



# Aryl substituted adamantane–dipyrromethanes: chromogenic and fluorescent anion sensors



Marija Alešković<sup>a</sup>, Nikola Basarić<sup>a</sup>, Ivan Halasz<sup>b</sup>, Xing Liang<sup>c</sup>, Wenwu Qin<sup>c</sup>, Kata Mlinarić-Majerski<sup>a,\*</sup>

<sup>a</sup> Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

<sup>b</sup> Division of Material Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

<sup>c</sup> Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

## ARTICLE INFO

### Article history:

Received 19 September 2012

Received in revised form 22 November 2012

Accepted 11 December 2012

Available online 19 December 2012

### Keywords:

Adamantanes

Anion sensors

UV–vis spectrometry

Fluorescence spectrometry

Dipyrromethanes

## ABSTRACT

New adamantane–dipyrromethane anion receptors were synthesized and their photophysical properties and anion binding investigated. In addition, a nitro derivative has been characterized by single crystal X-ray analysis. In the crystal structure, the nitro derivative is complexed with CH<sub>3</sub>CN molecules, indicating that dipyrromethanes can in principle be employed as neutral molecule hosts. Anion binding ability in CH<sub>3</sub>CN solutions with TBA salts (F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, AcO<sup>−</sup>, HSO<sub>4</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup> and H<sub>2</sub>PO<sub>4</sub><sup>−</sup>) was investigated by UV–vis, fluorescence and/or <sup>1</sup>H NMR spectroscopy, and the association constants of the corresponding complexes were determined. The receptors form 1:1 complexes with the highest association constants with F<sup>−</sup> and AcO<sup>−</sup>. Change of the substituent at the phenyldipyrromethanes results in different photophysical properties, leading to different spectroscopic responses in the presence of anions. Therefore, differently substituted phenyldipyrromethanes can be used as colorimetric or fluorescent anion sensors.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Within the field of supramolecular chemistry there is a continuous flow of conducted research related to anion receptors due to highlighted importance and presence of anions in many scientific areas, as well as in biological and technological processes.<sup>1</sup> Although supramolecular chemists have designed various complex supramolecular systems based on acyclic and cyclic pyrrole receptors,<sup>2</sup> simple pyrrole anion receptors potent in complexing anions with high selectivity and affinity are still a topic of the investigation.<sup>3</sup> It is well known that even simple receptors bearing only two pyrrole units (i.e., DPQ systems) can bind anions with appreciable selectivity and high binding constants.<sup>4</sup> In addition, substitution of the pyrrole moiety with the additional H-bond donating groups, and/or introduction of a variety of chromophores leads to the development of very effective hosts and sensors.<sup>3</sup> Such systems are able to create structural recognition motifs for anionic species that can be very diverse in their nature, and can bind from simple inorganic anions<sup>1</sup> to macromolecules such as peptides or DNA.<sup>5</sup>

A current line of research in our group is oriented at the study of anionic receptors with polycyclic cage units, i.e., synthesis and investigation of anion binding properties of adamantylpyrrole<sup>6</sup> and

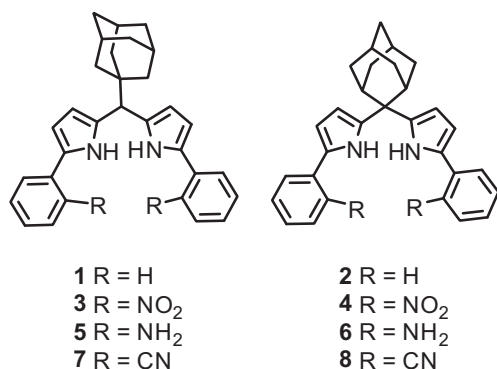
adamantylurea<sup>7</sup> derivatives. We have recently investigated a series of simple adamantane–dipyrromethanes wherein adamantane is a rigid spacer and pyrroles are the H-bond donors of the receptor system.<sup>6a,c</sup> Incorporation of the rigid and bulky adamantane moiety into receptors diminishes the rotational mobility of the pyrroles, which can lead to the preorganization of the receptors for the anion capture. Therefore, the stability constants of the complexes were higher than those of the phenyl substituted dipyrromethane receptor. Furthermore, <sup>1</sup>H NMR titration experiments performed in CDCl<sub>3</sub> and X-ray analysis revealed the unexpected stoichiometries of the complexes with F<sup>−</sup> and AcO<sup>−</sup>, wherein the anion is bound by four H-bonds in the cavity created between two dipyrromethane units from two host molecules.<sup>6a,c</sup>

