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A Case of Oxoanions Recognition Based on Combined Cationic and Neutral C–H Hydrogen Bond Interactions†

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Novel bidentate bis-(benzimidazolium) receptor containing pyrene as fluorescent signaling units has been synthesized. Fluorescent and NMR spectroscopy studies reveal that this receptor exclusively recognizes sulphate and hydrogenpyrophosphate in the competitive water-DMSO (1:9) medium; significant downfield shifts were observed for the C(2)-H protons of both the imidazolium groups, and appreciable downfield shifts were also observed for the inner naphthalene protons indicating their participation in hydrogen bonding with anions along with the C(2) imidazolium protons. The calculated association constants from ^{1}H NMR and fluorescence titrations demonstrate that the receptor binds sulphate stronger than hydrogenpyrophosphate anions

Introduction

The design and synthesis of receptors and sensor for anions has received considerable attention in recent years and continues to be highly topical.[1] Anions play a very important role in biology[2], pharmacy[3] and environmental processes.[4] Hydrogen bonding has been the most popular interaction used in the design of neutral anion receptors by the utilization as binding sites of ureas,[5] thioureas,[6] amides,[7] guanidines[8] pyrroles,[9] and imidazoles[10] moieties among others. Additionally electrostatic, Lewis acid-base[11] and more recently, anion–π interactions[12] and halogen bonding[13] have all been exploited in the construction of a wide variety of highly efficient receptors for anions.

The combination of the electrostatic and hydrogen bonding interactions have demonstrated to be a good strategy for anions recognition. In particular, imidazolium[14] and triazolium[15] have proved to be potent CH hydrogen bonding donor motifs as anion recognizing sites to be incorporated into molecular receptor framework by virtue of the positive charge and the presence of relatively acidic C-H groups. However, to the best of our knowledge, receptors with pure neutral CH H-bonding donor motifs have not yet been exploited for the purpose of oxoanions recognition.[16] In this context, we are interested in pursuing this goal to create receptors in which selectivity arises from the combined intrinsic anion preference of two distinct cationic and neutral CH hydrogen bond interactions. We report here the synthesis and a comparative study of the anion sensing properties of a novel charge-assisted bis-(benzimidazolium) receptor where a naphthalene spacer group is decorated with two arms containing as binding site benzimidazolium motif, end capped with a photoactive pyrene ring. This chemosensor molecule only recognizes sulphate and hydrogen pyrophosphate anions in aqueous solvent media (DMSO/H_2O 9:1).

Hydrogenpyrophosphate ($HP_2O_7^{3-}$) plays an important role in energy transduction in organisms. ATP hydrolysis, with the concomitant release of pyrophosphate, is central to many biochemical reactions.[17] Telomerase (a biomarker for cancer diagnosis) activity is measured by evaluating the amount of pyrophosphate in the PCR amplification of the telomerase elongation product.[18] Furthermore, a high level of pyrophosphate in synovial fluids is correlated to calcium pyrophosphate dehydrate disease (CPDD), a rheumatologic disorder.[19] Therefore, the detection and discrimination of this anion has been the main focus of the effort of several research groups. However, very few examples of effective selective fluorescent chemosensors[20] have been reported so far. To date, several different heterocyclic ring systems containing a pyrrolic NH group have been reported in the literature as hydrogen-bond donors to anions, bis(imidazoles),[21] and imidazole derivatives.[22]

