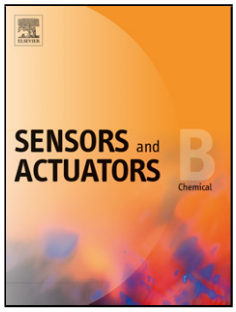

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Octatosylaminophthalocyanine: A reusable chromogenic anion chemosensor

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Graphical Abstract:

Keywords: Anion Binding, Phthalocyanines, Chromogenic Chemosensors, Anionic Coordination, Reversible Sensors

Abstract:

Detailed herein is the use of 2,3,9,10,16,17,23,24-octatosylaminophthalocyanine as a chromogenic chemosensor for anions. The host:guest complexes formed during the sensing event can be regenerated by acid treatment without loss of the sensing ability. This allows the phthalocyanine chemosensor to be reused. This system also responds in a colorimetric manner when exposed to the neutral solvent molecules, dimethyl sulfoxide and methanol. A single-crystal X-ray structure of the Pc **1**:2 MeOH complex was obtained. It illustrates the main interactions between the host:guest species in the solid state. Fits of the binding curves are consistent with this stoichiometry predominating in the solution state.

1. Introduction

New chemosensors capable of sensing target guests via changes in their optical features have attracted considerable attention lately due to their potential applications in the development of analytical devices. Species capable of binding and recognizing selectively anionic substrates are of particular interest due to the importance of anions in areas as diverse as nuclear waste treatment, environmental chemistry, and biology [1-5]. A particular challenge within this broad paradigm is to create colorimetric chemosensors for anions.

The design of chemosensors for anions is considered relatively more challenging than the corresponding task of designing sensors for cations due to *inter alia* the diversity of shapes encountered in the case of anions, the generally lower charge densities for anions as compared to cations, and pH effects that can serve to neutralize anions via protonation [6-9].

Ideally, chemosensors for anions should allow for an ability to selectively recognize and sense anionic analytes via color changes that can be followed readily by eye, through changes in absorption or fluorescence spectral features, or modulations in an electrochemical responses [10]. Recent publications in the area of anion sensing have exploited the anion binding properties of macrocycles, such as calix[4]pyrroles [11-14], porphyrins [15-18], *N*-confused porphyrins [19,20], saphyrins [21-23], porphyrazines [24], subphthalocyanines [25,26], as well as other anion-binding compounds [27]. Interestingly, however, in spite of being reported as gas sensors [28], to the best of our knowledge, phthalocyanines have never been successfully used as anion sensors. Here, we report the use of a particular phthalocyanine, 2,3,9,10,16,17,23,24-octatosylaminophthalocyanine (Pc **1**), as a chromogenic chemosensor for anions. We also show that this system responds to the neutral solvent molecules, dimethyl sulfoxide and methanol.

2. Experimental

2.1. Reagents

All reagents and solvents were used as received from commercial sources without further purification. The tetrabutylammonium salts of fluoride, chloride, bromide, dihydrogen phosphate, acetate, nitrate and nitrite were used as the anion sources; these salts were purchased from Sigma–Aldrich.

2.2. Apparatus

^{1}H and ^{13}C NMR spectra were recorded on a *Bruker Avance-300* spectrometer at 300.13 and 75.47 MHz, respectively. Tetramethylsilane was used as an internal reference. HRMS spectra were recorded on a *VG AutoSpec-M* spectrometer using 3-nitrobenzyl alcohol (NBA) as the matrix. Absorption spectra were recorded using a *Shimadzu UV-2501-PC*. Preparative thin-layer chromatography was carried out on 20 × 20 cm glass plates coated with silica gel (1 mm thick).

A suitable single-crystal was mounted on a Hampton Research CryoLoop using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6) purchased from Aldrich [29], with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected at 150(2) K on a Bruker X8 Kappa APEX II charge-coupled device (CCD) area-detector diffractometer (Mo K_α graphite-monochromated radiation, $\lambda = 0.71073$ Å) controlled by the APEX2 software package [30], and equipped with an Oxford Cryosystems Series 700 cryostream that was monitored remotely using the software interface Cryopad [31]. Images were processed using the software package SAINT+ [32]. Data were corrected for absorption by the multi-scan semi-empirical method implemented in SADABS [33]. The structure was solved by the direct methods of SHELXS-97 [34] and refined by full-matrix least squares on F^2 using SHELXL-97 [35]. All non-hydrogen atoms were directly located from the difference Fourier maps and successfully refined with anisotropic displacement parameters.

