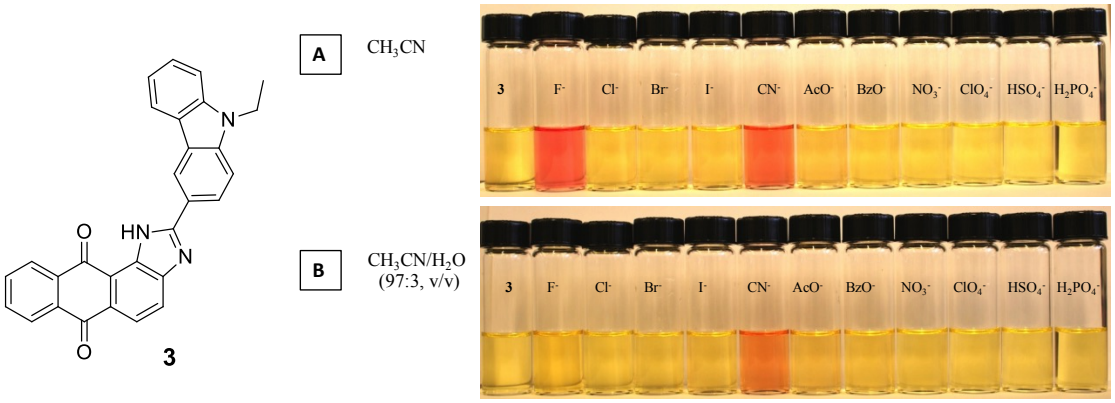
GRAPHICAL ABSTRACT

Cyanide and fluoride colorimetric sensing by novel imidazo-anthraquinones functionalized with indole and carbazole

Rosa M. F. Batista,[1] Elisabete Oliveira,[2,3] Susana P. G. Costa,[1] Carlos Lodeiro[2]*, M. Manuela M. Raposo[1]*



Cyanide and fluoride colorimetric sensing by novel imidazo-anthraquinones functionalized with indole and carbazole

Rosa M. F. Batista,[1] Elisabete Oliveira,[2,3] Susana P. G. Costa,[1] Carlos Lodeiro,[2]* M. Manuela M. Raposo[1]*

[1]*Center of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal*

[2] *BIOSCOPE Group, REQUIMTE-CQFB, Faculty of Science and Technology, Chemistry Department, Caparica Campus, University NOVA of Lisboa, 2829-516, Portugal.*

[3] *Veterinary Science Department, (CECAV), University of Trás-os-Montes and Alto Douro, 5001-801, Vila Real, Portugal.*

Abstract- Novel imidazo-anthraquinones functionalized with indole and carbazole have been synthesised and characterised and their evaluation as colorimetric chemosensors was carried out in acetonitrile as well as in acetonitrile/H_2O (97:3) in the presence of several anions such as F^-, Cl^-, Br^-, I^-, CN^-, NO_3^-, ClO_4^-, AcO^-, BzO^-, NO_3^-, ClO_4^-, HSO_4^- and $H_2PO_4^-$. Additionally, their behaviour in the presence of H^+ and OH^- was also studied. Upon addition of CN^- and F^- to acetonitrile solutions of compounds **1**-**3**, a marked colour change from yellow to orange was observed and the fluorescence emission of **1** and **2** was switched "on". The recognition in organic aqueous solution lead to the selective and sensitive naked-eye detection (mM) of CN^- for all receptors, with an easily detectable colour change from yellow to orange. The binding stoichiometry between the receptors and the anions was found to be 2:1. The binding process was also followed by ^1H NMR titrations showing that two different binding modes occurred in the presence of fluoride or cyanide anions, which is in agreement with the spectrophotometric titrations.

Keywords*:* Imidazole; Anthraquinone; Fluoride; Cyanide; Aqueous media; Naked-eye detection.