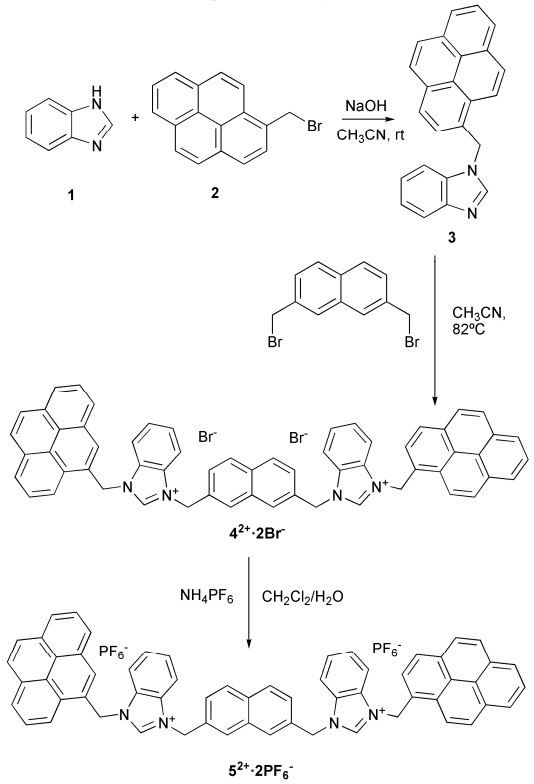
The development of sulphate selective anion receptors is currently an area of intense interest due to the important roles this anion plays in biological systems and disease[23] and the appreciation of the role they could play in radioactive waste remediation.[24] Considerable effort has been devoted to the synthesis of receptors that might allow the removal of sulfate from the highly basic nitrate-rich mixtures produced by pretreatment of the original radioactive waste with NaOH.[25] Consequently, one of the current challenges in anion recognition chemistry involves the preparation of receptors that

show high sulfate/nitrate selectivity.[26] Sulfate recognition in aqueous media is difficult because of its high hydration energy (ΔG_h= -1080 kJ/mol *vs* -300 kJ/mol for nitrate),[27] and extreme hydrophilicity according to the Hofmeister series.[28]

Results and discussion

Synthesis

The bis-(benzimidazolium) target receptor derivative $\mathbf{5^{2+}\cdot 2PF_6^-}$ has been prepared in a 31% overall yield by a stepwise procedure which involves initial reaction of 1*H*-benzo[*d*]imidazole **1** with 1-(Bromomethyl)pyrene **2** in acetonitrile in 1:1 molar ratio in the presence of a slight excess of NaOH to give the pyrenemethyl benzimidazole **3** in 73% yield. Subsequent reaction of two equiv of compound **3** with 2,7-Bis(bromomethyl)naphthalene in acetonitrile at reflux temperature afforded the bis-(benzimidazolium) $\mathbf{4^{2+}}$ as bromide salt in 42% yield, which was readily converted into the desired $\mathbf{5^{2+}\cdot 2PF_6^-}$ in quantitative yield by several washings with aqueous NH_4PF_6 (Scheme 1). All the prepared compounds have been fully characterized using standard techniques: ^{1}H NMR, ^{13}C NMR and FAB mass spectrometry.



Scheme 1: Synthesis of the bis-(benzimidazolium) receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$.

Anion binding studies

The anion binding properties of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ toward $HP_2O_7^{3-}$, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, NO_3^-, F^-, Cl^-, Br^-, I^-, AcO^-, ClO_4^-, BF_4^- and $C_6H_5CO_2^-$ anions as tetrabutylammonium salt and the organic phosphate derivatives ATP, ADP and AMP as sodium salt, was initially investigated using ^{1}H NMR titration experiments through the addition of aliquots of the different anions to solutions of the receptors in DMSO and DMSO/D_2O 9:1.

Receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ exhibits the characteristic signals corresponding to the naphthalene ring: one singlet at δ = 7.95 ppm and two doublets around δ = 7.5 -7.7 ppm and the end-capped pyrene rings: complex set of signals in the range δ = 8.0 ppm δ = 8.6 ppm. Additionally the methylene protons of the two arms naphthalene-CH_2-imidazolium ring and pyrene-CH_2-imidazolium ring appear as two different singlets at δ = 5.88 ppm and δ = 6.57 ppm respectively, whereas the imidazolium protons appear as a singlet at δ = 9.83 ppm. Although the ^{1}H NMR spectra of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO-d_6 and DMSO-d_6/D_2O 9:1 are very similar, it is necessary to underline that in the aqueous solvent mixture the imidazolium protons were absent.

The addition of increasing amount of SO_4^{2-} anions to a solution of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO-d_6 promote an important and progressive downfield shifts for the signal corresponding to the imidazolium protons from δ = 9.83 to δ = 11.58 ppm (Δδ = 1.75 ppm) and the H_c protons of the naphthalene central ring from δ = 7.95 to δ = 8.62 ppm (Δδ = 0.67 ppm) indicating a direct interaction of the SO_4^{2-} anions with these protons. The naphthalene-CH_2-imidazolium and pyrene-CH_2-imidazolium protons were also downfield shifted although in less extension (Δδ = 0.1 ppm) (Figure 1). Similar changes were observed after addition of $HP_2O_7^{3-}$ anions although all the signals were considerably broader than in $\mathbf{5^{2+}\cdot SO_4^{2-}}$ (See SI).