2.3 Synthesis

2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine (Pc 1). Magnesium filings (10 mg) and pentan-1-ol (*ca*. 1 mL) were heated at 150 °C (reflux) until a slurry was formed (ca. 1 h). Octan-1-ol (0.5 mL) was added, followed by 4,5-ditosylaminophthalonitrile (465 mg, 1 mmol). The reaction mixture was then heated at 185 ºC for 12 hours. The reaction mixture was cooled to room temperature and poured into a 1:10 water/methanol mixture (100 mL). The solid was collected, dissolved in a mixture of $CHCl_3$/acetic acid (5:1) and the solution was washed with distilled water (4 x 100 ml). The organic solution was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The dark green solid was dissolved in dry THF (20 mL) in a 50 mL flask equipped with a water condenser. Trifluoroacetic acid (2 mL) was added and the mixture was heated at 50 ºC for 3 hours, with the removal of the coordinated metal cation being monitored during this time by UV-Vis spectroscopy and TLC) analysis. The reaction mixture was cooled to room temperature and water (*ca.* 10 mL) was added until a precipitate was formed. Methanol (2 mL) was added leading to further precipitation. The precipitate was then collected by filtration. After redissolving in a minimal amount of $CHCl_3$, the solid obtained in this way was purified by column chromatography over silica gel using $CHCl_3$ as the eluent. The green

fraction was collected and crystalized from $CHCl_3$/hexanes affording pure Pc **1** (300 mg, 64% yield). ^{1}H NMR ($CDCl_3$): δ -3.46 (s, 2H, NH), 2.11 (s, 12H, CH_3), 2.93 (s, 12H, CH_3), 6.67 (d, *J* = 8.2 Hz, 8H, *m*-Ts H), 7.10 (d, *J* = 8.2 Hz, 8H, *o*-Ts H), 7.79 (d, *J* = 8.2 Hz, 8H, *m*-Ts H), 7.92 (s, 4H, NH), 8.00 (d, *J* = 8.2 Hz, 8H, *o*-Ts H), 8.04 (d, *J* = 8.2 Hz, 8H, α-Pc H), 8.61 (s, 4H, α-Pc H), 8.80 (s, 4H, α-Pc H); 8.89 (s, 4H, NH). MS (MALDI-TOF) m/z: 1868 $[M+H]^+$.