1. Introduction

The search for new chemosensors for anion detection through hydrogen bonding interaction has been a dynamic research area due to the importance of anions in a broad variety of medicinal, environmental and biological processes. Colorimetric as well fluorimetric chemosensors for anions are appealing approaches in this area since both can offer qualitative and quantitative information. Moreover, the change of color associated to a signalling event detected by naked eye is especially attractive due to the low cost or unnecessary equipment *(1)*.

Recently, angular annulation of imidazole to other systems such as anthraquinone lead to versatile expanded imidazole receptors with more acidic NH due to the change of the electronic properties of the imidazole substituents. These imidazo-anthraquinone derivatives were able to detect fluoride and cyanide in organic solvent as well as in aqueous solutions *(2)*. Cyanide *(3)* and fluoride *(4)* anions play an important role in chemical, environmental and biochemical processes and therefore their straightforward recognition is vital.

On the other hand, reports regarding imidazo-anthraquinones functionalized with heterocycles at position 2 of the imidazole ring are recent and unusual *(2c,5)*. Moreover, the acidity of the imidazole NH is expected to be enhanced by conjugation with indole and carbazole heterocycles which would lead to higher binding affinity for anions. Also, the annulation of these heterocycles to the imidazo-anthraquinone system could impart interesting photophysical properties and high thermal stabilities of the final conjugated heterocyclic systems.

Having in mind these considerations, we report here the synthesis and evaluation of the chemosensory ability of three new systems bearing indole and carbazole linked to position 2 of the imidazole. Receptors **1-3** were obtained in good to excellent yields using a simple synthetic methodology and an easy purification procedure. The naked-eye selective detection of the cyanide ion by these probes in an acetonitrile-water solution produced a noticeable change in colour from yellow to orange.

2. Results and discussion

2.1. Synthesis

Commercially available heterocyclic aldehydes and 1,2-diaminoanthraquinone were heated for 12 h in ethanol at reflux using formic acid as catalyst, to yield the respective imines which were subsequently cyclised to the imidazo-anthraquinones **1-3** in the

presence of lead tetraacetate in acetic acid at room temperature (Scheme 1) *(6)*. Recrystallization of the crude products from diethyl ether/chloroform gave the pure compounds **1-3** in excellent yields (81-95%), which were completely characterised by ^{1}H and ^{13}C NMR, IR and HRMS.

In the ^{1}H NMR spectra in DMSO-d_6 at 25 ºC, the chemical shift of the broad singlet concerning the imidazole NH proton appeared downfield in the range of 12.86-12.94 ppm indicating high acidity and strong hydrogen-bonding ability for all receptors.

Scheme 1

Table 1

The absorption and emission spectra of imidazo-anthraquinones **1-3** were measured in acetonitrile solution (10^{-6}-10^{-5} M) (Table 1). Compounds **1-3**, differing in the heterocycle at position 2 of the imidazole (indole or carbazole), and according to the electronic character of the substituent as well as the position of attachment, displayed maximum wavelength of absorption in the range 448-456 nm.

Receptors **1-2** exhibited negligible relative fluorescence quantum yields (less than 0.001) which were determined using a quinine sulphate solution in sulphuric acid (0.5 M) as standard (Φ_F = 0.54 *(7)*). The maximum wavelength of emission for compounds **1** and **2** were 640 and 650 nm, respectively, with very large Stokes' shifts (188 and 194 nm, respectively). On the other hand, compound **3** was not emissive.

2.2. Spectrophotometric and spectrofluorimetric titrations of compounds 1-3

Imidazo-anthraquinones **1-3** were evaluated as chemosensors by spectrophotometric titrations in the presence of halide spherical (F^-, Cl^-, Br^- and I^-), linear (OH^-, CN^-) and the bulky anions (AcO^-, BzO^-, NO_3^-, ClO_4^-, HSO_4^- and $H_2PO_4^{2-}$) in the form of tetrabutylammonium salts. A preliminary test in the presence of 100 equivalents of the anions revealed that compounds **1-3** responded significantly to the presence of F^- and CN^- with a distinct colour change from yellow to orange (Figure 1). All compounds were insensitive to the presence of the other anions.