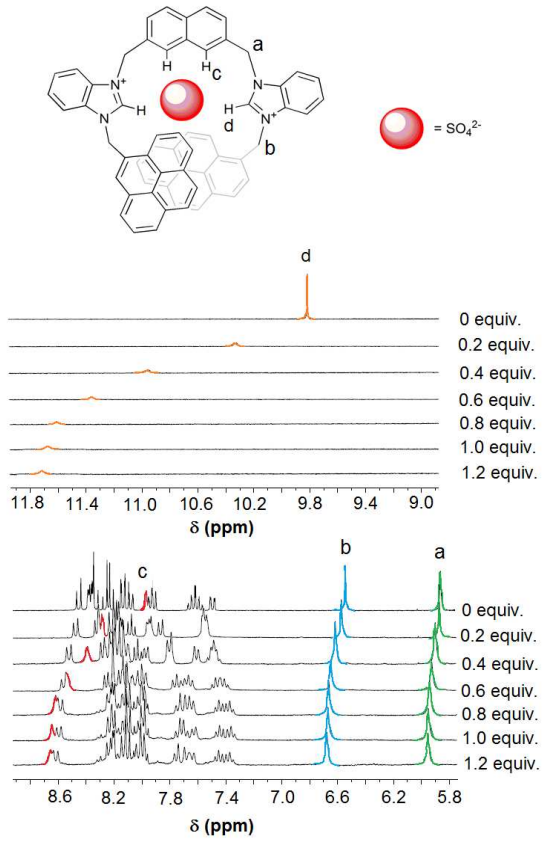


Figure 1. ^{1}H NMR spectral changes observed in receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ (c = 1 x 10^{-3} M in DMSO-d_6) during the addition of up to 1.2 equiv of SO_4^{2-} anions.

The same ^{1}H NMR titration experiments were also carried out in the more competitive medium DMSO-d_6/D_2O 9:1, the most

noticeable changes upon addition of $HP_2O_7^{3-}$ anions to a solution of $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO-d_6/D_2O 9:1 were the downfield shift of the H_c naphthalene protons ($\Delta\delta$ = 0.54 ppm), and the methylene protons in the arm naphthalene-CH_2-imidazolium ring ($\Delta\delta$ = 0.1 ppm). Unlike the shifts observed in DMSO-d_6, addition of $HP_2O_7^{3-}$ anions to the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ practically does not affect to the pyrene-CH_2-imidazolium protons (See SI). As expected, addition of SO_4^{2-} anions induces similar changes than those observed after addition of $HP_2O_7^{3-}$ anions to the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ in the same solvent.

Interestingly addition of even a large excess of $H_2PO_4^-$, HSO_4^-, NO_3^-, F^-, Cl^-, Br^-, I^-, AcO^-, ClO_4^-, BF_4^-, $C_6H_5CO_2^-$ATP, ADP and AMP ions to a solution of $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO-d_6 or DMSO-d_6/D_2O 9:1 did not induce significant changes in the ^1H NMR spectra of the receptor.

Job plot analysis of the titration data of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ with SO_4^{2-} and $HP_2O_7^{3-}$ anions in DMSO-d_6 and DMSO-d_6/D_2O 9:1 revealed a 1:1 receptor to anion binding stoichiometry (Figure 2).

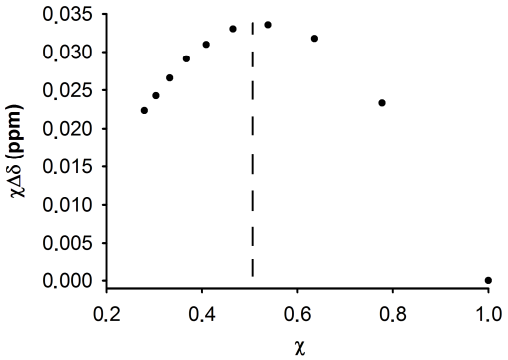


Figure 2. Job Plot experiment with a maximum at 0.5 indicating 1:1 stoichiometry for receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ and SO_4^{2-} in DMSO-d_6/D_2O.

