

**Iodine-catalysed synthesis of a novel *meso*-substituted dipyrromethane and its evaluation as a cation chemosensor**

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**Abstract:** The synthesis and characterization of a dipyrromethane functionalised with an arylthiophene bridge was achieved by using an iodine catalytic method. Evaluation of the chemosensory ability in the presence of several cations showed both chromogenic and fluorescent response, with  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cr}^{3+}$  among the most easily detected ions. The results suggest that the novel dipyrromethane behaves as a dual channel chemosensor, with higher selectivity and sensitivity for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ .

**Keywords:** Dipyrromethanes; Arylthiophene; Chromogenic and fluorogenic chemosensors; Metal cations.

## 1. Introduction

In recent years, *meso*-substituted dipyrromethanes have been frequently explored as potential ion sensors, providing valuable qualitative and quantitative information on molecular recognition processes. Some of these compounds exhibit very interesting photophysical properties, which can be triggered in the presence of some cations and anions and display as chromogenic and/or fluorescent changes [1]. Due to the acidic character of NH protons, these compounds are also able to interact with several anions. Also, the inclusion of strong charge-transfer substituents often enhances their fluorescence properties. In this regard, chromophores based on (oligo)thiophene and arylthiophene derivatives are known to display fluoroionophoric properties and can also be used for various optical applications [2].

However, most common methods for the synthesis of these molecules can be laborious and time-consuming, requiring a great excess of pyrrole and a tightly controlled atmosphere [3]. Recently, a new method based on molecular iodine-catalysis has been proposed as a fast, inexpensive and good-yielding procedure with reduced reaction times. Using molecular iodine as a catalyst withdraws the requirement of strong and expensive acid-catalysts, such as TFA [4].

Bearing in mind the above facts and our research interests, we now report the synthesis and characterization of a dipyrromethane functionalized with an arylthiophene bridge. The evaluation of the chemosensory ability in the presence of several ions was also carried out in acetonitrile solution.

## 2. Experimental

### 2.1. General procedure for the synthesis of compound 1

Formyl-arylthiophene (1 mmol), pyrrole (10 mmol) and iodine (0.1 mmol) were added to dichloromethane (10 mL). The mixture was stirred for 1h at room temperature and reaction progress was monitored by TLC. After total conversion of the aldehyde, the reaction was stopped by addition of NaOH 0.1 M (2 mL). The mixture was washed several times with dichloromethane and water and the organic phase was dried with anhydrous MgSO<sub>4</sub>. After filtration, the solvent was evaporated and the crude residue was purified by chromatography using a gradient of diethyl ether/petroleum ether as eluent.

**2,2'-((5-Phenylthiophene-2'-yl)methylene)bis(1H-pyrrole) (1)** was obtained as a brown solid (60%) mp = 100-101 °C. UV (acetonitrile):  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 300 (6.51). IR (nujol):  $\nu$  ( $\text{cm}^{-1}$ ) 3409 (NH), 3320 (NH), 1597, 1560, 1302, 1259, 1111, 1028, 947.2, 738.9, 718.4.  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  = 5.75 (s, 1H, CH), 5.95-5.97 (m, 2H, 2 x H-4), 6.03-6.05 (m, 2H, 2 x H-3), 6.73-6.75 (m, 2H, 2 x H-5), 6.81 (dd,  $J$  = 3.6 and 1.2 Hz, 2H, 2 x H-3'), 7.27-7.29 (m, 2H, H-4', H-4''), 7.38-7.42 (m, 2H, H-3'', H-5''), 7.60-7.63 (m, 2H, H-2'', H-6''), 9.83 (s, 2H, 2 x NH) ppm.  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  = 40.27, 107.19, 108.22, 118.00, 123.34, 125.97, 127.00, 128.01, 129.77, 133.32, 135.48, 143.32, 148.33 ppm.