Figure 1

Additionally, the acid-base behaviour of imidazo-anthraquinones **1**-**3** was also evaluated in the presence of H^+ and OH^-, which presented spectral changes in the ground and excited state, with the exception of compound **3** which was not emissive and therefore only changes in the ground state were observed.

In acidic media all compounds showed a blue shift in the absorption band ($\Delta\lambda$ = 30-45 nm), as well as in the emission band ($\Delta\lambda$ = 35-45 nm) followed by a quenching in the emission fluorescence of ca. 60%. As an example, the absorption and emission titration of compound **1** with increasing amount of acid is presented in Figure 2. A blue shift was observed from 450 nm to 415 nm ($\Delta\lambda$= 35 nm), followed by a decrease at 450 nm, and an increase at 415 nm, with the appearance of an isosbestic point at 437 nm. The emission band at 640 nm was blue shifted ($\Delta\lambda$ = 35 nm) and quenched. The observed quenching in the fluorescence emission was probably due to the formation of a hydrogen-bond interaction between the protonated nitrogen located in the imidazo unit and the oxygen atom of the carbonyl in the antraquinone chromophore *(8)*.

Figure 2

In basic media, the contrary effect was observed, in which a red shift in the absorption was detected, as well as an enhancement in the emission intensity. With exception of compound **3**, which was not emissive, compounds **1** and **2** showed the same behaviour in the ground and excited states with increasing amount of OH^- (see Figure 3 for titration of compound **1**). In the absorption spectra, a red shift from 450 to 500 nm was seen with an isosbestic point at 476 nm (Fig. 3A). An enhancement in the emission intensity of ca. 40 % was seen (Fig. 3B), which can be attributed to the deprotonation of the imidazo NH suppressing the hydrogen-bond formation.

Figure 3

Detection of anions by the deprotonation of the imidazo NH occurs via hydrogen bonding favoured by the proximity between the carbonyl oxygen from the anthraquinone moiety and the nitrogen of the imidazo.

In the ground state, a similar behaviour was observed for all compounds studied, in the presence of fluoride, as well as, in the excited state for compounds **1** and **2** *(9)*.

Interaction with fluoride in acetonitrile induced a red shift from 450 nm to 520 nm in the absorption band, with an isosbestic point at 478 nm. On the other hand, in the emission spectra an enhancement of *ca.* 40 % in the intensity, as well as a red shift of 25 nm was also observed. In Figure 4 is shown the spectrophotometric and spectrofluorimetric titration for compound **1** in the presence of fluoride as representative example.

Figure 4

The addition of cyanide to imidazo-anthraquinones **1-3** resulted only in colorimetric changes and in Figure 5 the spectrophotometric titration of compound **3** in the presence of cyanide is presented as a representative example.

Figure 5

Having in mind practical applications of imidazo-anthraquinones **1-3** in aqueous media and early reports in which selectivity to cyanide over fluoride was achieved by increasing the water percentage in organic solvent aqueous mixtures *(2e,3n)*, an anion selectivity assay in acetonitrile/H_2O (97:3, v/v) was carried out. In Figure 1b the comparison of the sensory study of compound **3** in organic (acetonitrile) and aqueous media is presented, showing that selectivity for cyanide was improved in aqueous media. In the aqueous mixture, it was possible to distinguish cyanide from fluoride since a change in colour from yellow to orange was only observed in the presence of cyanide (Figure 1b).