<sup>1</sup>H NMR spectroscopy is a very informative technique for the binding studies since it also gives structural information. However, it is not applicable in sensor technology. On the other hand, sensors with optical response (UV–vis or fluorescence) are of particular interest because detection of a substrate can be achieved fast and with low detection limits, the methods are inexpensive, easy to use, and the instrumentation is highly accessible. In addition, receptors with ‘naked eye detection’ are getting even more popular because semiquantitative analysis can be performed outside the typical laboratory environment. It is known that chromophores, which are directly attached to the binding region of the receptor usually exhibit significant spectral changes (chromogenic or fluorogenic).<sup>8</sup>

\* Corresponding author. E-mail address: [majerski@irb.hr](mailto:majerski@irb.hr) (K. Mlinarić-Majerski).

Hence, even simple chromophore-based anion hosts can be very effective in signalling process of molecular recognition, as it is shown in many examples from the literature.<sup>4,9</sup> Therefore, our next step in the design of anion sensor molecules was introduction of a chromophore into the adamantane–dipyrromethane receptors so that the observation of binding can be monitored by spectrophotometric methods.

Herein we report the synthesis and anion binding studies of new receptors **1–8**. The receptor molecules bear the adamantane–dipyrromethane moiety and aryl groups directly attached to the pyrroles. The aryl groups were functionalized with electron-withdrawing groups (CN or NO<sub>2</sub>), which should electronically enhance the binding ability of the nearby pyrrole H-bond donors, or electron-donating group that should introduce additional hydrogen bonding sites (NH<sub>2</sub> groups). The rigid adamantane moiety of the receptors composed of adamant-1-yl or adamant-2,2-diyl group should have different conformational freedom and effect the anion binding ability and selectivity. Depending on the H-bonding ability, and the availability of H-bonds for the complexation (determined by the electronic and structural effects) the study should highlight the optimal substitution of the receptor molecules and favourable structural motifs for strong and selective anion binding. The investigated anions in this report are characterized by different size, geometry and basicity (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>).

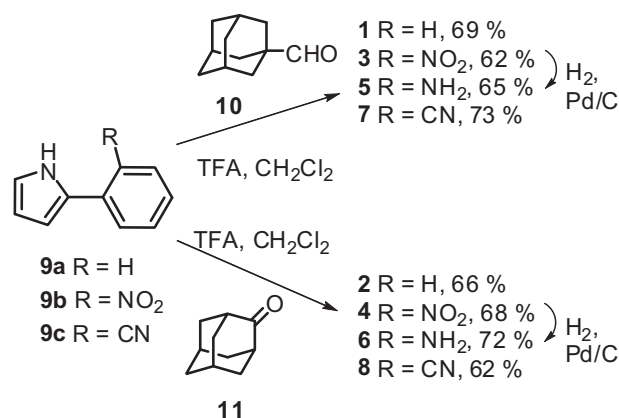


## 2. Results and discussion

### 2.1. Synthesis

New dipyrromethane derivatives **1–4**, **7** and **8** were obtained in very good yields from the corresponding adamantane carbonyl derivatives **10** or **11** and 2-phenylpyrrole precursors **9a–c**,<sup>10</sup> which were obtained in an optimized Suzuki coupling reaction between *N*-Boc-2-pyrrole boronic acid and the corresponding aryl bromide. Amino derivatives **5** and **6** were obtained by catalytic hydrogenation from the nitro analogues **3** and **4**, respectively (Scheme 1).