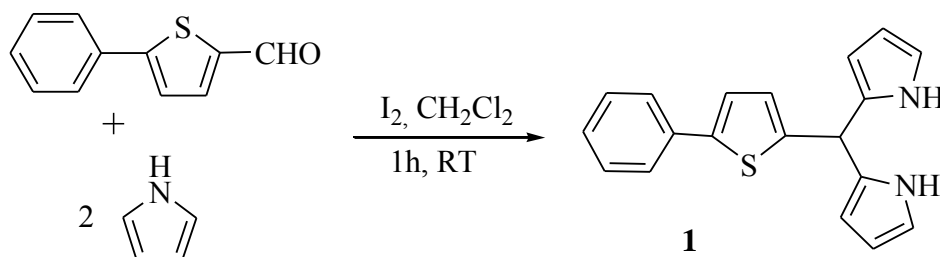
## 2.2. Spectrophotometric and spectrofluorimetric titrations

All spectrophotometric titrations were performed as follows: a stock solution of compound **1** ( $1 \times 10^{-4}$  M) was prepared by dissolving an appropriate amount of the solid in  $\text{CH}_3\text{CN}$  in a 100 mL volumetric flask. Titration solution ( $1 \times 10^{-5}$  M) was prepared by appropriate dilution of the stock solution. Titrations of compound **1** were carried out by addition of microliter amounts of standard solutions of the metal cations (in the form of hexahydrated tetrafluoroborate or perchlorate salts) in  $\text{CH}_3\text{CN}$ . All measurements were performed at 298 K. Fluorimetric titrations were performed under the same conditions described for absorption spectra.

## 3. Results and discussion

### 3.1. Synthesis

Dipyrromethane **1** was synthesized by condensation of pyrrole with formyl-arylthiophene in the presence of iodine, in dry dichloromethane, by stirring for 1 h at room temperature (Scheme). The product was obtained as a solid with high purity and a yield of 60% after column chromatography (Table 1).



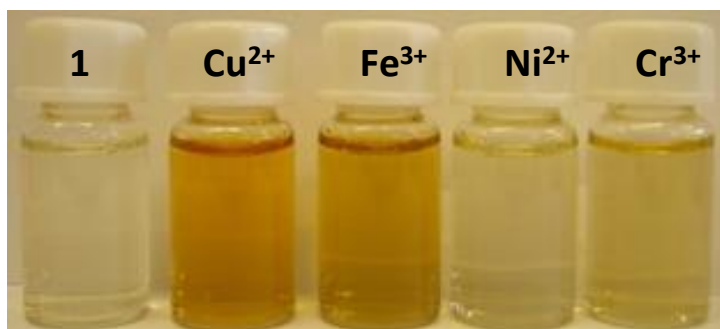
**Scheme.** Synthesis of dipyrromethane **1**.

**Table 1.** Yield, IR,  $^1\text{H}$  NMR and UV-Vis data for dipyrromethane **1**, in acetonitrile solution.

Cpd.	Yield (%)	$\delta$ (ppm)		IR ( $\text{cm}^{-1}$ )	UV/Vis	
		CH	NH	NH	$\lambda_{\text{max}}$ (nm)	$\log \epsilon$
<b>1</b>	60	5.75	9.83	3409 3320	300	4.51