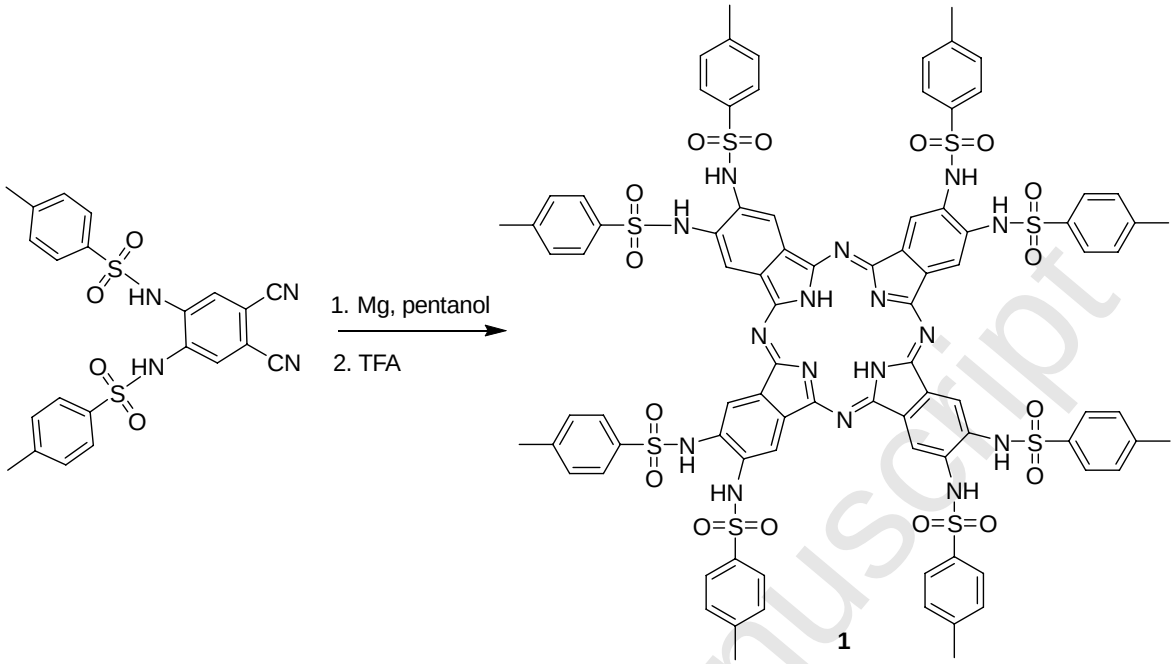
2.4 Anion binding studies

Anion binding studies were carried out by means of UV-Vis spectroscopic titrations in three different solvents, namely THF, $CHCl_3$, and DMSO. The titrations were performed using a stock solution of Pc **1** (6.3×10^{-6} M) upon the addition of aliquots of an anion solution (5.3×10^{-3} M). The variation on the absorbance caused by the addition of the anion, at a selected wavelength, was used to obtain binding isotherms. The binding isotherms were analyzed assuming a 1:2 binding stoichiometry via a non-linear regression analysis in accord with the following equation [36]: $(\Delta A/l)=([C]x(K_{11}.\Delta\varepsilon_{11}.[anion]+K_{11}.K_{12}.\Delta\varepsilon_{12}[anion]^2)/(1+K_{11}.[anion]+K_{11}.K_{12}.[anion]^2$. As noted above, binding isotherms were obtained for experiments conducted in THF, $CHCl_3$, and DMSO at 22 ºC. Measurements were repeated 2-3 times and found to be reproducible within a 15-20% error range. The consistency between the calculated and experimentally observed binding profiles was taken as evidence of the proposed 1:2 binding stoichiometry. Support for this conclusion came from so-called Job plot analyses (*vide infra*).

3. Results and discussion

3.1 Synthesis and characterization

2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine (Pc **1**) was prepared in 64% yield by cyclotetramerization of the corresponding ditosylaminophthalonitrile (Scheme 1), following a modification of a previously reported method [37]. Porphyrin derivatives bearing two or four tosylamino groups have been reported as efficient anion chemosensores [38,39]. Structurally related compounds, quinoxalinebis(sulfonamide) systems, have also been studied as anion-sensing compounds [40]. It was thus expected that upon exposure to anions, Pc **1** would likewise undergo a colour change. Less clear was the extent of this colour and the nature of the substrate specificity. The present study was thus undertaken with the goal of testing whether Pc's could be used to generate viable colorimetric anion sensors. As detailed below, Pc **1** does in fact act as a useful anion sensor in several organic solvents. It also interacts with several neutral substrates, as evidenced by the colorimetric response produced in the presence of methanol and DMSO.



Scheme 1

The UV-Vis spectrum of Pc **1** (Figure 1) changes significantly in different solvents: It is green in THF, but bluish in chloroform. In THF, it shows a split Q band with maximum absorption values (λ_{max}) at 681 and 710 nm, while in chloroform an intense Q band at ca. 640 nm is seen, along with a weaker one at 680 nm. In DMSO, the absorption spectrum of Pc **1** is characterized by a broad Q band centred around 720 nm and the solution is purplish in color. The solvatochromic effect observed in the case of Pc **1** is ascribed to a combination of hydrogen bonding and deprotonation of the peripheral NH-Ts groups. Such deprotonation events are expected to correlated with the solvent basicity and be modulated by other solvent-based supramolecular interactions that might involve the tosyl units.

