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Aryl substituted adamantane–dipyrromethanes: chromogenic and fluorescent anion sensors

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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_3CN molecules, indicating that dipyrromethanes can in principle be employed as neutral molecule hosts. Anion binding ability in CH_3CN solutions with TBA salts (F^-, Cl^-, Br^-, AcO^-, HSO_4^-, NO_3^- and $H_2PO_4^-$) was investigated by UV–vis, fluorescence and/or ^1H 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^- and AcO^-. 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.

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.[1] Although supramolecular chemists have designed various complex supramolecular systems based on acyclic and cyclic pyrrole receptors,[2] simple pyrrole anion receptors potent in complexing anions with high selectivity and affinity are still a topic of the investigation.[3] 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.[4] 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.[3] 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[1] to macromolecules such as peptides or DNA.[5]

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[6] and adamantylurea[7] 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.[6a,c] 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, ^1H NMR titration experiments performed in $CDCl_3$ and X-ray analysis revealed the unexpected stoichiometries of the complexes with F^- and AcO^-, wherein the anion is bound by four H-bonds in the cavity created between two dipyrromethane units from two host molecules.[6a,c]

^1H 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).[8]

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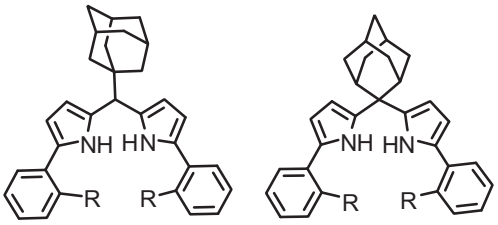
Hence, even simple chromophore-based anion hosts can be very effective in signalling process of molecular recognition, as it is shown in many examples from the literature.[4,9] Therefore, our next step in the design of anion sensor molecules was introduction of a chromophore into the adamantane–dipyrromethane 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_2), 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_2 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^-, Cl^-, Br^-, AcO^-, NO_3^-, HSO_4^- and $H_2PO_4^-$).



1 R = H
3 R = NO_2
5 R = NH_2
7 R = CN

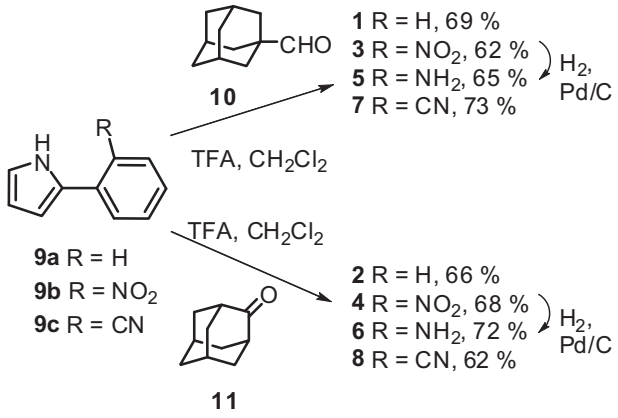
2 R = H
4 R = NO_2
6 R = NH_2
8 R = CN

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**,[10] 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_3CN. In addition, we measured quantum yields of fluorescence and lifetimes of the singlet excited states in CH_3CN and cyclohexane (Table 1). In CH_3CN solution all receptors exhibit a strong absorption band at ≈300 nm (log ε/M^{-1} cm^{-1}≈4.2–4.6). On substitution of the phenylpyrrole, additional low-energy absorption bands can be seen in the spectra, for **3** and **4** at ≈410 nm (log ε/M^{-1} cm^{-1}≈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_3CN solution with the maxima at 360–450 nm, and relatively strong emission with Φ=0.4–0.7.



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_3CN 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_3CN). 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 2.9×10^8 and 6.9×10^8 s^{-1}, and in CH_3CN the constants are 2.1×10^8 and 1.7×10^8 s^{-1}. These findings suggest that excitation to S_1 leads to an increase of the dipole moment. That is, excitation to S_1 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^-, Cl^-, Br^-, AcO^-, NO_3^-, HSO_4^- and $H_2PO_4^-$, were performed by UV–vis and fluorescence titrations in CH_3CN 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[11] 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^-, AcO^- and $H_2PO_4^-$) to the CH_3CN solution of **1** or **2** induced pronounced changes in their UV–vis spectra. For example, addition of F^- to the CH_3CN 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

Table 1
Photophysical properties of **1**–**8**

Compd	Solvent	λ_{abs}/nm	log ε/M^{-1} cm^{-1}	λ_{em}/nm	Φ[a]	τ[b]/ns
1	CH_3CN	304	4.59	360	0.55±0.01	2.63±0.02
	Cyclohexane	—[c]	—[c]	338	0.30±0.01	1.02±0.01
2	CH_3CN	306	4.52	380	0.66±0.02	3.01±0.02
	Cyclohexane	—[c]	—[c]	358	0.53±0.02	1.59±0.01
3	CH_3CN	299 and ~405	4.37 and 3.65	—	—	—
4	CH_3CN	302 and ~415	4.31 and 3.48	—	—	—
5	CH_3CN	280 and 320	4.28 and 4.29	381	0.41±0.01	2.85±0.01
6	CH_3CN	285 and 320	4.26 and 4.33	378	0.43±0.05	3.07±0.01
7	CH_3CN	304 and 348	4.30 and 4.26	430	0.70±0.02	7.97±0.01
	Cyclohexane	—[c]	—[c]	411	0.44±0.01	3.5±0.4 (32) 6.3±0.3 (68)
8	CH_3CN	304 and 355	4.27 and 4.26	450	0.52±0.02	9.33±0.09
	Cyclohexane	—[c]	—[c]	421	0.43±0.03	3.93±0.01 (75) 7.1±0.3 (25)

[a] Measured by use of quinine sulfate in 0.05 M aqueous H_2SO_4 as reference.
[b] Measured by single photon timing method.
[c] Compound not soluble in cyclohexane.

Table 2
The association constants (log β±σ(log β)) of the complexes of receptors **1**–**8** with anions determined by UV–vis and fluorescence titrations[a]

Compd	Method	F^-	Cl^-	Br^-	AcO^-	NO_3^-	$H_2PO_4^-$	HSO_4^-
1	UV–vis	4.50±0.02	<2	—[b]	3.80±0.10	—[b]	3.48±0.01	<2
	Fluo	4.31±0.02	1.99±0.07	≈1	3.97±0.02	—[b]	3.25±0.01	<2
							3.29±0.02[c]	
2	UV–vis	4.51±0.03	3.02±0.04	1.99±0.03	4.03±0.03	<2	3.11±0.02	—[b]
	Fluo	4.78±0.02	3.13±0.03	<2	4.06±0.02	—[b]	3.02±0.02	1.67±0.20
					3.78±0.04[c]		3.25±0.09[c]	
3	UV–vis	4.99±0.02	2.21±0.04	—[b]	3.95±0.03	—[b]	3.40±0.01	1.68±0.02
4	UV–vis	5.31±0.03	2.98±0.03	2.13±0.02	3.88±0.05	<2	3.44±0.01	1.77±0.05
5	UV–vis	4.04±0.07	—[b]	—[b]	4.56±0.12	—[b]	2.75±0.04	5.96±0.02[d]
	Fluo	3.71±0.04	<2	—[b]	4.81±0.20	—[b]	2.78±0.06	8.04±0.02[d]
							2.61±0.13[c]	
6	UV–vis	3.84±0.04	2.94±0.07	<2	4.27±0.20	<2	2.55±0.06	5.97±0.02[d]
	Fluo	4.09±0.01	2.18±0.08	<2	3.95±0.06	2.57±0.20	2.83±0.03	8.10±0.02[d]
							2.58±0.14[c]	
7	UV–vis	5.31±0.04	2.35±0.02	1.63±0.04	4.04±0.02	—[b]	4.07±0.01	1.92±0.01
	Fluo	4.96±0.02	2.37±0.03	<2	4.05±0.01	—[b]	3.97±0.01	2.42±0.04
					4.08±0.03[c]		4.14±0.04[c]	
8	UV–vis	5.33±0.03	3.18±0.02	2.08±0.02	3.78±0.06	<2	3.55±0.01	1.88±0.05
	Fluo	5.18±0.03	3.16±0.04	2.19±0.09	4.09±0.01	2.43±0.10	3.43±0.01	<2
					4.07±0.02[c]			

[a] The titrations were performed at 25 °C in a CH_3CN solution. The anions were added as TBA salts. The complexes are formed in 1:1 stoichiometry giving β/mol^{-1} dm^3, 1:1 stoichiometry is confirmed by mole ratio method.
[b] No binding interaction observed.
[c] The average association constants were determined from *direct* emission fluorimetric titration by processing data taken from one fluorescence wavelength or ratiometric fluorimetric titration.
[d] The titration data gave the best fit to 1:2 model (receptor/anion) giving β/mol^{-2} dm^6.

