



Highly selective optical chemosensor for cyanide in aqueous medium



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ABSTRACT

New cyanide selective chromogenic chemosensors based on metal-phthalocyanines containing four tosylamino groups were developed. These new receptors have high sensitivity for several anions (AcO^- , F^- , CN^- , NO_2^- , H_2PO_4^- and OH^-) over other anions, such as: Br^- , Cl^- , NO_3^- and HSO_4^- . The experiments were conducted by UV–vis spectroscopy in DMSO and THF solutions. The selectivities were also checked in DMSO:water mixtures. In solutions containing water the highest selectivity was obtained for CN^- anion. The host:guest complexes formed during the sensing event can be undo by acid treatment with a solution of trifluoroacetic acid without loss of the sensing ability of the chemosensors allowing their reuse.

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1. Introduction

Anions are one of the most important species in the natural world and are involved in many vital processes, being ever-present in the environment [1–4]. Anions are also critical to the preservation of life as we know it. Indeed, the transport, recognition or transformation of anions are involved, at some level, in almost every possible biochemical processes [5–8]. Anionic species are larger in size, having varied shapes in comparison to the metal ions, consequently a higher degree of design and complementarity is required to make receptors that are selective for a particular anionic guest [1,9]. The design and preparation of materials able to recognize and host selectively anionic species have assumed great importance in several areas in the past few years and are still a challenge for organic and materials chemists [10–13]. The design and synthesis of chemosensors able to detect anions by colorimetric, fluorescent or electrochemical means is still an important aspect but the main challenge is to the design chemosensors with high selectivity and sensitivity [14,15]. Among the different types of chemosensors, chromogenic chemosensors have many advantages due to their simplicity, low-cost, and rapid tracking of analytes.

Therefore, this type of chemosensors are getting popular due to their capability to detect analytes by naked eye, that is, without resort to any instrument [16,17].

One of the most interesting anions to monitor is the cyanide ion (CN^-) due to its environmental, biological and industrial importance. Cyanide is one of the most toxic and harmful anions to human health and environment, since it can suppress the transport of oxygen. Because its wide application in various fields, such as mining, metallurgy, photographic processing, synthesis of nylon and other synthetic fibers and resins, the development of simple methods that are selective and sensitive toward CN^- detection, especially in aqueous and physiological conditions, continues to be an important topic of research [18–29]. In general, the anion chemosensors incorporate N–H containing groups, such as: amide, urea/thiourea, pyrrole, among others [30–32].

In biological and environment systems, the host:guest interactions with anions occur typically in aqueous solution. Therefore much attention has been paid to develop anion chemosensors that could work in aqueous phase. However, chemosensors that are able to recognize anions in water are scarce [11,21–23,33–36]. The problem is that hydration of the anion makes difficult (or prevents) the chemosensor to recognize it.

Recently, we have shown that a free-base phthalocyanine bearing two tosylamino groups in each isoindole ring of the macrocycle is an efficient chromogenic anion chemosensor [15]. That octatosylaminophthalocyanine displays different colors in the presence of

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various test anions and, since it is possible to undo the host:guest complexes, it can be reused without loss of sensing ability [15]. A major drawback of the octatosylaminophthalocyanine is the difficult and low yielding process of preparing the required 4,5-ditosylaminophthalonitrile precursor [37]. In order to surpass this shortcoming, we decided to develop a new family of phthalocyanines bearing only four tosylamino groups and to evaluate their sensing abilities for anions. Our main goal was to increase the overall yield of the phthalocyanines, starting from commercially available precursors, and to confirm if the presence of two vicinal tosylamino groups is, or not, mandatory for the anion sensing ability.

The results show that robust and selective anion chemosensors (a free-base phthalocyanine and the corresponding Mg(II) and Zn(II) complexes) can be prepared in high yields starting from 4-aminophthalonitrile and *p*-toluenesulfonyl chloride. The structures of the new phthalocyanines were confirmed by NMR, UV–vis and mass spectra.

2. Experimental

2.1. Reagents

All reagents and solvents were used as received from commercial sources without further purification. Tetrabutylammonium salts of acetate, bromide, chloride, cyanide, nitrate, nitrite, dihydrogen phosphate, hydrogen sulfate and hydroxide were used as the anion sources. These salts were purchased from Sigma–Aldrich.

2.2. Apparatus

^1H 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 the internal reference. HRMS spectra were recorded on LTQ Orbitrap XL mass spectrometer using 3-nitrobenzyl alcohol (NBA) as matrix. Absorption spectra were recorded using a Shimadzu UV-2501-PC.

2.3. Synthesis

4-Tosylaminophthalonitrile (1)

Pyridine (1 mL) was added to a solution of 4-aminophthalonitrile (100 mg, 0.69 mmol) and *p*-toluenesulfonyl chloride (152 mg, 0.76 mol) in toluene (1 mL). The reaction was stirred at 70 °C, under nitrogen atmosphere for 3 h. After this time, the toluene and pyridine was evaporated under reduced pressure. The reaction mixture was neutralized with a solution of saturated sodium carbonate, washed with water, extracted with dichloromethane and the organic phase was dried with anhydrous sodium sulfate. Compound **1** was crystallized from dichloromethane/hexane (230 mg, 89% yield). mp = 147.8 °C. ^1H NMR (300.13 MHz, DMSO- d_6): δ 2.36 (s, 3 H, CH₃), 6.72 (s, 1H, NH), 7.42 (d, J = 8.2 Hz, 2H, *o*-Ts H), 7.52 (dd, J = 8.7, 2.3 Hz, 1H, H-5), 7.61 (d, J = 2.3 Hz, 1H, H-3), 7.79 (d, J = 8.2 Hz, 2H, *m*-Ts H), 7.98 (d, J = 8.7 Hz, 1H, H-6). ^{13}C NMR (75.47 MHz, DMSO- d_6): δ 21.1 (CH₃), 108.1, 115.6, 115.95, 116.04, 121.8, 121.9, 126.9, 130.2, 135.6, 135.8, 142.9, 144.5. HRMS (ESI) m/z : calculated for C₁₅H₁₂N₃O₂S (M + H)⁺: 298.0650; found: 298.0636.