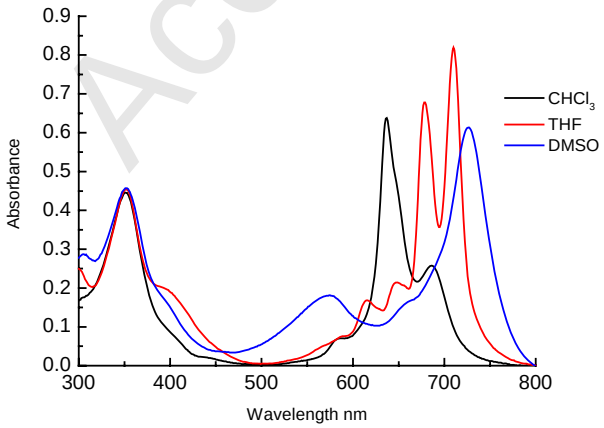


Figure 1. Absorption spectra of Pc **1** (6.3×10^{-6} M) as recorded in $CHCl_3$, THF, and DMSO.

3.2 UV-Vis anion studies

Tests of anion binding were carried out at 22 ºC and were monitored by UV-Vis spectroscopy. THF, $CHCl_3$, and DMSO were used as solvents. Upon addition of the different anions, significant variations on the UV-Vis spectrum of the Pc **1** were observed (Figures 2 and SI1-19). The absence of a precise isosbestic point under conditions of the titration was taken as an indication that multiple complexation equilibria are involved. Good fits to a 1:2 binding profile were obtained as noted in Section 2.4 above. The data obtained by Job's method (cf. Supporting Information) were also consistent with a 1:2 stoichiometry for the Pc:anion complex. An exception is observed when DMSO is added to a THF solution of Pc **1**; in this case the data proved consistent with the formation of a 1:1 complex.

Analyses of the change in absorption intensity data as a function of anion concentration allowed the anion binding interactions between Pc **1** and the anions chosen for study to be quantified. To do this, the observed data points were fitted to a 1:2 binding profile using a non-linear regression analysis as detailed in the Experimental Section. This allowed the affinity constants (*K*) to be determined in thee different solvents (Table 1). The highest affinity constants were observed in THF and $CHCl_3$.

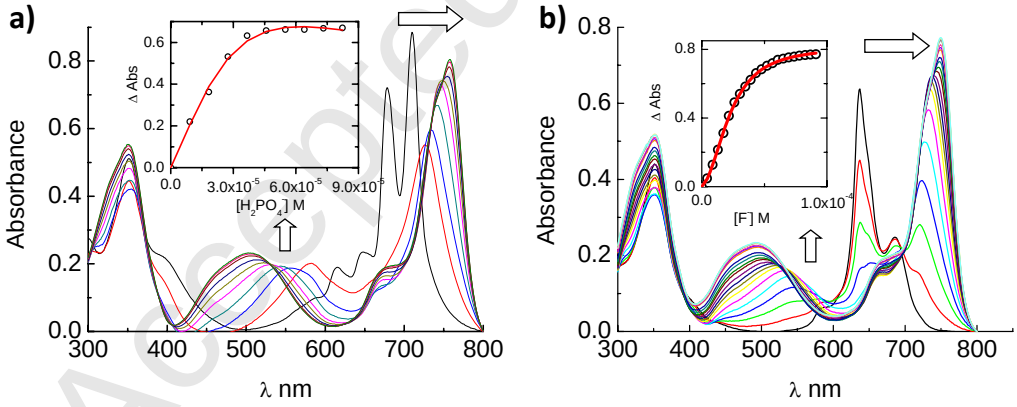


Figure 2. Spectral changes associated with the titration of Pc **1** with: **a)** dihydrogen phosphate anion in THF; **b)** fluoride anion in $CHCl_3$. The insets show the binding profiles and the generated fits. See text for fitting details.

Table 1: Affinity constants (M^{-2}) for various test anions (as the tetrabutylammonium salts) and selected neutral molecules at 22 ºC as determined in three different solvents.

THF	**$CHCl_3$**	**DMSO**
K (M^{-2})	*K* (M^{-2})	*K* (M^{-2})

F^-	$2.64x10^9$	$1.21\ x10^9$	$2.60\ x10^8$
Cl^-	$7.55\ x10^7$	$4.48\ x10^6$	$2.54\ x10^6$
Br^-	$1.08\ x10^5$	$1.58\ x10^4$ [a]	
AcO^-	$9.59\ x10^8$	$9.23\ x10^8$	$1.25\ x10^7$
$H_2PO_4^-$	$1.38\ x10^7$	$3.67\ x10^6$	$3.70\ x10^5$
NO_2^-	$2.36\ x10^6$	$1.99\ x10^4$ [a]	
NO_3^-	$1.94\ x10^4$	[b]	[a]
MeOH	$3.21\ x10^8$	[a]	[a]
DMSO	$1.05\ x10^5$ [c]	[a]	[a]

[a] Not calculated; [b] Spectral changes deemed too small to allow for accurate affinity constant determinations; [c] Binding isotherms were analysed by a 1:1 non-linear regression (*K* in M^{-1}).