### 3.2. Spectrophotometric and spectrofluorimetric titrations of compound **1** with cations in acetonitrile

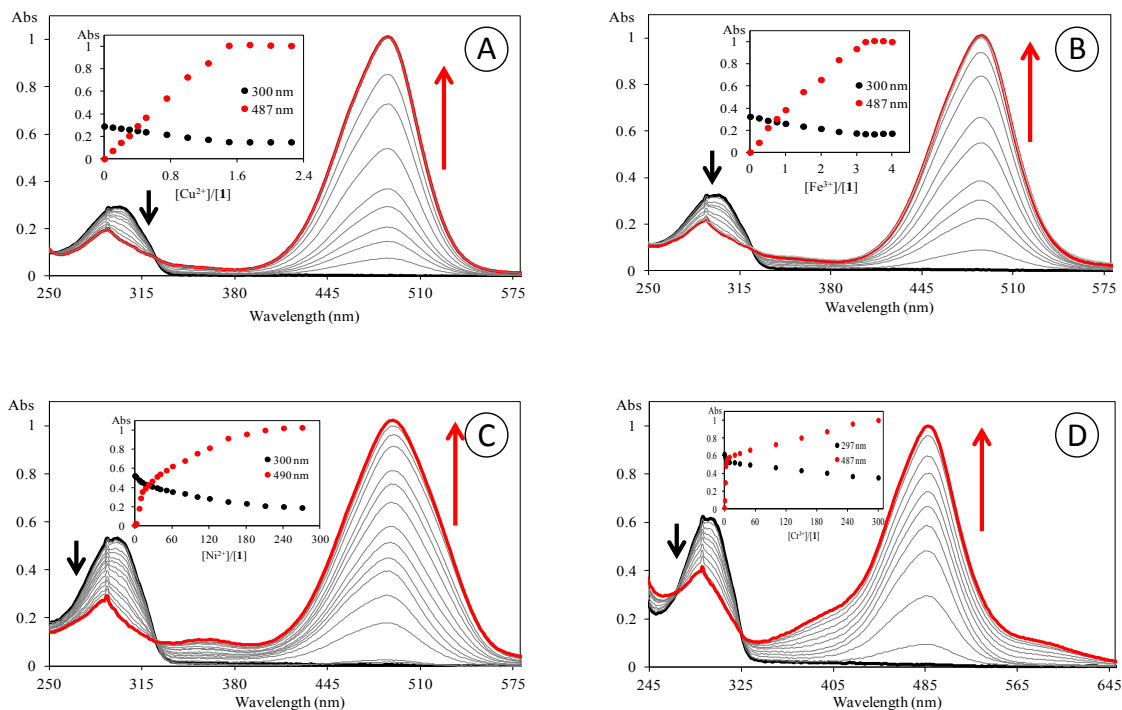
To explore the sensing ability of dipyrromethane **1** in solution in the presence of  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ , a preliminary sensing study was performed with addition of 50 equivalents of metal ion to a 100  $\mu\text{M}$  acetonitrile solution of compound **1**. For  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Zn}^{2+}$ , no visible colour changes were seen, whereas the remaining cations showed a change from colourless to pale yellow ( $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ ) or orange ( $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ ) (Figure 1).



**Figure 1.** Colour change of acetonitrile solutions of compound **1** in the presence of 50 equivalents of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ .