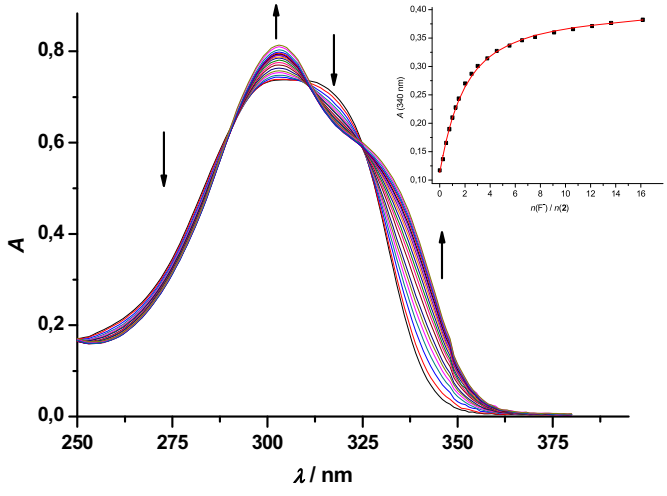


Fig. 1. UV–vis titration of the CH_3CN solution of **2** (c=2×10^{-5} M) with addition of F^-. The spectra were corrected for dilution. Inset: absorbance of the CH_3CN solution of **2** at 340 nm versus mole ratio of F^-/**2** (■ exp. values, —calcd values).

smaller (Cl^-, Br^- and HSO_4^-) or no (NO_3^-) changes in the UV–vis spectra, so in some cases fitting was rather difficult, and therefore, some log β values were estimated to be <2. The observed changes of the UV–vis spectra of receptors **1** and **2** enable their application as sensors for F^-, Cl^- or $H_2PO_4^-$. Particularly noticeable is the change on addition of F^-, which may enable use of **1** and **2** as 'naked eye' colorimetric sensors (graphical abstract).

In contrast to the hyperchromic changes observed in the UV–vis spectra, addition of basic anions (F^-, AcO^-, $H_2PO_4^-$, and Cl^-) to the CH_3CN solution of **1** and **2** resulted in fluorescence quenching (Fig. 2 and Supplementary data, Figs. S64–S77). The quenching was not observed on addition of a large excess of less basic anions (Br^-, HSO_4^-, and NO_3^-). Non-linear curve-fitting after the fluorescence titration by the Specfit program enabled estimation of the stability constants compiled in Table 2. The constant determined by UV–vis and fluorescence titration generally agree very well. However, some smaller differences between the values obtained by these two methods can be observed for the most basic anion F^-, which may be attributed to a partial proton transfer taking place in the excited state. For example, in the fluorescence spectra of **2**, on addition of F^-, a new shoulder appears in the fluorescence spectra at ≈500 nm,

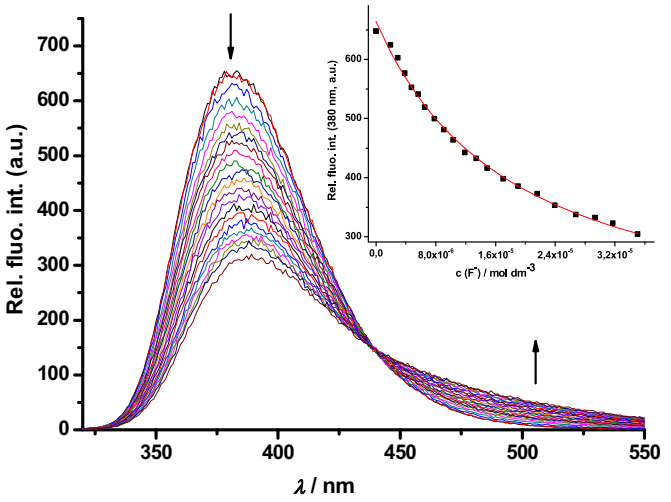


Fig. 2. Fluorescence titration of the CH_3CN solution of **2** ($c=2\times10^{-6}$ M) with addition of F^-, λ_{ex}=310 nm. The spectra were corrected for dilution. Inset: fluorescence emission of the CH_3CN solution of **2** at 380 nm versus concentration of F^- (■ exp. values, — calcd values).

which may be attributed to the fluorescence of the deprotonated receptor **2**. F^- is a strong base that can deprotonate pyrrole NH while simultaneously forming the HF_2^- species.[12] Furthermore, it is known that molecules exhibit different acidity and basicity in the S_0 and S_1 states.[13] Therefore, smaller differences between the association constants obtained from UV–vis and fluorescence may be due to the change of the acidity/basicity of the molecules on excitation. Nevertheless, the pronounced quenching of fluorescence for hosts **1** and **2** with F^-, not seen with other anions, renders them as fluorogenic sensors for F^- (Fig. 3).

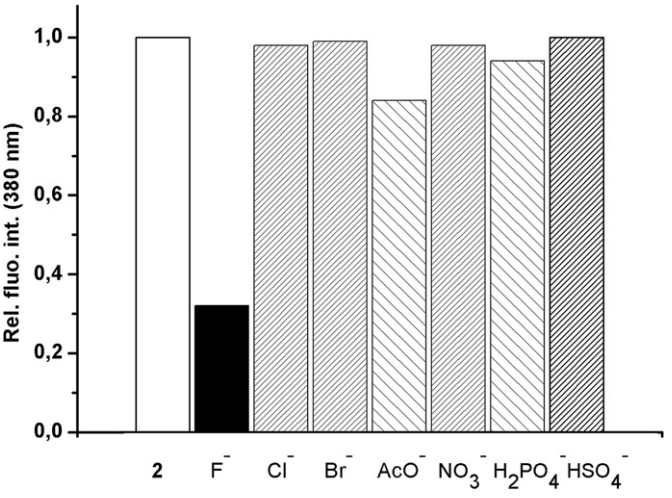


Fig. 3. Application of **2** as fluorogenic anion sensor (comparison of the fluorescence emission of **2** in the CH_3CN after addition of 100 equiv of different TBA salts).

The findings obtained by UV–vis and fluorescence titrations for receptors **1** and **2** strongly indicate formation of the ground state complexes of the receptors with anions. All the complexes are formed in stoichiometry 1:1. Overall, the most stable complexes are observed with the most basic anions F^-, $H_2PO_4^-$ and AcO^-. The binding of the anions is accomplished through hydrogen bonds with two pyrrole NH protons, in contrast to the previous series of adamantane–dipyrromethanes, wherein formation of 1:2 (host/anion) stoichiometries was observed.[6a,c] Probably, in the receptors **1** and **2** binding site is somewhat shielded by the phenyl substituents, so it would be sterically very demanding to surround the anions with two receptors.

Compared to nonsubstituted receptors **1** and **2**, amino derivatives **5** and **6** were anticipated to form more stable complexes with anions due to an introduction of the additional hydrogen bond donors (NH_2 groups). The amino groups along with the pyrrole NH protons could in principle create an optimal surrounding for the stabilization of the negative charge of anion through a net of hydrogen bonds and thus increase the stability of the complex. Although the anticipated trend of increased association constants was not observed (Table 2), amino derivatives **5** and **6** showed selective spectral response in the presence of F^- and HSO_4^- in the UV–vis and fluorescence spectra. On the other hand, little evidence of anion binding was seen for other tested anions (Cl^-, Br^- and NO_3^-), so in some cases calculated association constants are rather uncertain or the recognition can not be observed at all by UV–vis or fluorimetric titration experiments.