Therefore, spectrophotometric titrations were also conducted in acetonitrile/H_2O (97:3, v/v) for imidazo-anthraquinones **1-3** in the presence of increasing amounts of cyanide (Figure 6). UV-vis titrations of compounds **1-3** (10^{-5} M in acetonitrile/H_2O (97:3, v/v) with cyanide showed a moderate decrease and a small bathochromic shift of the absorption band together with a simultaneous growth of a new red-shifted band. As an example, compound **1** exhibited an absorption band at 450 nm and a yellow colour in acetonitrile/H_2O (97:3, v/v) solution. Upon addition of increasing amounts of cyanide, this band progressively decreased while a new absorption band at 550 nm increased in intensity ($\Delta\lambda$ = 100 nm) (Figure 6A). This induced an obviously visible colour

modulation from yellow to orange, suggesting the formation of a charge transfer complex between the anion and the anthraquinone receptors.

Figure 6

The association constants were calculated using the HypSpec program *(10)* from the results obtained in acetonitrile and acetonitrile/H_2O (97:3, v/v) (Table 2). The best result was obtained for compound **3** due to the higher acidity of hydrogen bond donor NH of the imidazole in carbazole derivative **3** compared to receptors **1** and **2** probably due to the large conjugated imidazo-anthraquinone-carbazole system. The limits of detection (LOD) and quantification (LOQ) at 520 nm were determined in acetonitrile and acetonitrile /H_2O (97/3, v/v), (Table 3) (*11*). Thus, for compound **3** in acetonitrile, the limit of detection (LOD) was found to be 3.31 μM for CN^- and 4.97 μM for F^-. Taking into account these results, the limit of quantification (LOQ) for CN^- and F^- that might be sensed in acetonitrile is *ca.* 9.68 μM and 13.38 μM, respectively. On the other hand in acetonitrile /H_2O (97/3, v/v) the LOD for CN^- was found to be 3.0 mM. Earlier reports of the limits of detection of the cyanide ion were in the range of mM to μM *(3d-n)*.

Table 2

Table 3

2.3. ^{1}H NMR titrations

The sensory behaviour observed with the spectrophotometric and spectrofluorimetric titrations was also complemented by performing ^{1}H NMR titrations in order to gain further insight into the binding mode between the receptor and the anions under study. Due to the limited solubility of compounds **1-3** in deuterated acetonitrile, the titrations were carried out in DMSO-d_6 for the fluoride anion (Figure 7) and acetone-d_6 for the cyanide anion at room temperature (Figure 8), taking into account the fact that cyanide could exhibit an analogous behaviour to that of fluoride in DMSO solution *i.e.* an increase in the basicity that could lead to the deprotonation of the imidazole NH *(12)*. In both solvents, the signal of the imidazole NH appearing downfield in the absence of anion suggested high acidity and strong hydrogen-bonding ability.

Figure 7

In DMSO-d_6, upon addition of 0.5 equivalents of F^-, the NH proton signal of **3** disappeared, suggesting a strong hydrogen bonding interaction between the anion and the imidazole NH. After addition of 1.5 equiv of F^-, one triplet signal started to develop at 15.5-16.5 ppm, which became quite prominent after addition of 3.0 equiv of F^-. Appearance of this triplet suggested the formation of HF_2^- ion and thus confirmed the deprotonation of the imidazole NH. This was also supported by the upfield shifts of the H4, H5 (~0.48 ppm) and H4' (~0.21 ppm) protons of the anthraquinone and carbazole nuclei, respectively, due to the increased electron density delocalized on the entire conjugated system. This deprotonation process is also confirmed by titration experiments with tetrabutylammonium salts of fluoride and hydroxide, in which it was possible to see the identical spectral changes (Figures 3 and 4).

Figure 8

In acetone-d_6, the signal of the imidazole NH appeared downfield at 12.2 ppm, but it suffered a dramatic shift to 5.7 ppm ($\Delta\delta \sim 6.5$ ppm) in the presence of cyanide (0.5 equivalents). The same upfield shift trend was seen for all other protons, upon continued addition of cyanide till 3 equivalents. This shielding effect is probably due the formation of the charge transfer complex between the anion and the receptor, resulting in an increase in the electron density in the system. The identity of the NH signal at 5.7 ppm was confirmed by disappearance after addition of D_2O (Figure 8).

