 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 spectra shows the deprotonated form **1** and **2**. Insets: absorption at 432 and 533 nm for **1**, and 445 and 525 nm for **2**.

**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$_4^-$).

**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$_4^-$.

**Schemes**

**Scheme 1.**



i. KHSO$_4$, MeOH, rt

ii. TCQ, ACN

*n* = 1,2

**1- 2**
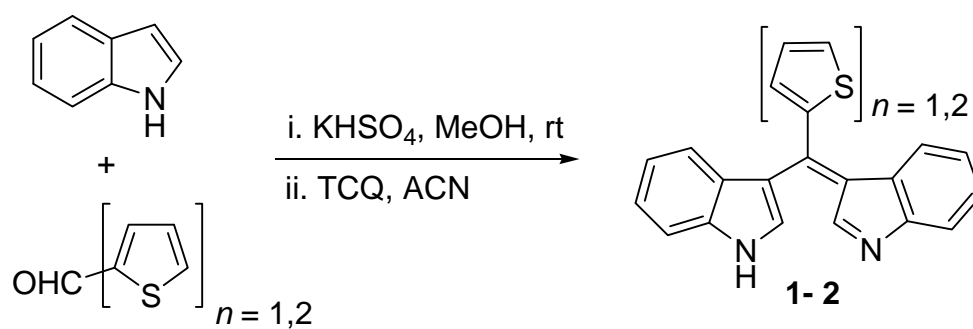
**Tables**

**Table 1**

| Product | Yield (%) | $\delta_H$ (ppm)[a] N=CH | NH | IR $\nu$ (cm$^{-1}$)[b] | UV-vis $\lambda_{max}$ (nm)[c] (log $\varepsilon$) |
|:---:|:---:|:---:|:---:|:---:|:---:|
| **1** | 40 | 8.63 | 13.97 | 3442 (NH) | 432 (4.04) |
| **2** | 76 | 8.69 | 13.89 | 3427 (NH) | 445 (4.15) |

**Table 2**

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

**Figure 1.**

**Figure 2.**



X = Cl⁻, Br⁻, I⁻, NO₃⁻ or ClO₄⁻

**Figure 3.**