An addition of F^- to the CH_3CN solution of **5** or **6** induced quenching of the fluorescence with concomitant bathochromic shift of the spectral maximum. The fluorescence emission intensity at 380 nm decreases, with an increase at ≈400 nm (Fig. 4). Addition of a large excess of other basic anions (i.e., $H_2PO_4^-$) to the solutions of hosts **5** or **6** quenched florescence without shifting the maximum in the spectra. The shifting of the maximum in the fluorescence spectra was not seen with other receptors with either of the tested anions. Therefore, receptors **5** and **6** can be applied as ratiometric fluorescence sensors for F^-.

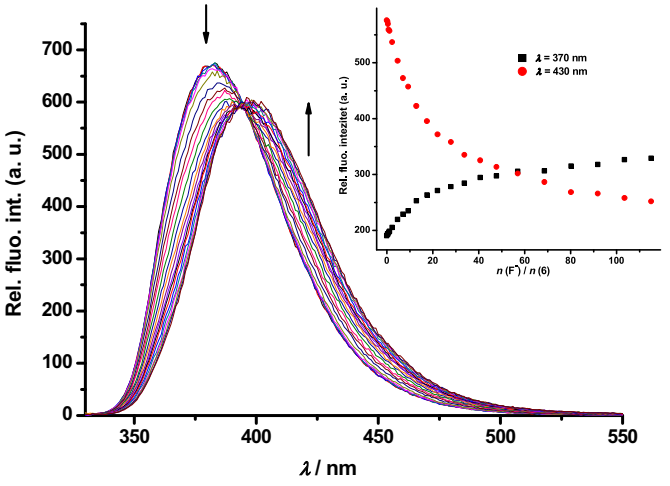


Fig. 4. Fluorescence titration of the CH_3CN solution of **6** ($c=4\times10^{-6}$ M) with the addition of F^-, λ_{ex}=320 nm. The spectra were corrected for dilution. Inset: emission of the CH_3CN solution of **6** at 370 and 430 nm versus mole ratio of F^-/**6**.

Basic F^- can in principle induce deprotonation of the pyrrole NH, which in turn, may be responsible for the observed bathochromic shift.[11] However, the binding of F^- in CH_3CN by **5** or **6** showed a small hyperchromic effect ($\Delta A\approx0.03$) and a small bathochromic shift ($\Delta\lambda\approx0.5$) in the UV–vis spectra (see Supplementary data, Figs. S36 and S43). If F^- had deprotonated the pyrrole NH, the generated negative charge would induce an enhancement in the intensity of the electrical dipole with the direct consequence of a significant red shift of the absorption band. Since it was not observed, we can conclude that the observed spectral change in the fluorescence spectra is result of the hydrogen bonded complex with F^-, and not of deprotonation. Probably, the introduction of the electron-donating group decreased acidity of the pyrrole NH. Additionally, we performed ^1H NMR titrations of **6** with F^- in CD_3CN to probe for the NH deprotonation and get structural information about the complex

geometries. The addition of even a small quantity of F^- (0.125 equiv) resulted in a significant change in the ^1H NMR spectra of **6**, and the excess of F^- shifted the NH signal downfield for ≈5 ppm (see Supplementary data, Fig. S113). Since we have not observed disappearance of the NH signal, deprotonation does not take place in the concentration range for ^1H NMR experiments. Consequently, we can say that receptors **5** and **6** have selective ratiometric fluorescence response only in the presence of F^-.

UV–vis titrations of receptors **5** and **6** with HSO_4^- showed some unexpected spectral changes. Upon addition of $TBAHSO_4$ to the solution of **6** in CH_3CN, absorption bands at ≈285 and ≈320 nm disappeared and the new band at ≈300 nm arose (Fig. 5). Such a change in the UV–vis spectra of **5** and **6** was not seen in the titrations with other tested anions, even in the presence of a large excess. More interestingly, the analysis of the experimental data indicated complexes of 1:2 (host/anion) stoichiometry with much higher association constants. Unique spectral response in the presence of HSO_4^- and specific stoichiometry of the complex call in question if the changes observed in the UV–vis spectra are due to different process then H-bonding complexation. Bowman-James,[14] and Gale[3g] have reported that HSO_4^- (an acidic anion) induces protonation of the receptors, which have basic (amino) substituents. Therefore, we tentatively assign the observed spectral changes to the proton transfer between the HSO_4^- and the amino groups. Furthermore, in the fluorescence titrations of **5** or **6** in CH_3CN solution with $TBAHSO_4$, quenching of the fluorescence was observed with only a small shift of the spectral maximum (Fig. 6). Analysis of the experimental data gave approximately two orders of magnitude higher values of the binding constants than those that were determined by UV–vis. Consequently, the UV–vis and fluorescence titration experiments with HSO_4^- indicate that binding of HSO_4^- is not a simple process, since it is probably accompanied by proton transfer.

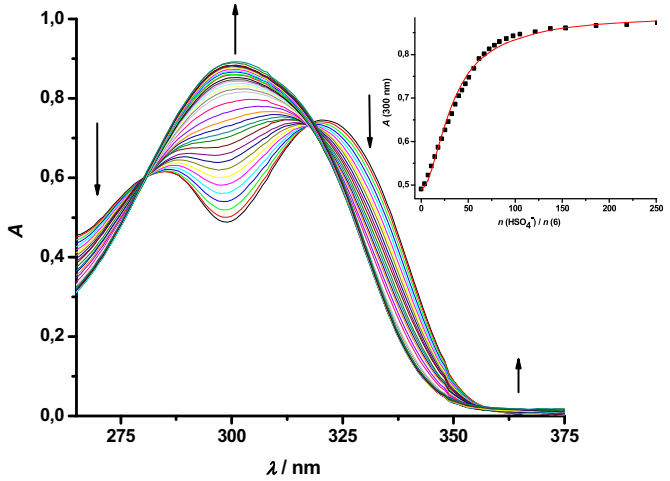


Fig. 5. UV–vis titration of the CH_3CN solution of **6** ($c=3\times10^{-5}$ M) with addition of HSO_4^-. The spectra were corrected for dilution. Inset: absorbance of the CH_3CN solution of **6** at 300 nm versus mole ratio of HSO_4^-/**6** (■ exp. values, — calcd values).

Therefore, the estimated binding constants do not represent real association constants corresponding to the complex of 1:2 stoichiometry, but to a cumulative constant comprising the stability constant of the H-bonded complex, proton transfer (PT), and the stability constant of the ion pair formed by PT. Different values of the association constants obtained from UV–vis and fluorescence titrations are probably due to the change of basicity of the amino group of the receptors on excitation to S_1.

Nitro analogues **3** and **4** are nonfluorescent, so we could only perform UV–vis titrations. Similar to the titrations of receptors **1** and **2**, addition of Cl^-, Br^-, HSO_4^- and NO_3^- to the CH_3CN solution of **3** and **4** had a negligible influence on the UV–vis spectra. The estimated stability constants of the corresponding 1:1 complexes are similar to those obtained for unsubstituted analogues **1** and **2** (Table 2), and in some instances (Br^-, NO_3^-) no anion coordination was observed. On the contrary, more basic anions such as F^-, AcO^- and $H_2PO_4^-$ induced more pronounced changes in the UV–vis spectra (Fig. 7). Generally, an increase of the absorbance at ≈300 nm is observed, and only in the titration with F^- a small bathochromic shift of the absorption band occurred (≈5 nm). Addition of anions induced larger spectral shifts on the low-energy band (350–550 nm). However, due to a low absorptivity of the band, these changes are not applicable for the sensing. Although it was expected that nitro compounds **3** and **4** (compared to dipyrromethanes **1** and **2**) would form complexes with much higher association constants, only a small increase of the complex stability was observed for F^- (Table 2).