The association constants were obtained by fitting the titration data to a 1:1 host-guest binding model using the WinEQNMR[29] program. The association constants obtained for the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ with SO_4^{2-} and $HP_2O_7^{3-}$ anions in DMSO-d_6 were above of the limits of the program $K_a > 10^4$ M^{-1}, nevertheless titration data obtained in the more competitive solvent medium (DMSO-d_6/D_2O 9:1) allowed the calculation of the association constants of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ with SO_4^{2-} anions (K = 1835 ± 167 M^{-1}) and with $HP_2O_7^{3-}$ anions (K = 374 ± 2 M^{-1}). Interestingly, it is noticeable that the resulted association constant for SO_4^{2-} anions is almost five times bigger than for $HP_2O_7^{3-}$ anions.

^{31}P spectral changes were also studied after addition of 1 equiv of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ to a solution of $HP_2O_7^{3-}$ anions in DMSO-d_6 and DMSO-d_6/D_2O 9:1. The ^{31}P NMR spectrum of the $HP_2O_7^{3-}$ shown a single peak in both solvents which was shifted $\Delta\delta$ = -1.80 ppm and $\Delta\delta$ = -2.48 ppm after addition of one equivalent of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ to a solution of the anions in DMSO-d_6 and DMSO-d_6/D_2O 9:1 respectively.

The sensing properties of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ was also investigated by UV-vis and fluorescence measurements in the aqueous mixture DMSO/H_2O 9:1 toward the previously mentioned set of anions.

The absorption spectrum of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO/H_2O 9:1 shows the characteristic pyrene absorption bands at λ = 268, 279, 316, 331 and 347 and are collected in the Table 1. The addition of the above-mentioned set of anions to a solution of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ (2.5 x 10^{-5} M in DMSO/H_2O 9:1) proved that only the addition of $HP_2O_7^{3-}$ and SO_4^- promotes small changes in the UV-vis spectrum of receptor. The absorption bands of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ at λ = 268, 279, 331 and 347 nm gradually decreases during the addition of $HP_2O_7^{3-}$ and SO_4^- anions with concomitant increase of the band at 316 nm (Table 1), two clear isosbestic points at λ = 282 and 326 nm were observed during the titration, indicating the formation of a well-defined host-guest species (Figure 3). Due to the small changes observed in the UV-vis spectrum it was not possible an accurate determination of the association constants using this technique.

Table 1. UV-Visible data of $\mathbf{5^{2+}\cdot 2PF_6^-}$, $\mathbf{5^{2+}\cdot HP_2O_7^{3-}}$ and $\mathbf{5^{2+}\cdot SO_4^{2-}}$ in DMSO/H_2O 9:1.

Compound	λ_{max}[nm](10^{-3} ε[$M^{-1}\cdot cm^{-1}$])
$\mathbf{5^{2+}\cdot 2PF_6^-}$	268 (74.92), 279 (101.16), 316 (22.84), 331 (51.32), 347 (73.60)
$\mathbf{5^{2+}\cdot HP_2O_7^{3-}}$	268 (65.08), 279 (88.12), 316 (26.72), 331 (49.84), 347 (66.36)
$\mathbf{5^{2+}\cdot SO_4^{2-}}$	268 (63.00), 279 (87.48), 316 (21.08), 331 (47.64), 347 (67.84)

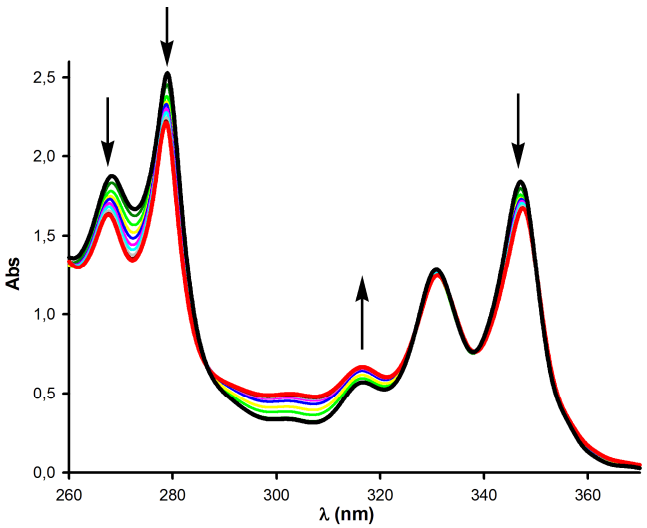


Figure 3. Changes in the absorption spectra of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO/H_2O 9:1 (2.5×10^{-5} M) upon addition of $HP_2O_7^{3-}$ anions at 20 °C. Arrows indicate the absorptions that increase or decrease during the titration.

Receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ exhibits a weak fluorescence in DMSO/H_2O 9:1 when excited at λ_{exc} = 360 nm. The emission spectrum shows the typical pyrene monomeric emission bands at 379, 397 and 418 nm, and another broad red-shifted and structureless band with a maximum at 481 nm ascribed to the

pyrene excimer emission. The calculated quantum yield for receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ was ϕ = 0.024 and the ratio between the excimer and monomer emission bands was I_E/I_M = 0.29 (Table 2).

Emission binding studies of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO/H_2O 9:1 (c = $2.5\cdot 10^{-5}$ M) with the same set of anions were performed and a sizable fluorescence intensity enhancement of the monomer and the excimer bands was only observed upon addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions (Figure 4).

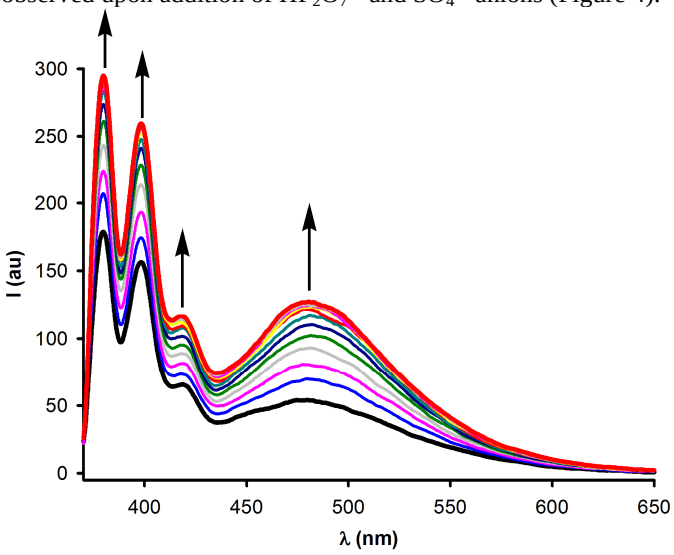


Figure 4. Changes in the fluorescence spectrum of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ (2.5×10^{-5} M) in DMSO/H_2O 9:1 upon addition of SO_4^{2-} anions at 20 °C. (λ_{exc} = 360 nm). Arrows indicate the emission that increase during the titration.

Addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions promotes a clear perturbation of the emission spectrum of the receptor. Firstly, it undergoes a remarkable increase of the quantum yield from 0.024 to 0.058 and 0.042 after addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions respectively. Secondly, the ratio between the intensity of the excimer and the monomer bands increases from 0.29, corresponding to the free receptor to 0.41 for $HP_2O_7^{3-}$ and 0.43 for SO_4^{2-} anions. Thirdly, the ratio between the intensity of the host-guest (HG) and the receptor (R) (I_{HG}/I_R) at λ = 481 nm for $HP_2O_7^{3-}$ and SO_4^{2-} increases 2.77 and 2.36 fold, respectively (Table 2 and Figure 5). The increment of the fluorescence intensity, especially in the monomer emission bands, is the result of the rigidity effect causes by the anion coordination which reduces the number of available vibrational and rotational non-radiative decay processes.[30] In addition, the presence of the anion induces a intramolecular π-π interaction between the two pyrene units and as a consequence the enhancement of the excimer band with the addition of the anions is higher than the monomer band (Table 2).

Table 2. Ratio of different parameters of the emission spectrum of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ after addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions in DMSO/H_2O (9:1).