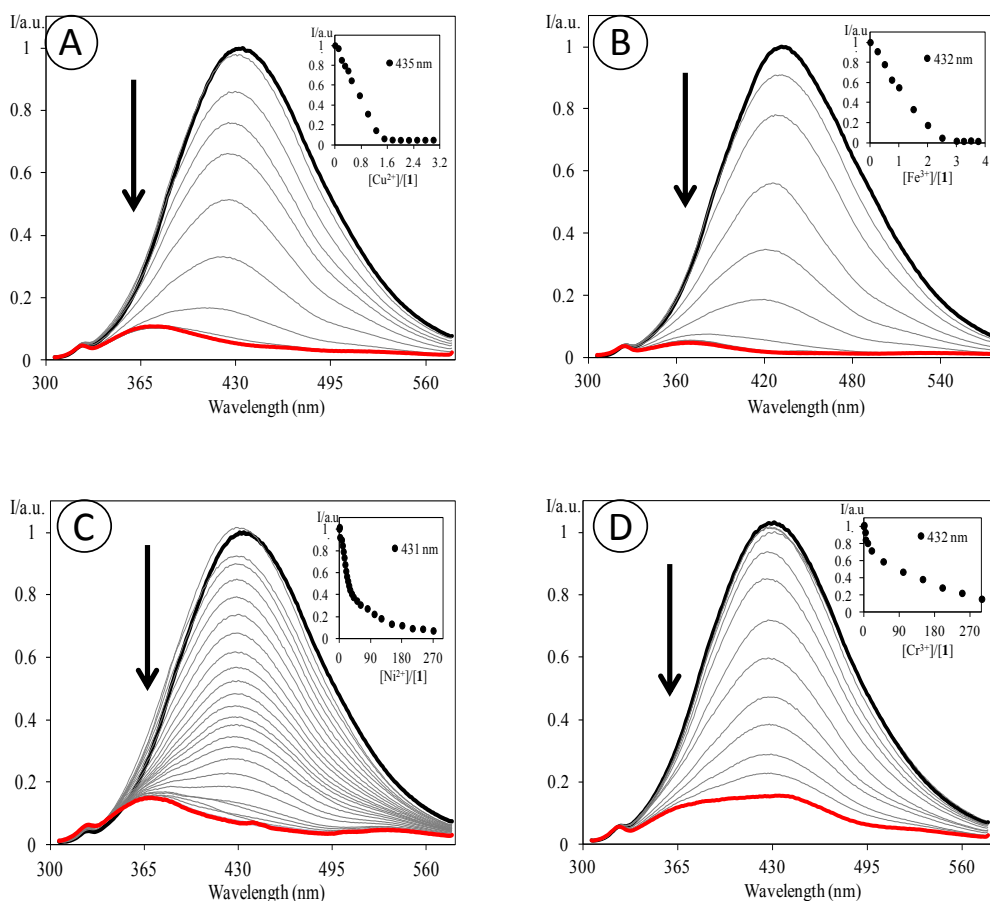
Considering the result of the preliminary test, spectrophotometric titrations of the selected cations were undertaken in acetonitrile solution. It was found that for all cations the band at the wavelength of maximum absorption decreased and a new red-

shifted band appeared at about 490 nm (Figure 2). Chromogenic selective detection was possible for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , which required only 2-3 equivalents to reach a plateau.



**Figure 2.** Spectrophotometric titrations of compound **1** in the presence of  $\text{Cu}^{2+}$  (A),  $\text{Fe}^{3+}$  (B),  $\text{Ni}^{2+}$  (C) and  $\text{Cr}^{3+}$  (D), in acetonitrile solution ( $[\mathbf{1}] = 10 \mu\text{M}$ ,  $T = 298 \text{ K}$ ). Inset: normalised absorption as a function of added metal equivalents.

Spectrofluorimetric titrations were also performed in acetonitrile solution, by exciting at the wavelength of maximum absorption of compound **1**. A CHEQ (chelation enhancement of the quenching) effect in the fluorescence emission was observed for all cations, with a slight blue-shift (10-15 nm) of the emission band especially with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  (Figure 3). The number of metal equivalents necessary for complete quenching of the initial fluorescence intensity is in agreement with the values obtained in the spectrophotometric titrations: once again, compound **1** is more sensitive to the presence of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , whereas  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  required a much larger amount of metal (250 and 300 equivalents, respectively).



**Figure 3.** Spectrofluorimetric titrations of compound **1** in the presence of  $\text{Cu}^{2+}$  (A),  $\text{Fe}^{3+}$  (B),  $\text{Ni}^{2+}$  (C) and  $\text{Cr}^{3+}$  (D), in acetonitrile solution. ( $[\mathbf{1}] = 10 \mu\text{M}$ ,  $T = 298 \text{ K}$ ,  $\lambda_{\text{exc}} \mathbf{1} = 300 \text{ nm}$ ). Inset: normalised emission at 431 nm, 432 nm and 435 nm as a function of added metal equivalents.

#### 4. Conclusions

Dipyrromethane **1** was synthesized in good yield (60%) using a simple experimental procedure. The evaluation of the chemosensory ability showed that compound **1** exhibited both chromogenic and fluorogenic response for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  behaving as a dual channel chemosensor. Moreover, higher selectivity and sensitivity was possible for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ . Further experiments are expected to bring more data on analogous compounds, which will hopefully display identical chemical and photophysical behaviour.

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