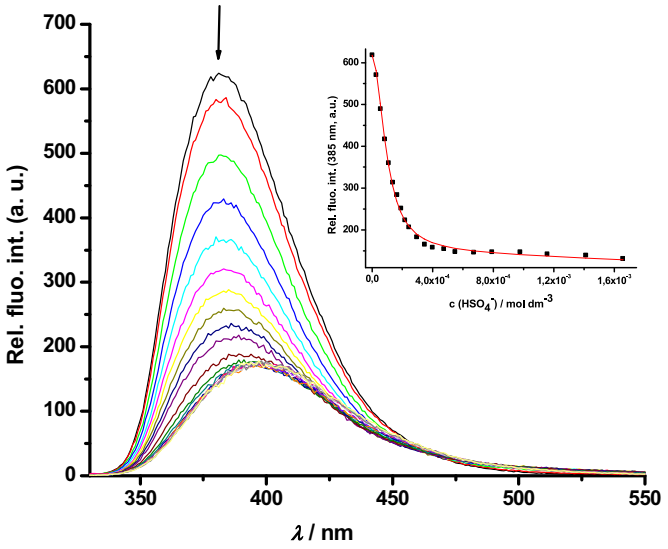


Fig. 6. Fluorescence titration of the CH_3CN solution of **6** ($c=3\times10^{-6}$ M) with the addition of HSO_4^-, λ_{ex}=320 nm. The spectra were corrected for dilution. Inset: emission of the CH_3CN solution of **6** at 385 nm versus concentration of HSO_4^- (■ exp. values, — calcd values).

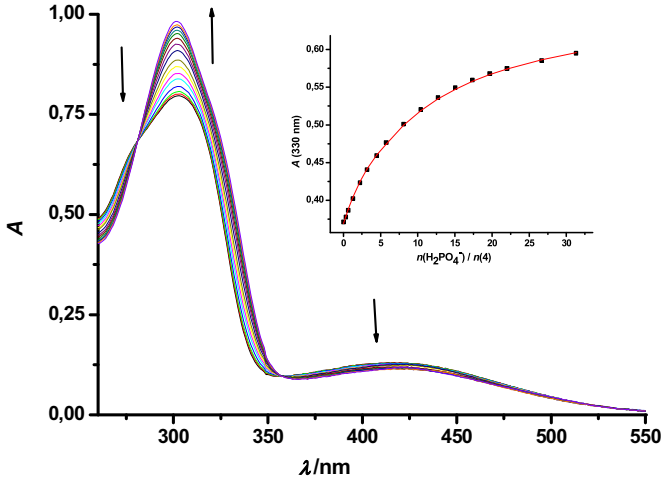


Fig. 7. UV–vis titration of the CH_3CN solution of **4** ($c=4\times10^{-5}$ M) with addition of $H_2PO_4^-$. The spectra were corrected for dilution. Inset: absorbance of the CH_3CN solution of **4** at 330 nm versus mole ratio of $H_2PO_4^-$/**4** (■ exp. values, — calcd values).

From the numerous attempts to grow single crystals of new receptors and/or their complexes, only crystals of receptor **4** were suitable for X-ray analysis. Interestingly, in the crystal structure of **4**, the molecule adopts a conformation with two pyrrolyl moieties pointing to the same directions. The pyrroles NH form two hydrogen bonds with neutral CH_3CN molecule (Fig. 8). Similar conformations were observed earlier in the crystal structures of the anion complexes of unsubstituted dipyrromethanes.[6c] On the other hand, in the crystal structure of the unsubstituted dipyrromethane receptors, the pyrroles adopt a conformation wherein NH are pointing to the opposite directions.[6c] Thus, as demonstrated by the crystal structure of the CH_3CN complex, most probably the structure of receptor **4** is preorganized for binding of anions or neutral molecules.

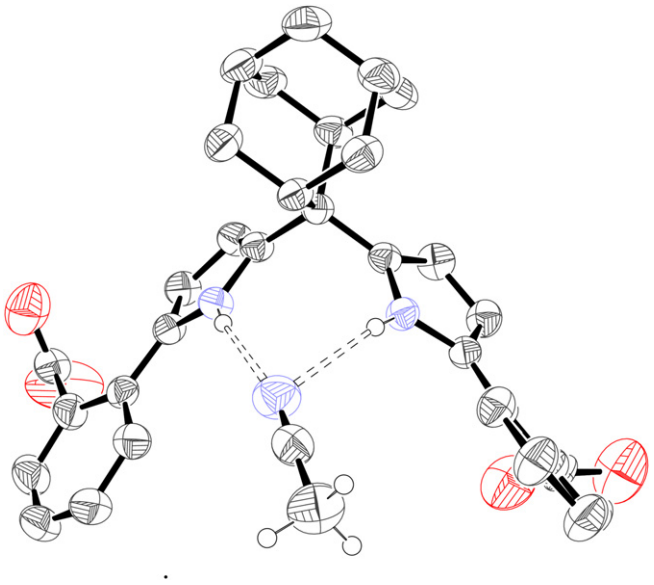


Fig. 8. *ORTEP* view of the asymmetric unit of compound **4**. Thermal ellipsoids are drawn at 50% probability. Acetonitrile molecule forms two hydrogen bonds towards pyrrole nitrogen atoms: N2–H2n···N5 (d(N2–H2n)=0.871 Å, d(H2n–N5)=2.432 Å, ∠(N2–H2n–N5)=161.8°) and N1–H1n···N5 (d(N1–H1n)=0.827 Å, d(H1n–N5)=2.324 Å, ∠(N1–H1n–N5)=154.1°).

In line with other dipyrromethane receptors, the cyano-substituted derivatives **7** and **8** form the most stable complexes with basic anions F^-, AcO^- and $H_2PO_4^-$ (Table 2) and have a low affinity towards Cl^-, Br^- and HSO_4^-, but no binding of NO_3^- was observed. An addition of TBAF to the CH_3CN solution of **8** caused red shift of the absorption band (≈15 nm) and a small hyperchromic effect ($\Delta A \approx 0.15$, Fig. 9). Furthermore, formation of three clear isosbestic points (288, 325 and 360 nm) indicated existence of two coloured species in equilibrium, i.e., molecules of the receptor and its complex. Therefore, from the UV–vis titration of **7** and **8** with F^- there was no indication that the deprotonation of the pyrrole NH takes place, even though we increased its acidity by CN group.

In the fluorescence titration of the CH_3CN solutions of **7** and **8**, quenching of the emission was observed by addition of F^- (Fig. 10), $H_2PO_4^-$ and AcO^- whereas a large excess of other anions did not induce any significant change (see Supplementary data, Figs. S92–S105). The binding of F^- by cyano receptors, as well as conformation changes of the receptors upon binding were investigated by ^{1}H NMR titration of **8** with TBAF in CD_3CN. The addition of 2.5 equiv of F^- to the CD_3CN solution of **8** shifted the pyrrole NH signal downfield from the initial value of δ 9.2–14.8 ppm (see Supplementary data, Fig. S114). In the aromatic region of the ^{1}H spectrum, a prominent downfield shift was also observed to the signal of the *ortho*-phenyl proton ($\Delta\delta \approx 0.8$ ppm), and only negligible

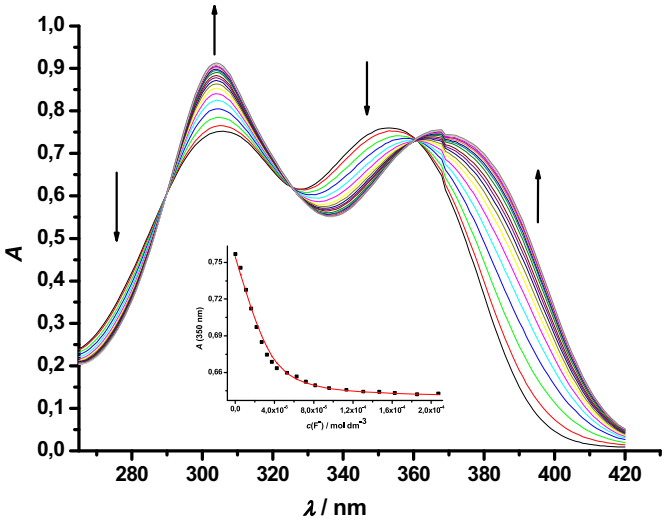


Fig. 9. UV–vis titration of the CH_3CN solution of **8** (c=4×10^{-5} M) with addition of F^-. The spectra were corrected for dilution. Inset: absorbance of the CH_3CN solution of **8** at 350 nm versus concentration of F^- (■ exp. values, — calcd values).