For the use of new receptors as optical sensors it is important to investigate their photophysical properties. Therefore, we measured UV–vis and fluorescence spectra of **1–8** in CH<sub>3</sub>CN. In addition, we measured quantum yields of fluorescence and lifetimes of the singlet excited states in CH<sub>3</sub>CN and cyclohexane (Table 1). In CH<sub>3</sub>CN solution all receptors exhibit a strong absorption band at ≈ 300 nm ( $\log \epsilon/M^{-1} \text{ cm}^{-1} \approx 4.2\text{--}4.6$ ). On substitution of the phenylpyrrole, additional low-energy absorption bands can be seen in the spectra, for **3** and **4** at ≈ 410 nm ( $\log \epsilon/M^{-1} \text{ cm}^{-1} \approx 3.5$ ), for **5** and **6** at 320 nm, and for **7** and **8** at 350 nm. All receptors except nitro derivatives **3** and **4**, which are nonfluorescent, display structureless fluorescence spectra in a CH<sub>3</sub>CN solution with the maxima at 360–450 nm, and relatively strong emission with  $\Phi=0.4\text{--}0.7$ .



Scheme 1.

### 2.2. Photophysical properties of **1–8**

Decay of the fluorescence measured by single photon timing (SPT) can be fitted to single exponential function (except for **7** and **8** in cyclohexane), giving fluorescence lifetimes in the range 2–9 ns.

Comparison of the UV–vis and fluorescence spectra of **1**, **2**, **7** and **8** taken in CH<sub>3</sub>CN and cyclohexane reveal that increase of solvent polarity induces small solvatochromic shifts in the absorption and relatively large shift in the fluorescence spectra. For example, Fig. S7 (see Supplementary data) demonstrates the influence of the solvent polarity on the fluorescence spectra of **8** (taken in cyclohexane, ethyl acetate, and CH<sub>3</sub>CN). Furthermore, fluorescence lifetimes and fluorescence quantum yields increase with the increase of the solvent polarity, corresponding to a decrease of both deactivation rate constants, radiative and non-radiative. For example, for **1** in cyclohexane  $k_F$  and  $k_{NR}$  are  $2.9 \times 10^8$  and  $6.9 \times 10^8 \text{ s}^{-1}$ , and in CH<sub>3</sub>CN the constants are  $2.1 \times 10^8$  and  $1.7 \times 10^8 \text{ s}^{-1}$ . These findings suggest that excitation to S<sub>1</sub> leads to an increase of the dipole moment. That is, excitation to S<sub>1</sub> has a partial CT character that is more stabilized in more polar solvents. Therefore, it is anticipated that binding of anions should induce changes in both absorption and fluorescence spectra (vide infra). It is interesting to note that fluorescence spectra of **2** and **8** are ≈ 10–20 nm bathochromically shifted compared to **1**, and **7**, respectively. This finding demonstrates that change of the aliphatic adamantane spacer also changes the photophysical properties. Presumably, there is some vibronic coupling between two arylpyrrole moieties in 2,2-bissubstituted adamantyl derivatives **2** and **8**.

### 2.3. Anion binding studies

The binding studies of new receptors **1–8** with the TBA salts of the following anions: F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, were performed by UV–vis and fluorescence titrations in CH<sub>3</sub>CN solution. Dependences of the UV–vis and fluorescence spectra on anion concentrations were processed by multivariate non-linear regression analysis by use of Specfit program<sup>11</sup> to determine the complex stoichiometries and the stability constants. The stability constants are compiled in Table 2. In addition, some of the fluorescence titrations were performed by a ratiometric method to additionally verify the obtained values of the stability constants and demonstrate the applicability of the receptor molecules as fluorescence ratiometric sensors (vide infra).

Addition of basic anions (F<sup>-</sup>, AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) to the CH<sub>3</sub>CN solution of **1** or **2** induced pronounced changes in their UV–vis spectra. For example, addition of F<sup>-</sup> to the CH<sub>3</sub>CN solution of **2** resulted in a small bathochromic shift and an increase of the absorbance at ≈ 300 nm (Fig. 1). Formation of three clear isosbestic points (293, 309 and 325 nm) indicated a presence of two coloured species in an equilibrium. Addition of less basic anions made

Download English Version:

<https://daneshyari.com/en/article/5218674>

Download Persian Version:

<https://daneshyari.com/article/5218674>

[Daneshyari.com](https://daneshyari.com)