3. Conclusions

Novel indole and carbazole functionalized imidazo-anthraquinones **1-3** were synthesized in good to excellent yields and completely characterised. The photophysical properties of compounds **1-3** were studied by UV-vis and fluorescence spectroscopy and their ability as colorimetric and fluorimetric sensors towards anions was studied in acetonitrile as well as in a mixture of acetonitrile/H_2O (in a 97:3 proportion). Higher sensitivity and selectivity for cyanide ion was observed in an aqueous solution with straightforward naked-eye detection from yellow to orange and moderate sensitivity with a mM-level detection limit. The binding process was also followed for fluoride and

cyanide anions by ^{1}H NMR titrations showing that a deprotonation of the receptor occured in presence of fluoride while in the presence of cyanide it was observed the formation of a charge transfer complex, which is in agreement with the spectrophotometric titrations.

4. Experimental

4.1. Synthesis general

All melting points were measured on a Stuart SMP3 melting point apparatus. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh). IR spectra were determined on a BOMEM MB 104 spectrophotometer. NMR spectra were obtained on a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H and 100.6 MHz for ^{13}C using the solvent peak as internal reference at 25 ºC. All chemical shifts are given in ppm using δ_H Me_4Si = 0 ppm as reference and *J* values are given in Hz. Assignments were made by chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear correlation techniques. Low and high resolution mass spectrometry analyses were performed at the "C.A.C.T.I. - Unidad de Espectrometria de Masas", at University of Vigo, Spain. All commercially available reagents were used as received.

4.2. General procedure for the synthesis of compounds 1-3

i) Preparation of the imines

The aldehydes (0.20 mmol) and 1,2-diaminoanthraquinone (0.24 mmol) were dissolved separately in ethanol (4 mL/mmol). The ethanolic solution of aldehyde and formic acid (0.04 mL/mmol of aldehyde) was added to the solution of 1,2- diaminoanthraquinone heated at reflux. The reaction mixture was heated under reflux overnight.

ii) Cyclisation of the imines

After cooling, the ethanolic solution was evaporated and the crude imine was dissolved in a small volume of acetic acid (5 mL/mmol of imine). To this solution, lead tetraacetate was added (0.20 mmol) and the mixture was stirred overnight at room temperature. Addition of water to the reaction mixture gave a solid which was isolated by filtration and purified by recrystalization from diethyl ether/chloroform.

4.2.1. 2-(1*H*-indol-3'-yl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione (1). Dark red solid (95%). Mp = 318.7-321.1 ºC. IR (KBr): ν = 3420, 1665, 1623, 1584, 1489, 1444, 1371, 1327, 1289, 1245, 1154, 1134, 1064, 1006, 931, 895, 840, 739, 714 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.22-7.25 (m, 2H, H-5' and H-6'), 7.49-7.52 (m, 1H, H-4'), 7.92-7.95 (m, 2H, H-8 and H-9), 8.06 (s, 2H, H-4 and H-5), 8.21-8.27 (m, 2H, H-7 and H-10), 8.58-8.61 (m, 1H, H-7'), 8.91 (d, 1H, *J* = 3.0 Hz, H-2'), 11.90 (s, 1H, N*H'*), 12.93 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6): δ = 105.22 (C3'), 112.07 (C4'), 117.34 (C11a), 120.86 (C4 and C6'), 121.76 (C7'), 122.54 (C5'), 123.40 (C5), 125.65 (C3'a), 126.79 (C7 and C10), 129.91 (C2'), 132.58 (C11b), 133.14 (C5a), 133.38 (C10a and C6a), 134.18 (C9), 134.41 (C8), 136.57 (C7'a), 150.57 (C3a), 155.97 (C2), 182.25 (C=O), 183.45 (C=O). UV/Vis (CH_3CN, nm): λ_{max} (log ε) = 452.0 (4,00). MS: *m/z* (FAB, %): 364 ($[M+H]^+$, 24), 363 (M^+, 10), 307 (38), 289 (18), 155 (31), 154 (100). $C_{23}H_{14}N_3O_2$; calcd 364.1086; found 364.1097.