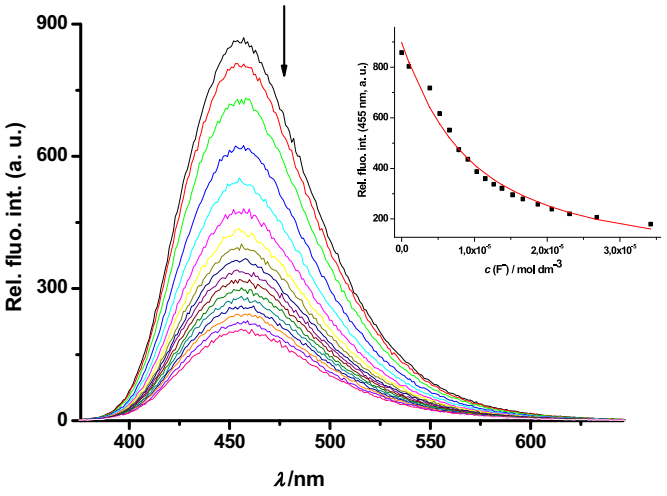


Fig. 10. Fluorescence titration of the CH_3CN solution of **8** (c=4×10^{-6} M) with the addition of F^-, λ_{ex}=355 nm. The spectra were corrected for dilution. Inset: emission of the CH_3CN solution of **8** at 455 nm versus concentration of F^- (■ exp. values, — calcd values).

shifting of the other signals. Since addition of basic F^- did not result in the disappearance of the pyrrole NH signals, we can discard deprotonation of the pyrrole NH, at least in the concentration range for the NMR experiments. Stoichiometry of the 1:1 complex was confirmed by mole ratio method, which was also performed by ^{1}H NMR spectroscopy (Fig. 11).

Since we were not able to grow single crystals of complexes of **7** or **8**, we studied conformation of the receptor **8** and its complex in the solution by NMR, using NOESY experiments. The interactions seen in the NOESY spectrum of receptor **8** showed that there is a free rotation around the single bond between the pyrrole and the phenyl ring, as well as between the pyrrole and the adamantane moiety (Scheme 2). Thus, the NOESY experiment did not indicate the existence of a preferable conformer of **8**.

In the presence of F^-, on the other hand, the interactions between the pyrrole NH protons and the *ortho*-phenyl protons can be seen, in accordance with the observed shift of the phenyl signal in the titration experiments. The finding suggests that the complexation of F^- leads to the conformation in which pyrrole groups

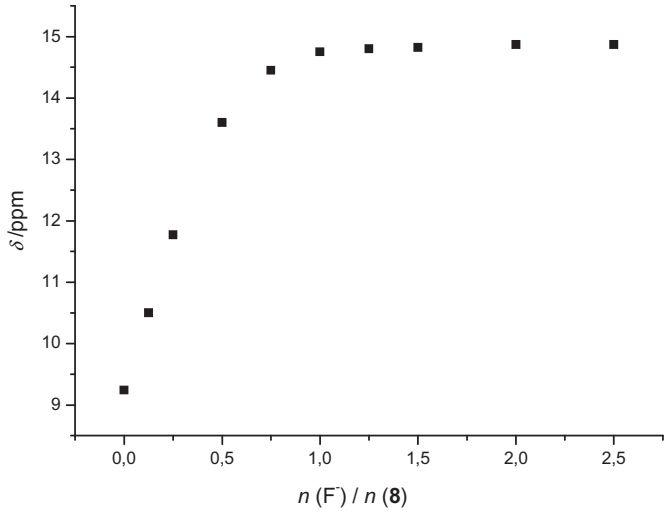
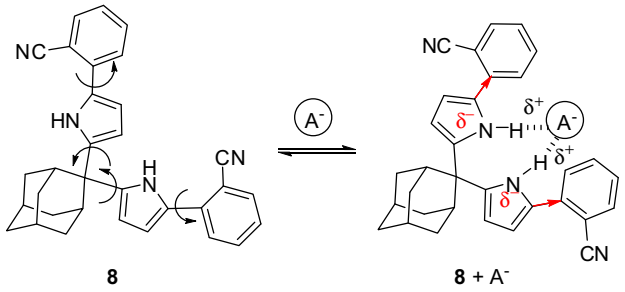


Fig. 11. Mole ratio method for stoichiometry determination of complex **8**·F^- in CD_3CN.



Scheme 2.

are oriented in the same direction forming the H-bonds with the anion, while the cyanide groups are turned out from the cleft with the anion (Scheme 2).

It is known that modification of binding sites by introduction of electron-withdrawing groups increases the acidity of nearby hydrogen bond donors. In turn, this increases the strength of the interactions within the complex and results in the formation of complexes with higher association constants.[15] Accordingly, it was anticipated that introduction of the NO_2 and CN groups to the receptor molecules would improve the binding ability for anions, compared to the unsubstituted analogues **1** and **2**, increasing the corresponding association constants. Whereas nitro group only increased stability of the F^- complexes, cyano derivatives displayed stronger binding with all anions except AcO^-. However, the effect of the electron-withdrawing groups was more demonstrated through the spectral changes observed on titration with anions. Absorption spectra of the receptors with NO_2 (**3** and **4**) and CN substituents (**7** and **8**) have partial charge transfer character. The hydrogen bond interaction between anion and the pyrroles increases the electron density on the pyrroles, which further increases the charge transfer character in both ground and excited states. Therefore, we observed large spectral changes in the titration experiments with **7** and **8**, which render them as useful UV–vis and fluorescence sensors for anions.

3. Conclusion

New adamantane–dipyrromethane anion receptors **1**–**8** were synthesized and their binding ability in the CH_3CN solutions with various TBA salts (F^-, Cl^-, Br^-, AcO^-, HSO_4^-, NO_3^- and $H_2PO_4^-$) was investigated by UV–vis, fluorescence and/or ^1H NMR spectroscopy. Overall, the most stable complexes were formed with basic anions F^-, AcO^- and $H_2PO_4^-$. Since these anions are very different in their geometry it is obvious that the basicity of the anion played the most important role in the molecular recognition process regardless of the change in the functionality of the receptors binding site. However, there is a slight difference in the stability constants of the complexes between the adamant-1-yl and adamant-2,2-diyl substituted receptors and other halide anions tested. The receptors **2**, **4**, **6** and **8**, which have a 2-adamantyl backbone, form the complexes with Cl^- and Br^- with about an order of magnitude higher association constants than the receptors **1**, **3**, **5** and **7** (Table 2). This valuable finding is important for designing the next generation of the receptor molecules with the polycyclic rigid spacers.

4. Experimental section

4.1. General

^1H and ^{13}C NMR spectra were recorded on a on a Bruker Spectrometer at 300 or 600 MHz. All NMR spectra were measured in deuterated solvents using tetramethylsilane as a reference. High-resolution mass spectra (HRMS) were measured on an Applied Biosystems 4800 Plus MALDI TOF/TOF instrument. IR spectra were recorded on FT-IR ABB Bonem MB 102 spectrophotometer. UV–vis spectra were recorded on Varian Cary 100 spectrometer equipped with a thermostating device. For fluorescence measurements, Cary Eclipse Varian and Hitachi F-4500 spectrofluorimeters were used. Fluorescence decay histograms were obtained on an Edinburgh instrument OB920. Single crystal was measured on an Oxford Diffraction Xcalibur 3. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected.