Compound	I_{HG}/I_R[a]	$(I_E/I_M)_{HG}/(I_E/I_M)_R$[b]	Φ_{HG}/Φ_R[c]
$\mathbf{5^{2+}}$ $\mathbf{HP_2O_7^{3-}}$	2.77	1.41	2.41
$\mathbf{5^{2+}\cdot SO_4^{2-}}$	2.36	1.48	1.75

[a] Ratio between the fluorescence intensity at λ = 481 nm after the addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions to the receptor. [b] Ratio between I_E/I_M after the addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions to the receptor. [c] Ratio of the quantum yield Φ after the addition of $HP_2O_7^{3-}$ and SO_4^{2-} anions to the receptor.

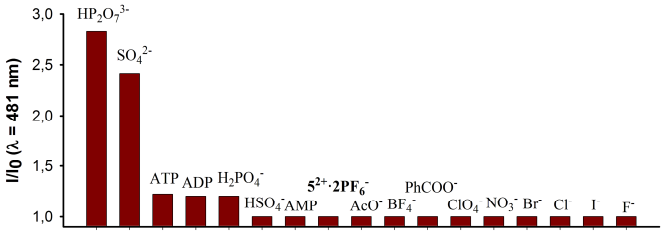


Figure 5. Normalized fluorescence intensity (I/I_0) of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ at λ = 481 nm in DMSO/H_2O 9:1, with respect to the free receptor, after addition of up to 20 equiv of several anions. Emission is monitored at λ_{exc} = 360 nm.

Specfit[31] analysis of the fluorogenic response of $\mathbf{5^{2+}\cdot 2PF_6^-}$ in DMSO/H_2O (9:1) with $HP_2O_7^{3-}$ and SO_4^{2-} anions reveal an association constant *K* for SO_4^{2-} (K = 2100 M^{-1}) considerably stronger than the calculated for $HP_2O_7^{3-}$ anions (K = 357 M^{-1}) which is in agreement with the association constants calculated previously by ^{1}H NMR.

The calculated detection limits for $HP_2O_7^{3-}$ and SO_4^{2-} anions in DMSO/H_2O 9:1 were: $2.69\cdot 10^{-5}$ M for $HP_2O_7^{3-}$ anions and $1.22\cdot 10^{-5}$ M for SO_4^{2-} anions.

The receptor $\mathbf{5^{+}\cdot 2PF_6^-}$can be used as fluorescent "naked eye" chemosensor molecule for $HP_2O_7^{3-}$ and SO_4^{2-} anions due to the increase of the fluorescence intensity of the excimer band (Figure 6).

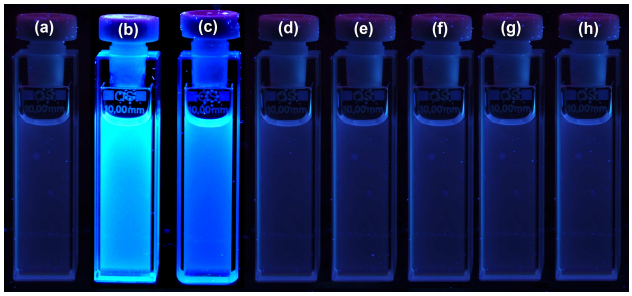


Figure 6. Visual changes in the fluorescence emission of receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ (a) in DMSO/H_2O (9:1) after addition of (b) $HP_2O_7^{3-}$, (c) SO_4^{2-}, (d) ATP, (e) ADP, (f) $H_2PO_4^-$, (g) HSO_4^- and (h) AMP anions

Taking into account the results obtained from ^{1}H NMR titrations data of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ with SO_4^{2-} and $HP_2O_7^{3-}$ anions, we tentatively propose binding modes like those outlined in Figure 8. In the case of SO_4^{2-} anions the two negative oxygen atoms S-O^- are bonded to the two benzimidazolium rings of the receptor. The cooperative action of the H_c inner aromatic proton of the naphthalene ring with the two oxygen S=O reinforce the binding of the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ with SO_4^{2-} anions. In the case of the $HP_2O_7^{3-}$ anion, we propose a similar binding mode in which, the two benzimidazolium rings are bonded to the two negative oxygen atoms of the P_α P-O^- of the $HP_2O_7^{3-}$ while the other oxygen atom of the P=O group is simultaneously bonded to both H_c inner aromatic protons of the naphthalene ring.

