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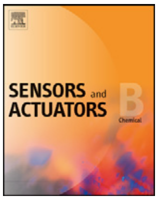

1-Arylazo-5,5-dimethyl dipyrromethanes: Versatile chromogenic probes for anions

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ABSTRACT

1-Arylazo-5,5-dimethyl dipyrromethanes (azo-DPM's) have been synthesized by electrophilic substitution reactions of 5,5-dimethyl dipyrromethanes in aqueous solution in 23–68% yields. The solution phase binding studies of azo-DPM's have been investigated by naked eye, absorption and proton NMR spectroscopy. The receptors, appended with electron-withdrawing groups display enhanced affinity and selectivity for F^-, $H_2PO_4^-$ and AcO^- than electron-donating groups in different solvents. Furthermore, the solvatochromic responses of 2,5-bis(4′-nitrophenyl)azo-pyrrole have been examined by visual and UV–vis spectroscopy with or without structurally different anions in a variety of solvents. The present studies of anion receptors may be used in environmental sensors, molecular electronics and development of molecular switches.

1. Introduction

The design and synthesis of neutrally charged anion receptors that possess high affinities and inherent selectivity for a variety of targeted anions represents a well appreciated challenge in supramolecular chemistry. The interest in this problem reflects in part the significant role played by anions in many biological and chemical systems [1–4]. Here, materials capable of reversible anion-induced color changes are particularly attractive as they require little or no instrumentation for practical uses [5,6].

Dipyrromethanes have emerged as useful intermediates for the synthesis of porphyrins [7–10], related polypyrrolic macrocycles [11,12] and pigments [13]. In most cases, the *meso* position has either no substituents or a single aryl or alkyl substituent. However, limited examples of 5,5-dialkyl/diaryldipyrromethanes are available in the literature [14,15]. Apart from their synthesis little attention has been paid to explore these important building blocks as versatile anion receptors and sensors. In an elegent work [16], Dehaen and coworkers have explored the ability of dialkyl dipyrromethanes to recognize neutral phenols in membrane systems similar to calix[4]pyrrole [17,18]. The quinoxaline derivatives, bearing dipyrromethane substituents and 2,6-diamidopyridine dipyrromethane hybrid macrocycles display augmented affinity towards variety of anions [19,20]. Recently we and other had reported that 2-arylazo-meso-octamethylcalix[4]pyrrole dyes can be used as chromogenic anion sensors [21,22], hence the easily available 1-arylazo-dipyrromethanes might be ideal candidate for sensing and binding of different anions.

Herein, we report the synthesis of chromogenic azo-DPM's **2–5** which allow not only for selective and sensitive colorimetric detection but also easy colorimetric differentiation of F^-, $H_2PO_4^-$ and AcO^- of different geometries.

2. Results and discussion

5,5-Dimethyldipyrromethane, **1** was synthesized by minor modification in the literature procedures [23]. The reaction of **1** with one equivalent of freshly prepared aryldiazonium chloride in the presence of catalytic amount of $NaHCO_3$ afforded 1-arylazo-5,5-dimethyl dipyrromethanes, **2–5** in moderate yields (Scheme 1). It is worthy to mention here that using quantitative amount of diazonium salt (1.0 equiv.) in the reaction, the formation of monopyrrole degradation product was not recognized, as frequently encountered with excess of aryldiazonium salts [24]. However, the reaction of **1** with p-nitrophenyldiazonium chloride (1.0 equiv.) under basic conditions gave monopyrrole degradation product, 2,5-bis(4′-nitrophenyl)azo-pyrrole, **6** in significant amount. Indeed due to the formation of this degradation product, **6** (isolated up to 20% yield), the lower yield of 1-(4′-nitrophenyl)azo-5,5-dimethyldipyrromethane, **5** was obtained. The synthesized azo-DPM's **2–5** were characterized by IR, UV–vis, ^1H NMR, ^{13}C NMR and ESI-mass spectroscopic techniques.

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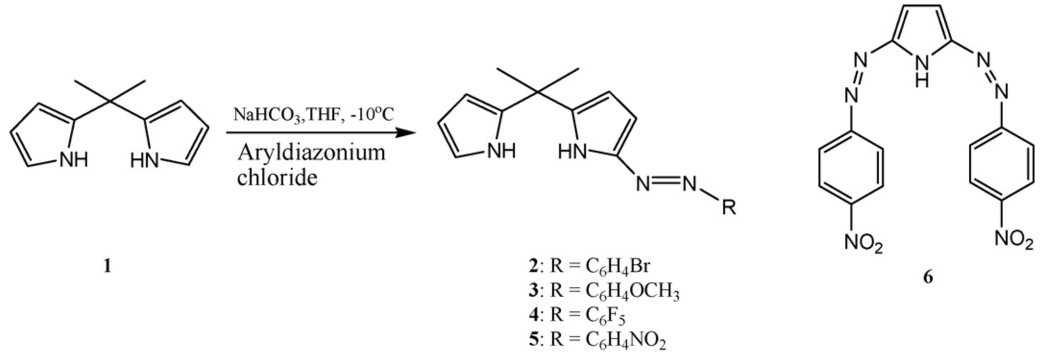

Scheme 1. Diazo-coupling reaction of 5,5-dimethyl dipyrromethanes.