Adamantane-1-carbaldehyde (**10**),[16] adamantane-2-one (**11**),[17] and 2-phenylpyrrole precursors (**9a**–**c**)[10] were prepared according to the procedure described in the literature. The new receptors **1**–**4**, **7** and **8** were additionally dried in Memmert vacuum drying oven to remove residual solvent.

4.2. General procedure for preparation of receptors 1–4, 7 and 8

In a two-neck flask under a stream of nitrogen carbaldehyde **10** or ketone **11** (1 mmol) and the corresponding phenylpyrroles **9a**–**c** (2 mmol) were dissolved in a small volume of dry CH_2Cl_2 (ca. 5–10 mL). By use of a syringe, to the reaction mixture was added TFA (0.1 mmol) and the mixture was stirred at rt, while the progress of the reaction was followed by TLC using CH_2Cl_2 as an eluent. Upon the disappearance of the starting 2-phenylpyrrole, the reaction was quenched by the addition of an aqueous solution of NaOH (0.1 M, ~20 mL) and the layers were separated. The aqueous layer was extracted two more times using CH_2Cl_2 (2×20 mL), the organic extracts were washed with water (20 mL), collected and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated on a rotary evaporator and the obtained dark residue was purified by chromatography, crystallization or washing with solvent.

*4.2.1. 1-[Di(5-phenyl-1H-pyrrol-2-yl)methyl]adamantane (**1**).* Obtained by reacting adamantane-1-carbaldehyde (**10**, 103 mg, 0.63 mmol) with 2-phenylpyrrole (**9a**, 180 mg, 1.26 mmol) in the presence of TFA (10 μL, 0.13 mmol) in dry CH_2Cl_2 (5 mL). After stirring over 7 days at rt the reaction was quenched and worked-up following the general procedure. After two chromatographies on silica gel using 0→50% CH_2Cl_2 in hexane as eluent reaction furnished 187 mg of product **1** in the form of colourless crystals. The obtained compound was further dried on 60 °C and 1000 Pa for 3 days. Colourless crystals, 187 mg, 69%; mp 92–94 °C; UV (CH_3CN) λ_{max} (log ε): 304 nm (4.59 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3430 (m), 2901

(m), 2845 (w), 1604 (w), 1506 (m), 753 (s), 692 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58–1.72 (m, 12H), 1.97 (br s, 3H), 3.62 (s, 1H), 6.17–6.24 (m, 2H), 6.44–6.52 (m, 2H), 7.12–7.19 (m, 2H), 7.29–7.34 (m, 4H), 7.37–7.44 (m, 4H), 8.27 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.6 (3×CH), 36.7 (3×CH_2), 37.0 (C), 40.4 (3×CH_2), 51.9 (CH), 106.2 (2×CH), 108.5 (2×CH), 123.3 (4×CH), 125.7 (2×CH), 128.7 (4×CH), 130.2 (2×C), 131.2 (2×C), 132.6 (2×C) ppm; HRMS calculated for $C_{31}H_{33}N_2$ ($[M+H]^+$): 433.2644; observed: 433.2650.

*4.2.2. 2,2-Di(5-phenyl-1H-pyrrol-2-yl)adamantane (**2**).* Obtained by reacting adamantane-2-one (**11**, 95 mg, 0.63 mmol) with 2-phenylpyrrole (**9a**, 180 mg, 1.26 mmol) in the presence of TFA (10 μL, 0.13 mmol) in dry CH_2Cl_2 (5 mL). After stirring over 5 days at rt the reaction was quenched and worked-up following the general procedure. After two chromatographies on silica gel using 0→50% CH_2Cl_2 in hexane as eluent reaction furnished 173 mg of product **2** in the form of colourless crystals. The obtained compound was further dried on 60 °C and 1000 Pa for 3 days. Colourless crystals, 173 mg, 66%; mp 75–77 °C; UV (CH_3CN) λ_{max} (log ε): 306 nm (4.52 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3448 (m), 2901 (m), 2853 (w), 1603 (m), 1503 (m), 1207 (w), 751 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.73–1.90 (m, 8H), 2.23–2.32 (m, 4H), 2.72 (br s, 2H), 6.11–6.19 (m, 2H), 6.32–6.39 (m, 2H), 7.08–7.16 (m, 2H), 7.26–7.38 (m, 8H), 7.97 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.3 (2×CH), 33.6 (4×CH_2), 33.9 (2×CH), 38.0 (1×CH_2), 45.4 (1×C), 105.7 (2×CH), 106.2 (2×CH), 123.3 (4×CH), 125.6 (2×CH), 128.6 (4×CH), 130.5 (2×C), 132.8 (2×C), 139.0 (2×C) ppm; HRMS calculated for $C_{30}H_{29}N_2$ ($[M-H]^+$): 417.2331; observed: 417.2323.

*4.2.3. 1-{Di[5-(2-nitrophenyl)-1H-pyrrol-2-yl]methyl}adamantane (**3**).* Obtained by reacting carbaldehyde **10** (362 mg, 2.2 mmol) with phenylpyrrole **9b** (835 mg, 4.4 mmol) in the presence of TFA (33 μL, 0.44 mmol) in dry CH_2Cl_2 (10 mL). After stirring over 4 days at rt the reaction was quenched and worked-up following the general procedure. After chromatography on silica gel using CH_2Cl_2 as eluent and the subsequent rechromatography on silica gel using 0→5% EtOAc in CH_2Cl_2 as eluent reaction furnished 712 mg of product **3** in the form of red crystals. The obtained compound was further dried on 35 °C and 1000 Pa for 20 h. Red crystals, 712 mg, 62%; mp 88–90 °C; UV (CH_3CN) λ_{max} (log ε): 299 nm (4.37 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3424 (m), 2901 (m), 2846 (m), 1605 (w), 1521 (s), 1349 (w), 778 (m), 743 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.57–1.63 (m, 9H), 1.64–1.68 (m, 3H), 1.98 (br s, 3H), 3.59 (s, 1H), 6.22 (dd, 2H, *J*=3.5, 2.7 Hz), 6.47 (dd, 2H, *J*=3.5, 2.7 Hz), 7.28 (dt, 1H, *J*=7.8, 1.1 Hz), 7.50 (dt, 1H, *J*=7.8, 1.2 Hz), 7.58 (dd, 1H, *J*=8.1, 1.2 Hz), 7.69 (dd, 1H, *J*=8.1, 1.1 Hz), 8.83 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 28.6 (3×CH), 36.6 (3×CH_2), 37.3 (C), 40.2 (3×CH_2), 51.8 (CH), 109.1 (2×CH), 111.7 (2×CH), 124.5 (2×CH), 124.7 (2×C), 126.3 (2×CH), 126.8 (2×C), 130.3 (2×CH), 132.2 (2×CH), 132.9 (2×C), 147.5 (2×C) ppm; HRMS calculated for $C_{31}H_{30}N_4NaO_4$ ($[M+Na]^+$): 545.2159; observed: 545.2136.