2(3),9(10),16(17),23(24)-Tetratosylaminophthalocyaninato magnesium(II) (Pc 1)

Magnesium filings (24.5 mg, 1.01 mmol) and pentan-1-ol (1.5 mL) were added in a sealed tube and heated at 150 °C until a slurry was formed (2 h). Octan-1-ol (1.5 mL) was added, followed by compound **1** (600 mg, 2.02 mmol). The reaction mixture was then heated at 180 °C for 12 h. After this time, the reaction

mixture was cooled to room temperature and poured into a 1:10 water/methanol mixture (100 mL). The precipitate was filtered and dissolved in a mixture of dichloromethane/methanol. The organic solution was washed with H₂O and then evaporated under reduced pressure. The residue was dissolved in dichloromethane/methanol and then it was precipitated with hexane leading to a green solid identified as phthalocyanine **Pc 1** (208 mg, 71% yield). ^1H NMR (300.13 MHz, DMSO- d_6): δ 2.26 (s, 12H, CH₃), 7.41 (d, J = 8.1 Hz, 8H, *o*-Ts H), 7.87–8.08 (m, 12H, *m*-Ts H + β -H), 9.11 (dd, 4H, J = 14.5, 1.6 Hz, α_2 -H), 9.21 (dd, 4H, J = 8.1, 1.6 Hz, α_1 -H), 11.17 (s, 4H, NH). ^{13}C NMR (75.47 MHz, DMSO- d_6): δ 20.9 (CH₃), 112.6, 113.0, 121.4, 123.7, 127.0, 130.0, 133.7, 136.8, 139.4, 139.8, 143.6, 152.2, 153.6. UV–vis (DMSO) λ_{max} (log ϵ): 360 (4.6), 690 (5.2) nm. HRMS (ESI) m/z : calculated for C₆₀H₄₅MgN₁₂O₈S₄ (M + H)⁺: 1213.2217; found: 1213.2165.

2(3),9(10),16(17),23(24)-Tetratosylaminophthalocyanine (Pc 2)

Phthalocyanine **Pc 1** (100 mg) was dissolved in dry THF (10 mL) in a 50 mL flask equipped with a water condenser. Trifluoroacetic acid (1 mL) was added and the mixture was heated at 50 °C for 3 h. The removal of the coordinated metal ion was monitored during this time by UV–vis spectroscopy and by TLC. The reaction mixture was cooled, neutralized with a KHCO₃ solution, washed with H₂O and the organic phase extracted with dichloromethane/methanol (95:5) and then concentrated. **Pc 2** was crystallized from dichloromethane/hexane and was obtained as a green solid (110 mg, 98% yield). UV–vis (DMSO) λ_{max} (log ϵ): 350 (4.1), 680 (4.4), 710 (5.1) nm. HRMS (ESI) m/z : calculated for C₆₀H₄₇N₁₂O₈S₄ (M + H)⁺: 1191.2523; found 1191.0396.

2(3),9(10),16(17),23(24)-Tetratosylaminophthalocyaninato zinc(II) (Pc 3)

In a sealed tube, phthalocyanine **Pc 2** (100 mg, 0.084 mmol) was dissolved in DMF (3 mL) and then the zinc acetate (36.7 mg, 0.210 mmol) was added. The reaction mixture was heated at 150 °C for 3 h (until the metalation was complete). During this period the formation of the complex was monitored by UV–vis spectroscopy and TLC. The reaction mixture was cooled, washed with H₂O and the organic phase extracted with dichloromethane/methanol (95:5) and concentrated. The product was then precipitated from dichloromethane/hexane. A green product was obtained, which was identified as phthalocyanine **Pc 3** (112 mg, 98% yield). UV–vis (DMSO) λ_{max} (log ϵ): 355 (4.5), 688 (5.2) nm. HRMS (ESI) m/z : calculated for C₆₀H₄₅N₁₂O₈S₄Zn (M + H)⁺: 1253.1658; found: 1253.1607.

2.4. Anion binding studies

Anion binding studies were carried out by means of UV–vis spectroscopic titrations in two different solvents: DMSO and THF. The titrations were performed using stock solutions of **Pc 1–3** (order 10^{−6} M) upon the addition of aliquots of an anion solution (order 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 accordance with the following equation [38]: $(\Delta A/l) = ([C] \times (K_{11} \cdot \Delta \epsilon_{11} \cdot [\text{anion}] + K_{11} \cdot K_{12} \cdot \Delta \epsilon_{12} \cdot [\text{anion}]^2) / (1 + K_{11} \cdot [\text{anion}] + K_{11} \cdot K_{12} \cdot [\text{anion}]^2))$. As noted above, binding isotherms were obtained for experiments conducted in THF and DMSO at 22 °C. 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 the so-called Job plot analyses.

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