In order to understand if the interactions between the anions and the Pc occur in the macrocycle core or/and at the tosylamino groups, we performed similar anion titrations with tetra-*tert*-butylphthalocyanine (Pc **2**, Figure 3). The addition of fluoride anion to a THF solution of Pc **2**, do not induce any perturbations in the UV-Vis spectra (see Figure SI20). These results are taken as an indication that, most probably, the spectral changes seen in the case of Pc **1** reflect binding-related changes that involve the peripheral tosylamino groups. Such an interpretation is in agreement with the results obtain via a single-crystal X-ray diffraction analysis of the 1:2 complex formed between Pc **1** and MeOH (*vide infra*).

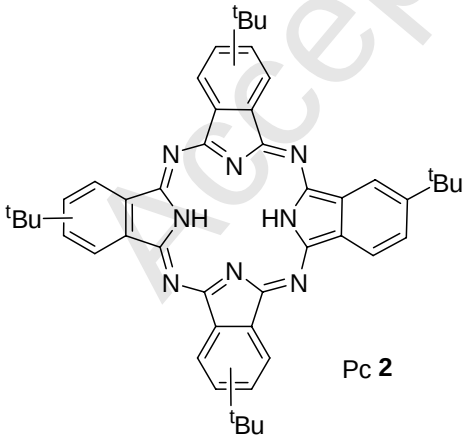


Figure 3. Tetra-*tert*-butylphthalocyanine ($H_2Pc^tBu_4$)

Based on the results in Table 1 we conclude that, irrespectively of the solvent used, Pc **1** interacts strongly with almost all the test anions included in the present study. Especially high affinities are seen for the fluoride and acetate anions. Across the board the following trend is observed: $F^- > AcO^- > Cl^- > H_2PO_4^- > NO_2^- > Br^- > NO_3^-$. Comparing the affinity constants in Table 1 with those typically seen for other neutral anion receptors [11-1824], reveals that those of Pc **1** are much higher.

A titration involving the treatment of Pc **1** in THF with MeOH and DMSO was also carried out in order to evaluate the competitive nature of these two solvents. The results are consistent with the expectation that DMSO is a less competitive solvent than MeOH. For instance, while MeOH forms a 1:2 host:guest complex in THF (as also observed in the solid state; see below) that is characterized by a high affinity constant (3.21×10^8 M^{-2}), DMSO forms a 1:1 complex (for which $K_a = 1.05 \times 10^5$ M^{-1}). Further underscoring the strength of the interactions seen in the case of MeOH is that the calculated affinity constants for MeOH binding in THF are higher than those found for most of the anions studied, with the exception of fluoride and acetate.

3.3 NMR spectroscopic studies of anion binding

The nature of the interactions between Pc **1** and the test anions of this study was probed using ^{1}H NMR spectroscopy. The addition of anions to a $CDCl_3$ solution of Pc **1** induced a progressive broadening of all signals corresponding to the protons of the tosylamino groups (NH-Ts). One such titration (involving tetrabutylammonium bromide) is shown in Figure 4. This line broadening behaviour, which is seen for all the tested anions to greater or lesser extent, is consistent with supramolecular interactions between the anion and the NH-Ts protons that also affect the resonances of the the aryl groups protons.