4.2.2. 2-(5'-methyl-1*H*-indol-3'-yl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione (2). Red solid (93%). Decomposition at T > 320 ºC. IR (Nujol): ν = 3427, 1661, 1583, 1567, 1376, 1325, 1245, 1152, 1006, 913, 842, 713 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 2.48 (s, 3H, CH_3), 7.04 (d, 1H, *J* = 7.2 Hz, H-6'), 7.38 (d, 1H, *J* = 8.1 Hz, H-7'), 7.92-7.94 (m, 2H, H-8 and H-9), 8.05 (s, 2H, H-4 and H-5), 8.21-8.26 (m, 2H, H-7 and H-10), 8.38 (s, 1H, H-4'), 8.86 (d, 1H, *J* = 3.0 Hz, H-2'), 11.78 (s, 1H, N*H'*), 12.86 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6): δ = 21.44 (CH_3), 104.73 (C3'), 111.68 (C7'), 117.20 (C11a), 120.81 (C4), 121.31 (C4'), 123.28 (C5), 124.06 (C6'), 126.15 (C3'a), 126.67 (C10), 126.73 (C7), 129.52 (C5'), 129.96 (C2'), 132.58 (C11b), 133.11 (C5a), 133.54 (C10a and C6a), 134.09 (C9), 134.33 (C8), 134.91 (C7'a), 150.60 (C3a), 156.06 (C2), 182.19 (C=O), 183.40 (C=O). UV/Vis (CH_3CN, nm): λ_{max} (log ε) = 456.0 (4,10). MS: *m/z* (FAB, %): 378 ($[M+H]^+$, 31), 377 (M^+, 14), 307 (36), 289 (18), 155 (33), 154 (100). $C_{24}H_{16}N_3O_2$; calcd 378.1243; found 378.1247.

4.2.3. 2-(9'-ethyl-9*H*-carbazol-3'-yl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione (3). Red solid (81%). Mp = 289.7-290.4 ºC. IR (liquid film): ν = 3447, 1659, 1584, 1526, 1489, 1441, 1325, 1292, 1154, 1007, 890, 842, 798, 751, 711, 604 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 1.35 (t, 3H, *J* = 7.2 Hz, CH_3), 4.47 (q, 2H, *J* = 7.2 Hz, CH_2), 7.28 (t, 1H, *J* = 7.5 and 6.9 Hz, H-7'), 7.49 (t, 1H, *J* = 7.2 Hz, H-6'), 7.64 (d, 1H, *J* = 8.4 Hz, H-8'), 7.72 (d, 1H,

J = 8.7 Hz, H-5'), 7.88-7.92 (m, 2H, H-8 and H-9), 8.04 (s, 2H, H-4 and H-5), 8.16-8.22 (m, 2H, H-8 and H-9), 8.27 (d, 1H, *J* = 8.4 Hz, H-1'), 8.49 (d, 1H, *J* = 8.7 Hz, H-2'), 9.30 (d, 1H, *J* = 1.5 Hz, H-4'), 12.94 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6): δ = 13.80 (*C*H_3), 37.22 (*C*H_2), 109.32 (C3' and C5'), 109.60 (C8'), 118.10 (C11a), 119.61 (C7'), 120.65 (C1'), 120.87 (C4'), 121.02 (C4), 122.32 (C8'a), 122.40 (C4'a), 124.15 (C5), 125.99 (C2'), 126.16 (C6'), 126.36 (C10), 126.76 (C7), 133.00 (C5a), 133.19 (C10a and C6a), 134.18 (C9), 134.39 (C8), 140.12 (C8'b), 141.03 (C4'b), 149.79 (C3a), 158.92 (C2), 182.23 (C=O), 183.28 (C=O). UV/Vis (CH_3CN, nm): λ_{max} (log ε) = 448.0 (4,09). MS: *m/z* (FAB, %): 442 ($[M+H]^+$, 100), 441 (M^+, 47), 307 (22), 155 (24), 154 (78). $C_{29}H_{20}N_3O_2$; calcd 442.1556; found 442.1559.