*4.2.4. 2,2-Di[5-(2-nitrophenyl)-1H-pyrrol-2-yl]adamantane (**4**).* Obtained by reacting ketone **11** (223 mg, 1.5 mmol) with phenylpyrrole **9b** (558 mg, 3 mmol) in the presence of TFA (33 μL, 0.44 mmol) in dry CH_2Cl_2 (10 mL). After stirring over 4 days at rt the reaction was quenched and worked-up following the general procedure. After chromatography on silica gel using 0→5% EtOAc in CH_2Cl_2 as eluent reaction furnished 518 mg of product **4** in the form of red crystals. The obtained compound was further dried on 35 °C and 1000 Pa for 20 h. Red crystals, 518 mg, 68%; mp 198–200 °C; UV (CH_3CN) λ_{max} (log ε): 302 nm (4.31 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3449 (s), 2926 (w), 2897 (w), 2878 (w), 1605 (w), 1521 (s), 1487 (m), 1333 (s), 1292 (m), 1206 (m), 1038 (m), 850 (w), 781 (m), 743 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.76 (br s, 2H), 1.82 (d, 4H, *J*=12.2 Hz), 1.86 (br s, 2H), 2.19 (d, 4H, *J*=12.2 Hz), 2.73 (br s, 2H), 6.15 (dd, 2H, *J*=3.5, 2.7 Hz), 6.38 (dd, 2H, *J*=3.5, 2.7 Hz), 7.20–7.24 (m, 2H), 7.43–7.48 (m, 2H), 7.54 (dd, 2H, *J*=8.1, 1.2 Hz), 7.66 (dd, 2H, *J*=8.1, 1.2 Hz), 8.79 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 27.1 (2×CH), 33.4 (4×CH_2), 33.5 (2×CH), 37.8 (CH_2), 45.3 (C), 106.3 (2×CH), 111.5 (2×CH), 124.5 (2×CH), 124.7 (2×C), 126.0 (2×CH), 126.9 (2×C), 130.2 (2×CH), 132.1 (2×CH), 140.5 (2×C), 147.3 (2×C) ppm; HRMS calculated for $C_{30}H_{29}N_4O_4$ ($[M+H]^+$): 509.2183; observed: 509.2187.

*4.2.5. 1-{Di[5-(2-cyanophenyl)-1H-pyrrol-2-yl]methyl}adamantane (**7**).* Obtained by reacting carbaldehyde **10** (120 mg, 0.7 mmol) with phenylpyrrole **9c** (245 mg, 1.4 mmol) in the presence of TFA (11 μL, 0.1 mmol) in dry CH_2Cl_2 (10 mL). After stirring over 6 days at rt the reaction was quenched and worked-up following the general procedure. To remove unreacted phenylpyrrole precursor **9c** the crude mixture was washed with the CH_2Cl_2 and hexane mixture. Analytically pure compound (256 mg) in the form of white powder was obtained by crystallization from methanol, which was further dried on 60 °C and 1000 Pa for 24 h. White powder, 256 mg, 73%; mp 216–218 °C; UV (CH_3CN) λ_{max} (log ε): 304 and 348 nm: (4.30 and 4.26 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3349 (m), 3325 (m), 2906 (s), 2850 (m), 2226 (s), 1594 (m), 1502 (s), 1268 (w), 1196 (w), 761 (s) cm^{-1}; ^1H NMR (CD_3CN, 600 MHz) δ 1.57–1.62 (m, 3H), 1.65–1.72 (m, 9H), 2.07–2.10 (br s, 2H), 3.79 (s, 2H), 6.29 (dd, 2H, *J*=3.5, 2.6 Hz), 6.78 (dd, 2H, *J*=3.5, 2.6 Hz), 7.26–7.32 (m, 2H), 7.59–7.63 (m, 4H), 7.68–7.72 (m, 2H), 9.47 (br s, 2H) ppm; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.56–1.75 (m, 12H), 1.99 (br s, 3H), 3.67 (s, 1H), 6.31 (dd, 2H, *J*=3.5, 2.7 Hz), 6.74–6.82 (m, 2H), 7.14–7.23 (m, 2H), 7.51 (dt, 2H, *J*=7.4, 1.3 Hz), 7.56–7.66 (m, 4H), 9.12 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.5 (3×CH), 36.6 (3×CH_2), 37.5 (C), 40.3 (3×CH_2), 52.0 (CH), 105.0 (2×C), 109.5 (2×CH), 110.8 (2×CH), 120.5 (2×C), 125.2 (2×CH), 126.1 (2×CH), 126.7 (2×C), 132.9 (2×C), 133.2 (2×C), 133.8 (2×CH), 135.4 (2×C) ppm; HRMS: calculated for $C_{33}H_{30}N_4$ ($[M]^+$): 482.2465; observed: 482.2462.

*4.2.6. 2,2-Di[5-(2-cyanophenyl)-1H-pyrrol-2-yl]adamantane (**8**).* Obtained by reacting ketone **11** (90 mg, 0.6 mmol) with phenylpyrrole **9c** (200 mg, 1.2 mmol) in the presence of TFA (8 μL, 0.1 mmol) in dry CH_2Cl_2 (10 mL). After stirring over 5 days at rt the reaction was quenched and worked-up following the general procedure. To remove unreacted phenylpyrrole precursor **9c** the crude mixture was washed with the CH_2Cl_2 hexane mixture. Analytically pure compound (172 mg) in the form of white powder was obtained by chromatography on preparative TLC with 10% diethyl ether in CH_2Cl_2 as eluent. The compound was further dried on 60 °C and 1000 Pa for 48 h. White powder, 172 mg, 62%; mp 230–231 °C; UV (CH_3CN) λ_{max} (log ε): 304 and 355 nm (4.27 and 4.26 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3446 (m), 3142 (m), 3377 (m), 3317 (m), 2902 (s), 2854 (m), 2226 (s), 1602 (s), 1498 (s), 1216 (m), 1055 (w), 757 (s) cm^{-1}; ^1H NMR (CD_3CN, 600 MHz) δ 1.77–1.86 (m, 8H), 2.14–2.20 (m, 4H), 2.96 (br s, 2H), 6.18 (dd, 2H, *J*=3.6, 2.7 Hz), 6.66 (dd, 2H, *J*=3.6, 2.7 Hz), 7.25–7.29 (m, 2H), 7.57–7.60 (m, 4H), 7.66–7.70 (m, 2H), 9.25 (br s, 2H) ppm; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.72–1.99 (m, 8H), 2.15–2.99 (m, 4H), 2.82 (br s, 2H), 6.22 (dd, 2H, *J*=3.6, 2.7 Hz), 6.67 (dd, 2H, *J*=3.6, 2.7 Hz), 7.08–7.19 (m, 2H), 4.41–7.51 (m, 2H), 7.53–7.61 (m, 4H), 9.12 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$,75 MHz) δ 27.1 (2×CH), 33.3 (2×CH), 33.5 (4×CH_2), 37.7 (CH_2), 45.5 (C), 104.5 (2×C), 106.6 (2×CH), 110.5 (2×CH), 120.8 (2×C), 124.9 (2×CH), 125.9 (2×CH), 126.6 (2×C), 132.8 (2×CH), 133.7 (2×CH), 135.6 (2×C), 140.9 (2×C) ppm; HRMS calculated for $C_{32}H_{28}N_4$ ($[M]^+$): 468.2387; observed: 468.2380.

4.3. General procedure for preparation of receptors 5 and 6

Nitro compounds **3** and **4** were submitted to hydrogenation on 10% Pd/C in abs methanol in a Paar apparatus at 60 psi of hydrogen on rt. After the disappearance of the characteristic red colour of the

compounds the catalyst was filtered off, and the solvent was evaporated under reduced pressure to afford crude products of amino derivatives **5** and **6**, which were further chromatographed on a silica gel column.

*4.3.1. 1-{Di[5-(2-aminophenyl)-1H-pyrrol-2-yl]methyl}adamantane (**5**).* Following the general procedure amino compound **5** was obtained by hydrogenation of nitro derivative **3** (100 mg, 0.2 mmol) dissolved in abs methanol (40 mL) with 10% Pd/C catalyst (40 mg). After 5 h under pressure of 4070 hPa of hydrogen the reaction was completed. Purification by chromatography on a silica gel column with 0→1% MeOH in CH_2Cl_2 as eluent afforded 58 mg of the product **5** in the form of colourless crystals. Colourless crystals, 58 mg, 65%; mp 113–115 °C; UV (CH_3CN) λ_{max} (log ε): 280 and 320 nm (4.28 and 4.29 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3420 (s), 2902 (s), 2846 (w), 1615 (m), 749 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.51–1.71 (m, 12H), 1.90–2.0 (br s, 3H), 3.59 (s, 1H), 3.93 (br s, 4H), 6.12–6.23 (m, 2H), 6.29–6.42 (m, 2H), 6.69–6.87 (m, 4H), 6.99–7.11 (m, 2H), 7.19–7.24 (m, 2H), 8.48 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.6 (3×CH), 36.7 (3×CH_2), 37.1 (C), 40.3 (3×CH_2), 51.7 (CH), 107.5 (2×CH), 107.8 (2×CH), 116.5 (2×CH), 119.1 (2×CH), 119.8 (2×C), 127.3 (2×CH), 127.6 (2×C), 127.9 (2×CH), 130.5 (2×C), 142.8 (2×C) ppm; HRMS calculated for $C_{31}H_{34}N_4$: 462.2778; observed: 462.2794.