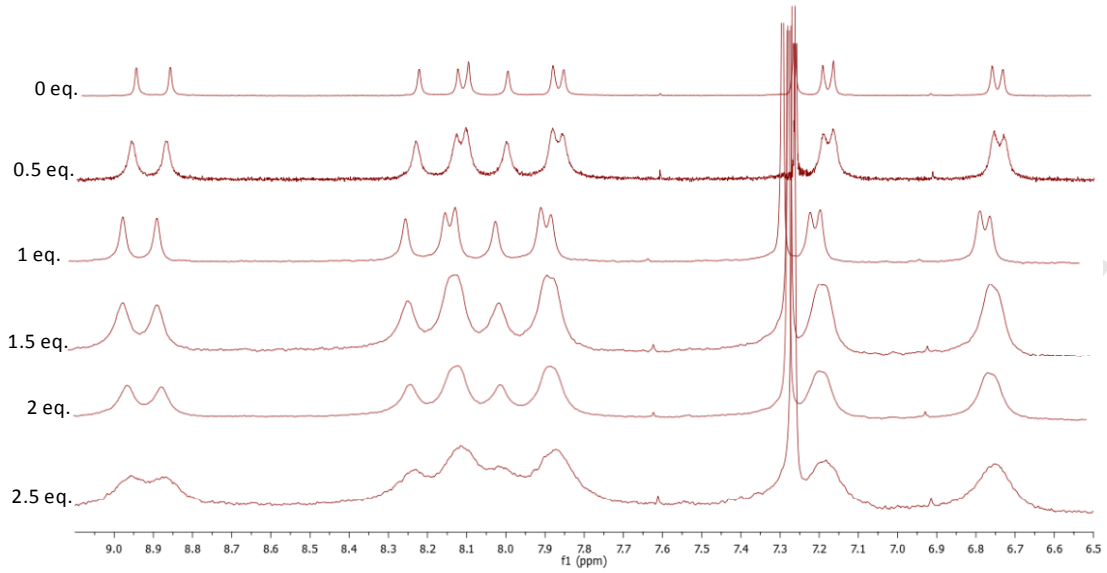


Figure 4. Partial ^{1}H NMR spectra of Pc **1** recorded in $CDCl_3$ upon the addition of 0.5 to 2.5 molar equivalents of tetrabutylammonium bromide.

3.4 X-ray studies

In order to gain further insights into the nature and type of the host-guest interactions in the solid state efforts were made to obtain diffraction grade single crystals of various putative complexes. Unfortunately, with the exception of the methanol adduct of Pc **1**, these efforts proved in vain. In the case of the methanol adduct, the structure was successfully elucidated using X-ray diffraction methods (see the SI for additions details involving this analysis; Table SI1). Based on the structure obtained (Figure 5), one can see that in the solid state two methanol molecules interact strongly with the Pc **1** macrocyclic unit by means of what are inferred to be strong and highly directional (N,O)–H···(N,O) hydrogen bonds. The interactions themselves may be divided into two main groups. The first concerns methanol molecules that act as hydrogen bond donors supporting O–H···N supramolecular interactions with the nitrogen atoms of the Pc isoindole moiety; the second involves the tosylamino groups, all of which donate their hydrogen atoms to two distinct methanol molecules. As can be inferred from an inspection of Figure 5 (including the side view), these supramolecular interactions in the solid state surround completely each individual molecule of Pc **1**. In light of the NMR spectroscopic data presented above, we conclude that identical interactions occur in solution.

In the solid state ancillary interactions are observed. For instance, an O1t–H1t···O2t hydrogen bonding interaction (Figure 5b and Table SI2) serves to interconnect the two types of

interactions aforementioned. It is also important to emphasize that all these supramolecular interactions are structurally very robust as reflected in the fact that all angles associated with the interactions are greater than 144º and the interatomic distances fall in the 2.698(5)-2.946(4) Å range (see Table SI2).

The individual supramolecular adducts are closely packed in the solid state with the overall structure being rather compact (cf. Figure SI23 in the SI). We note that the channels observed in the crystal structure are large enough to accommodate other molecular substrates and that in terms of size considerations, the methanol molecules could easily be replaced by other anions.