2.1. Anion binding studies of chromophoric azo-dipyrromethanes (2–5)

2.1.1. Naked eye detection

The anion sensing ability of compounds **2**–**5** was examined on a qualitative level by visual examination of the anion-induced color changes in the solution of sensors **2**–**5** (5.0×10^{-5} M in DMSO) before and after the addition of an anions (5.0×10^{-4} M in DMSO). All the sensors except **2** showed dramatic color responses in the presence of different anions at room temperature. For instance, the DMSO solutions of azo-sensors, **3** and **4**, appended with electron-donating ($-OCH_3$) and electron-withdrawing ($-C_6F_5$) substituents changed from light yellow to orange color, in the presence of F^- (Fig. 1A). Equally were found to be insensitive to the addition of a large excess of Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and AcO^- (up to 10 equiv.). However, the addition of large excess of acetate anion deepens the color of solution of **4**.

The most remarkable color based changes were observed with azo-sensor, **5** appended with nitrophenyl substituent (Fig. 1B). The addition of F^-, $H_2PO_4^-$ and AcO^- anions changed the color of the solution of **5** from yellow to blue, green and violet, respectively at low anion concentration, suggesting the significant binding of these anions with **5**.

Thus visual inspection of solutions of azo-DPM's before and after the addition of anions indicate that fluoride ion interact more strongly with **3**–**5** due to higher electro-negativity and smaller size compared to other anions [25,26]. Further, **5** proved to be a potential chromogenic anion sensor, not only for selective colorimetric detection but, at the same time, easy colorimetric differentiation of F^-, $H_2PO_4^-$ and AcO^-, which is still a challenge for most supramolecular chemists.

2.1.2. UV–vis spectroscopy

The complexation studies of azo-DPM's, **2**–**5** were carried out by UV–vis spectroscopy in DMSO at room temperature. Titrations were performed by adding aliquots of 20 μl of stock solutions (5.0×10^{-5} M) of anionic guests (F^-, Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and AcO^-) to the investigated derivatives, **2**–**5** (5.0×10^{-5} M).

In the absence of anions, the spectrum of **3** is characterized by the presence of one absorption maximum at 388 nm. Upon addition of F^-, the peak at 388 nm decreased while a broad shoulder at 430 nm appeared. Under the same conditions, no obvious spectral changes were observed upon addition of Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and AcO^-. This high selectivity of **3** toward F^- is presumably due to the strong basicity of F^-. The analogous binding pattern towards lighter halides, particularly fluoride and to a lesser extent acetate was observed with azo-sensor **4**.

Different from **4**, the azo-dipyrromethane, **5** resulted significant UV–vis spectral changes for F^-. For instance, the UV–vis spectra of **5** showed a characteristic absorption maximum at 438 nm. With the successive addition of fluoride anion, peak at 438 nm gradually decreased with a large bathochromic shift moving from 438 to 575 nm ($\Delta\lambda = 137$ nm, Fig. 2). Meanwhile a clear isobestic point was observed at 493 nm. The isobestic point in UV–vis spectra indicates that there is a balance in the solution and the complex has been formed between host and guest. The new absorption peak at 575 nm can be ascribed to the partial charge-transfer (CT) interactions between the electron rich donor nitrogen atom of pyrrole moieties and the electron-deficient p-nitrophenyl units.

An important additional observation made during these experiments is that the spectra as well as the color of the solution of receptor-F^- conjugates revert back to the original spectra corresponding to those receptors in the absence of anion upon addition of small aliquots of water/methanol. This phenomenon illustrates that the addition of a protic solvent destroys the complexation between **5** and F^-, demonstrating that interaction between **5** and F^- is, in essence, a hydrogen-bonding interaction.

Further, in a separate experiment, The UV–vis spectra of all azo-sensors **3**–**5** have been recorded in the presence of tetrabutylammonium hydroxide in DMSO and compared with UV–vis spectra of sensors in the presence of added salts. The results indicate that there is significant difference (>30 nm) in the absorption spectra

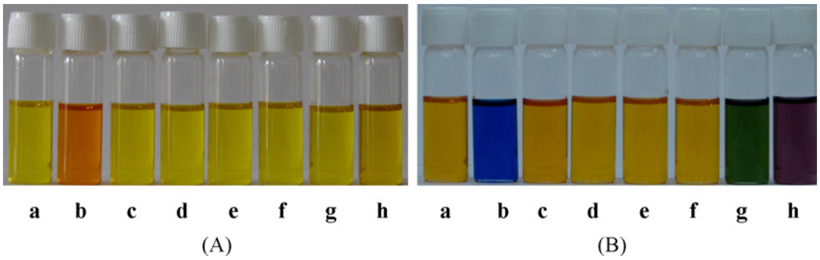

Fig. 1. (A) Color changes of **azo-3** (5.0×10^{-5} M) in DMSO with the addition of tetrabutylammonium anions (5.0×10^{-4} M): (a) = free receptor, (b) = fluoride, (c) = chloride, (d) = bromide, (e) = iodide, (f) = hydrogen sulfate, (g) = dihydrogen phosphate, (h) = acetate; (B) color changes of azo-5 (5.0×10^{-5} M) in DMSO with the addition of tetrabutylammonium anions (5.0×10^{-4} M); (a) = free receptor, (b) = fluoride, (c) = chloride, (d) = bromide, (e) = iodide, (f) = hydrogen sulfate, (g) = dihydrogen phosphate, (h) = acetate.