*4.3.2. 2,2-Di[5-(2-aminophenyl)-1H-pyrrol-2-yl]adamantane (**6**).* Following the general procedure amino compound **6** was obtained by hydrogenation of nitro derivative **4** (220 mg, 0.4 mmol) dissolved in abs methanol (75 mL) with 10% Pd/C catalyst (80 mg). After 6 h under pressure of 3999 hPa of hydrogen the reaction was completed. Purification by chromatography on a silica gel column with 2→10% diethyl ether in CH_2Cl_2 as eluent afforded 139 mg of the product **6** in the form of colourless crystals. White powder, 139 mg, 72%; mp 168–169 °C; UV (CH_3CN) λ_{max} (log ε): 285 and 320 nm (4.26 and 4.33 M^{-1} cm^{-1}); IR (KBr) ν_{max} 3430 (m), 3333 (m), 2902 (s), 2850 (s), 1610 (s), 1502 (s), 1474 (m), 1445 (w), 1200 (w), 773 (s), 745 (s) cm^{-1}; ^1H NMR (CD_3CN, 600 MHz) δ 1.77–1.83 (m, 8H), 2.17–2.21 (m, 4H), 2.9 (br s, 2H), 4.23 (s, 4H), 6.06 (dd, 2H, J=3.4, 2.8 Hz), 6.19 (dd, 2H, J=3.4, 2.8 Hz), 6.69 (dt, 1H, J=7.4, 0.9 Hz), 6.73 (dd, 1H, J=7.9, 0.9 Hz), 6.97–7.00 (m, 1H), 7.14 (dd, 2H, J=7.6, 1.4 Hz), 8.89 (br s, 2H) ppm; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71–1.91 (m, 8H), 2.19–2.33 (m, 4H), 2.70 (br s, 2H), 3.82 (s, 4H), 6.07–6.13 (m, 2H), 6.20–6.27 (m, 2H), 6.68–6.82 (m, 4H), 7.02 (dt, 1H, J=7.8, 1.3 Hz), 7.16 (dd, 1H, J=7.6, 1.1 Hz), 8.30 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.4 (2×CH), 33.6 (4×CH_2), 33.7 (2×CH), 38.0 (CH_2), 45.4 (C), 105.2 (2×CH), 106.8 (2×CH), 116.5 (2×CH), 119.1 (2×CH), 120.1 (2×C), 127.2 (2×CH), 127.8 (2×C), 127.9 (2×CH), 138.5 (2×C), 142.8 (2×C) ppm; HRMS calculated for $C_{30}H_{32}N_4$: 448.2621; observed: 448.2625.

4.4. UV–vis titrations

The receptor was dissolved in spectroscopic grade CH_3CN in the concentration range 10^{-5} M, corresponding to the maximum of absorbance in the range 0.6–0.9. The solution of the receptor was placed in a quartz cuvette (1 mL) and small volumes (5–20 μL) of the following anion solutions were added: TBAF (1 M in THF, containing <5 wt % H_2O, diluted with CH_3CN to 1×10^{-3} M), TBACl, TBABr, TBAOAc, $TBAHSO_4$ or $TBAH_2PO_4$ (from 1×10^{-3} to 1×10^{-1} M in CH_3CN). After each addition, UV–vis spectra were recorded. The titrations were performed at 25 °C. The spectrometric data were processed using SPECFIT program.

4.5. Fluorescence titrations

The receptor was dissolved in CH_3CN in the concentration range ≈10^{-5} M, corresponding to the absorbance maximum in the range ≈0.08. The solution of the receptor was placed in a quartz cuvette (3 mL) and small volumes (10 μL) of the solutions of anion are added: TBAF (1 M in THF, containing <5 wt % H_2O, diluted with CH_3CN to 1×10^{-3} M), or TBACl, TBABr, TBAOAc, $TBAHSO_4$ or $TBAH_2PO_4$ (from 1×10^{-3} to 1×10^{-1} M in CH_3CN). After each addition, fluorescence spectra were recorded. The titrations were performed at 25 °C. The obtained data were processed using SPECFIT program.

In other set of titrations experiments freshly prepared samples in 1-cm quartz cells were used to perform all UV–vis absorption and emission measurements. All spectra were recorded at 20 °C using undegassed samples. The titration experiments were carried out by adding small quantities of a stock solution of tetrabutylammonium salt in acetonitrile to a much larger volume (25 mL) of solutions of compounds. The data were processed as specified in Supplementary data.

4.6. ^1H NMR titrations

To a 0.5 mL of the CD_3CN solution of anion receptor (c≈0.01 M) was added a solution of TBAF (1 M in THF, containing <5 wt % H_2O) or $TBAHSO_4$ (≈0.1 M in CD_3CN). After each addition, ^1H NMR spectra were recorded.

4.7. Steady state and time-resolved fluorescence measurements

The compounds were dissolved in CH_3CN (HPLC grade), or cyclohexane (UV-spectroscopy grade) and the concentrations were adjusted to have absorbance at the excitation wavelength <0.1. Solutions were purged with argon for 30 min prior to analysis. The measurements were performed at 20 °C. Fluorescence quantum yields were determined by comparison of the integral of the emission bands with the quinine sulfate in 0.5 M H_2SO_4 (Φ=0.54).[18] Typically, three absorption traces were recorded (and averaged) and three fluorescence emission traces, excited at three different wavelengths. Three quantum yields were calculated and the mean value reported.

Fluorescence decay histograms were obtained on an Edinburgh instrument OB920, equipped with light emitting diode (excitation wavelength 310 nm), using time-correlated single photon counting technique in 1023 channels. Histograms of the instrument response functions (using LUDOX scatterer), and sample decays were recorded until they typically reached 3×10^3 counts in the peak channel. The half width of the instrument response function was typically ~1.5 ns. The time increment per channel was 0.02, 0.049 or 0.098 ns. Obtained histograms were fitted as sums of exponential using Gaussian-weighted non-linear least-squares fitting based on Marquardt–Levenberg minimization implemented in the software package of the instrument. The fitting parameters (decay times and pre-exponential factors) were determined by minimizing the reduced chi-square χ^2. Additional graphical method was used to judge the quality of the fit that included plots of surfaces ('carpets') of the weighted residuals versus channel number.

4.8. Crystallography

Single crystal was obtained by slow evaporation of CH_3CN/hexane (~1:1) solution of the receptor at the 4 °C. Single crystal diffraction data were collected from the crystal glued on a glass fibre tip. Diffraction intensity data were collected by ω-scans on an Oxford Diffraction Xcalibur 3 using graphite-monochromated Mo Kα radiation (λ=0.71073 Å) and reduced using the CrysAlis[19] program package. A summary of general and crystal data, intensity data collection and final refinement parameters are presented in Table S1 (Supplementary data). The structures were solved by direct methods using SHELXS.[20] The refinement

procedure by full-matrix least-squares methods based on F^2 values against all reflections included anisotropic displacement parameters for all non-H atoms. The positions of H-atoms each riding on its parent carbon atom were determined on stereochemical grounds. Hydrogen atoms bonded to pyrrole nitrogen atoms were located form difference Fourier map and isotropically refined. Refinements were performed using SHELXL-97.[20] The SHELX programs operated within the WinGX[21] suite. Molecular graphics were done with Mercury[22] and ORTEP.[23] Supplementary crystallographic data sets for the structures are available through the Cambridge Structural Database with deposition number CCDC900725. Copy of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.026.

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