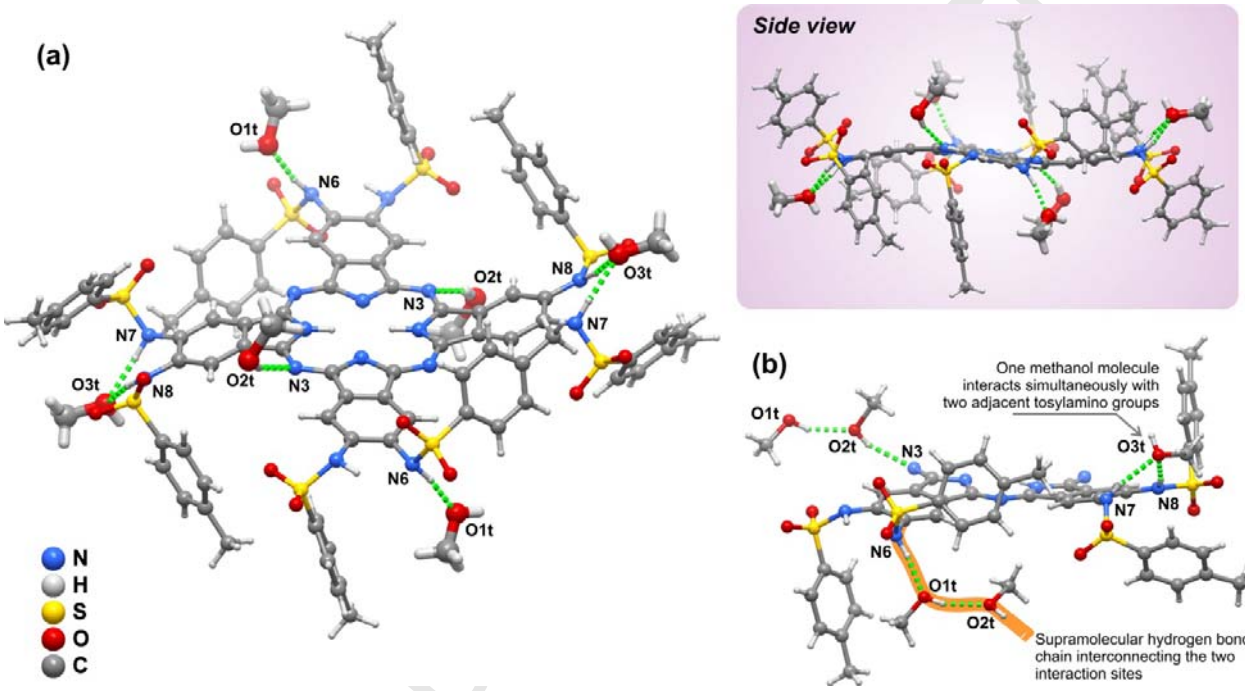


Figure 5 – (a) Perspective view of the molecular unit present in the crystal structure of the 1:2 complex between Pc **1** and MeOH seen in the solid state. Hydrogen bonding (dashed green lines) interactions involving neighbouring methanol molecules are also shown (represented in a larger ball-and-stick representation mode for clarity). **(b)** Detailed view of the various strong and highly directional N–H···O and O–H···O hydrogen bonds in which the molecular units of Pc **1** are involved. For geometrical details of the represented hydrogen bonds, see Table SI2. For clarity, symmetry codes used to generate equivalent atoms have been omitted.

3.2. Substrate-induced colour changes

Phthalocyanines are well recognized pigments whose colour can be tuned via the choice of coordinated metal cation. As demonstrated in the present study, the free-base form of Pc **1** also displays different colours in the presence of various test anions (studied in organic solvents as their TBA salts). For instance, when fluoride is added to a THF solution of Pc **1** the green colour

changes to pale orange (cf. Figure 6). Similarly, addition of bromide anion in THF produces a pale purple coloration. This phthalocyanine also allows an easy distinction between nitrate (for which exposure leads to a blue solution) and nitrite (leads to a pale pink solution) anions in this same solvent. Because of the striking changes in the colour of the original THF solution that are easily visible to the unaided eye, we conclude that Pc **1** may be used as a colorimetric anion sensor.

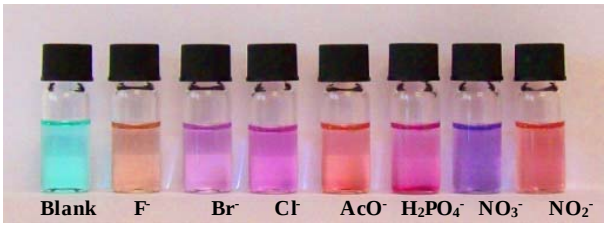


Figure 6. Changes in the colour of a THF solution of Pc **1** observed upon the addition of 10 equivalents of anions (as the corresponding tetrabutylammonium (TBA) salts).