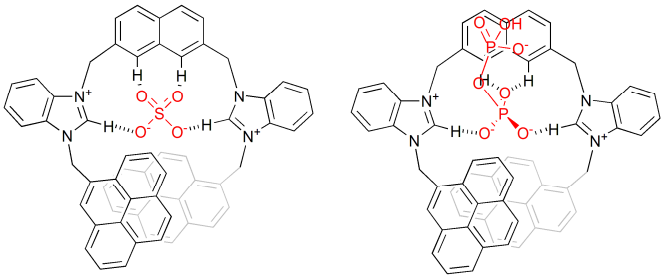


Figure 8. Proposed binding mode for receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ with SO_4^{2-} and $HP_2O_7^{3-}$ anions

Conclusions

The synthesis of a novel fluorescent bis-benzimidazolium chemosensor molecule has been achieved where a naphthalene spacer group is decorated with two arms containing as binding site an unsubstituted benzimidazolium motifs, end-capped with a photoactive pyrene ring. UV-vis and fluorescent spectroscopic as well as ^{1}H NMR anion titration studies reveal that the receptor $\mathbf{5^{2+}\cdot 2PF_6^-}$ shows a preferred association for sulphate and hydrogenpyrophosphate anions in the competitive DMSO/H_2O 9:1 medium. Fluorescence measurements show higher enhancements of the excimer emission band of the pyrene units than the monomer emission bands. Additionally ^{1}H NMR titration studies demonstrate that the presence of the naphthalene moiety in the receptor influences in the anions recognition even through combinations of cationic (imidazolium) and neutral (naphthalene) C-H hydrogen bonding: significant downfield shifts were observed for the C(2)-H protons of both imidazolium groups, and appreciable downfield shifts were also observed for the inner naphthalene protons indicating their participation in hydrogen bonding with anions along with the C(2) imidazolium protons. Interestingly the calculated association constant from ^{1}H NMR and fluorescence titrations for sulphate anions is around 5-times larger than for hydrogenpyrophosphate anions.

Acknowledgements

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Experimental Section

General comments

All reactions were carried out under N_2 and using solvents which were dried according to routine procedures. Melting points were determined on hot-plate melting point apparatus and are uncorrected. NMR spectra were recorded on 300, 400 and 600 MHz apparatus. The following abbreviations for stating the multiplicity of the signals in the NMR spectra were used: s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet). Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra. UV-vis and fluorescence spectra were carried out in the solvents and concentrations stated in the text and in the corresponding figure captions, using a dissolution cell with 10 mm pathlength, and they were recorded with the spectra background corrected before and after sequential additions of different aliquots of anions. Mass spectrometry was recorded on an HPLC-MS TOF instrument using positive ionization. Quantum yield values were measured with respect to anthracene as standard (Φ = 0.27±0.01) using the equation $\Phi_x/\Phi_s = (S_x/S_s)\ [(1\text{-}10^{-As})/(1\text{-}10^{-Ax})](n_s^2/n_x^2)$, where x and s indicate the unknown and standard solution, respectively, F is the quantum yield, S is the area under the emission curve, A is the absorbance at the excitation wavelength and n is the refractive index. Mass spectrometry was recorded on an HPLC-MS TOF instrument using positive ionization.

Synthesis

Synthesis of the 1-((pyren-1-yl)methyl)-1*H*-benzo[*d*]imidazole 3. (0.39 g, 73 %) To a solution of 1*H*-benzo[*d*]imidazole (0.188 g, 1.61 mmol) in acetonitrile (50 ml) was added dropwise an aqueous solution of 1M NaOH (2 mmol) and stirred during 10 min. 1-(Bromomethyl)pyrene (0,472 g, 1.61 mmol) was then added in one portion and the resultant mixture was stirred at room temperature for 16 hours. During the course of the reaction a white solid was formed which was separated by filtration and washed with water and diethylether, affording the desired compound **3**. ^{1}H NMR δ_H (400 MHz; $CDCl_3$) 8.26-8.23 (2H, m), 8.18 (2H, dd, *J* = 9.3Hz, *J* = 1.8Hz), 8.14-8.11 (2H, m), 8.08-8.04 (2H, m), 7.89-7.86 (1H, m), 7.86 (1H, s), 7.68 (1H, d, *J*=7.88), 7.43-7.41 (1H, m), 7.35-7.26 (2H, m), 6.07 (2H, s); ^{13}C NMR δ_C (100.61 MHz; $CDCl_3$) 144.9, 144.6, 144.1, 135.1, 132.5, 132.2, 131.5, 129.8, 129.5, 128.9, 128.4, 128.2, 127.2, 126.9, 126.8, 125.9, 125.5, 124.1, 123.3, 122.5, 121.4, 110.8, 47.9; MS (ESI): *m/z* calc. for $[M + H]^+$ 333.14, found 333.14. mp 190ºC.

Synthesis of the Bis-benzimidazolium receptor as bromide salt $\mathbf{4^{2+}\cdot 2Br^-}$. (0.13 g, 42.3%) To a solution of 1-[(pyren-1-yl)methyl]-1*H*-benzo[*d*]imidazole **3** (0.2 g, 0.6 mmol) in acetonitrile (125 ml) was added dropwise a solution of 2,7-bis(bromomethyl)naphthalene (40 ml) in acetonitrile (0.094 g, 0.3 mmol) and the resultant mixture was heated at reflux temperature for 3 days. The resulting precipitate solid was collected by filtration and washed with diethylether, giving the desired compound. ^{1}H NMR δ_H (300 MHz; DMSO) 9.85 (2H, s), 8.45 (2H, d, *J* = 9Hz), 8.38-8.31 (8H, m), 8.26 (2H, d, *J* = 9Hz), 8.21 (2H, d, *J* = 9Hz), 8.15-8.05 (6H, m), 7.97 (2H, s), 7.95-7.89 (4H, m), 7.66-7.55 (4H, m), 7.49 (2H, dd, *J* = 9Hz, *J* = 3 Hz), 6.54 (4H, s), 5.86 (4H, s); ^{13}C NMR δ_C (75.46 MHz; DMSO) 142.9, 132.3, 132.3, 132.3, 131.6, 131.5, 131.1, 130.7, 130.1, 128.8, 128.7, 128.7, 128.2, 127.8, 127.4, 127.2, 126.9, 126.7, 126.1, 126.0, 126.0, 125.8, 125.2, 124.2, 123.7, 122.3, 114.3, 114.0, 50.0, 48.5; MS (ESI): *m/z* calc. for $[M^+ + Br^-]^+$ 899.3, found 899.3; mp 248 decomposes.

Synthesis of the Bis-benzimidazolium receptor as hexafluorophosphate salt $\mathbf{5^{2+}\cdot 2PF_6^-}$. A solution of bis-(benzimidazolium) derivative as bromide salt $\mathbf{4^{2+}\cdot 2Br^-}$ (0.100g, 0.1 mmol) in CH_2Cl_2 (20 ml) was washed with a saturated solution of NH_4PF_6 in H_2O and stirred during 20 minutes (5 x 20 ml). The organic solvent was collected and dried with anhydrous Na_2SO_4. The solid was separated by filtration and the solvent was removed under reduced pressure, to give the

PF_6^- salt in quantitative yield. ^{1}H NMR δ_H (600 MHz; DMSO) 9.83 (2H,s), 8.46 (2H, *d*, *J* = 6 Hz), 8.39-8.37 (6H, m), 8.34 (2H, *d*, *J* = 6 Hz), 8.27 (2H, *d*, *J* = 6 Hz), 8.23 (2H, *d*, *J* = 6 Hz), 8.16-8.12 (4H, m), 8.09 (2H, *d*, *J* = 6 Hz), 7.98 (2H, s), 7.96-7.92 (4H, m), 7.67-7.60 (4H, m), 7.50 (2H, dd, J = 6 Hz, J = 1.7 Hz), 6.57 (4H, s), 5.88 (4H, s); ^{13}C NMR δ_C (150.903 MHz, DMSO) 142.7, 132.3, 132.3, 132.2, 131.6, 131.5, 131.1, 130.7, 130.1, 128.8, 128.7, 128.7, 128.2, 127.7, 127.3, 127.2, 126.9, 126.6, 126.1, 126.0, 125.9, 125.8, 125.1, 124.2, 123.6, 122.2, 114.2, 113.9, 50.0, 48.4; MS (ESI): *m/z* calc. for $[M^+ + PF_6]^+$ 963.31, found 963.31; mp 210 °C decomposes.

Notes and references

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