The possibility of using an "indicator paper" for an easy detection of anions in solution, in analogy to pH paper, is appealing. In order to evaluate this possibility, Pc **1** was adsorbed on regular filter paper (the paper was immersed in a THF solution of Pc **1** and then the solvent was evaporated at room temperature). Small pieces of the resulting blue paper were immersed in DMSO solutions containing various test anions. In some cases, a drastic change in colour was observed (Figure 7). Anions with higher affinities for Pc **1** (Table 1) induce a change of the paper colour to purple while anions with lower affinities give rise to only a small change in the initial colour. This rudimentary test shows that Pc **1**, even when adsorbed in paper, behaves as an anion sensor. Further studies are required to find the best paper to use as a support, the extent to which it is possible to differentiate amongst different anions in mixtures, and the limits of detection under various conditions of use. Further work along these lines is in progress.

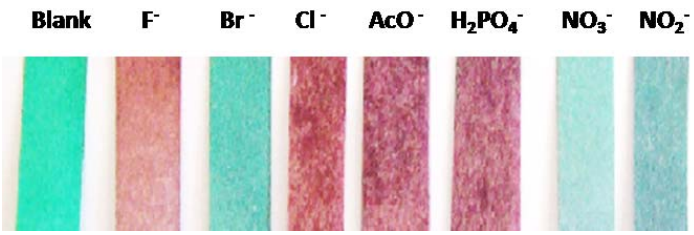


Figure 7. Photos of filter paper with adsorbed Pc **1** (blank; left side of figure) and (other images) after the treated filter paper is immersed in DMSO solutions containing the TBA salts of various test anions.

3.3. Reversibility of the host-guest system study

For practical use we believe a reversible sensor will prove advantageous. Towards this end, the reversibility of the host-guest complexes was studied. For these analyses, a $CHCl_3$ solution of the 1:2 Pc **1**•fluoride complex was prepared. It was then treated with a few drops of a solution of TFA in $CHCl_3$ (9.4×10^{-4} M). As can be seen from an inspection of Figures 8 and SI21, this acid treatment leads to a complete regeneration of the sensor. On this basis we conclude that the formation and dissociation of the complex Pc **1**•$2F^-$ is formally reversible. To confirm the reusability of our sensor, the resulting acid solution was washed with water, and the recovered Pc **1** was used again in anion binding studies with F^- (see Figure SI22). Again, a dramatic colour change was observed. Further, the same affinity constant was obtained when the same data analysis was performed [**Error! Bookmark not defined.**].

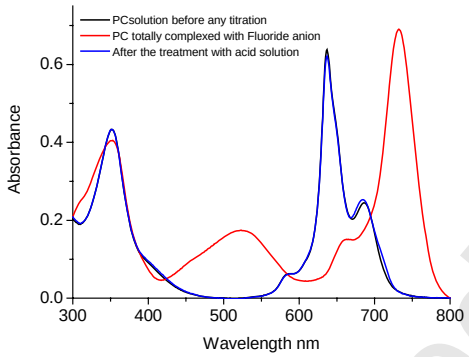


Figure 8. Treatment of the complex Pc **1**:$2F^-$ with a solution of TFA.

4. Conclusions

This work provides support for the notion that appropriately modified Pcs can act as viable chromogenic anion chemosensors. The phthalocyanine system of this study, Pc **1**, displays a high affinity for a number of test anions, as well as for dimethyl sulfoxide and methanol. A single crystal X-ray crystal structure of the complex formed between Pc **1** and methanol revealed a 1:2 binding stoichiometry in the solid state. It also revealed interactions that involve both the core and periphery of the phthalocyanine receptor. This structure is completely consistent with the stoichiometries inferred in solution for both the test anions and this particular solvent when analyzed in less polar media.

The strong colour changes seen upon exposure to anions lead us to predict that Pc **1** may have a role to play as an anion receptor whose function may be followed easily by the unaided eye. A particularly attractive feature is that it is possible to undo the host:guest complexes formed from

1 and thus reuse the Pc without loss of sensing ability. The immobilization of Pc **1**, or analogous Pcs, on recoverable/reusable matrixes may allow its use as a sensor under "green" conditions where leaching of the receptor material into the environment is contraindicated. Preliminary studies, involving the use of Pc **1** supported on filter paper, are promising in this latter regard.

Acknowledgments

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