4.3. Spectrophotometric/spectrofluorimetric titrations of compounds 1-3

Absorption spectra were recorded on a JASCO V-650 UV-visible spectrophotometer and fluorescence emission spectra on a HORIBA JY Scientific Fluoromax-4 spectrofluorimeter. The linearity of the fluorescence emission vs. concentration was checked in the concentration used (10^{-4} – 10^{-6} M). A correction for the absorbed light was performed when necessary. The titrations were performed as follows: stock solutions of the compounds (*ca*. 10^{-3} M) were prepared by dissolving an appropriated amount of compound in a 10 mL volumetric flask and diluting to the mark with acetonitrile or acetonitrile/H_2O. The solutions were prepared by appropriate dilution of the stock solutions still 10^{-5} – 10^{-6} M. Titrations of compounds **1**, **2** and **3** were carried out by the addition of microliter amounts of standard solutions of the anions in the form of tetrabutylammonium salts in acetonitrile. All the measurements were performed at 298 K. Relative fluorescence quantum yields were measured using a solution of quinine sulphate in sulphuric acid (0.5M) as a standard (Φ_F = 0.54) (*7*) for **1** to **3** and values were corrected for the refraction index of the solvents.

The detection (LOD) and quantification limits (LOQ) for the anions studied were calculated, by performing ten different analyses for the selected receptor (*11*).

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Captions

Table 1. Yields and UV-visible absorption data for compounds **1-3** in acetonitrile.
[a] For the N*H* of imidazo moiety in DMSO-d_6. [b] For the N*H* of indole moiety in DMSO-d_6. [c] For the NH stretching band.

Table 2. Association constants for compounds **1-3** in the presence of F^- and CN^- in acetonitrile and acetonitrile /H_2O (97:3, v/v). For all interactions, the stoichiometry suggested from Hyperquad software was 2:1 (L:A).
[a] No reliable results were obtained.

Table 3. Limit of detection (LOD) and limit of quantification (LOQ) of compound **3** for fluoride and cyanide ion in acetonitrile and acetonitrile /H_2O (97:3, v/v).

Scheme 1. Synthesis of imidazo-anthraquinone derivatives **1-3**.

Figure 1. Colour changes of compound **3** (2.0×10^{-5} M) in acetonitrile (A) and acetonitrile/H_2O (97:3, v/v) (B) seen in the presence of 100 equiv. of F^-, Cl^-, Br^-, I^-, CN, AcO^-, BzO^-, NO_3^-, ClO_4^-, HSO_4^- and $H_2PO_4^-$ in the form of tetrabutylammonium salts.

Figure 2. Spectrophotometric (A) and spectrofluorimetric titration (B) of compound **1** in acetonitrile with a standard solution of methanesulfonic acid in acetonitrile. (T= 298 K, [**1**] = 1×10^{-5} M, $\lambda_{\mathbf{1}exc}$ = 444 nm). In inset (A) is represented the absorption at 415nm and 450 nm; in inset (B) is represented the normalized emission at 640 nm.

Figure 3. Spectrophotometric (A) and spectrofluorimetric titration (B) of compound **1** in acetonitrile with a standard solution of $[(Bu)_4N]OH$ (T=298 K, [**1**] = 1×10^{-5} M, $\lambda_{\mathbf{1}exc}$ = 480 nm). In inset (A) is represented the absorption at 450 nm and 500 nm.

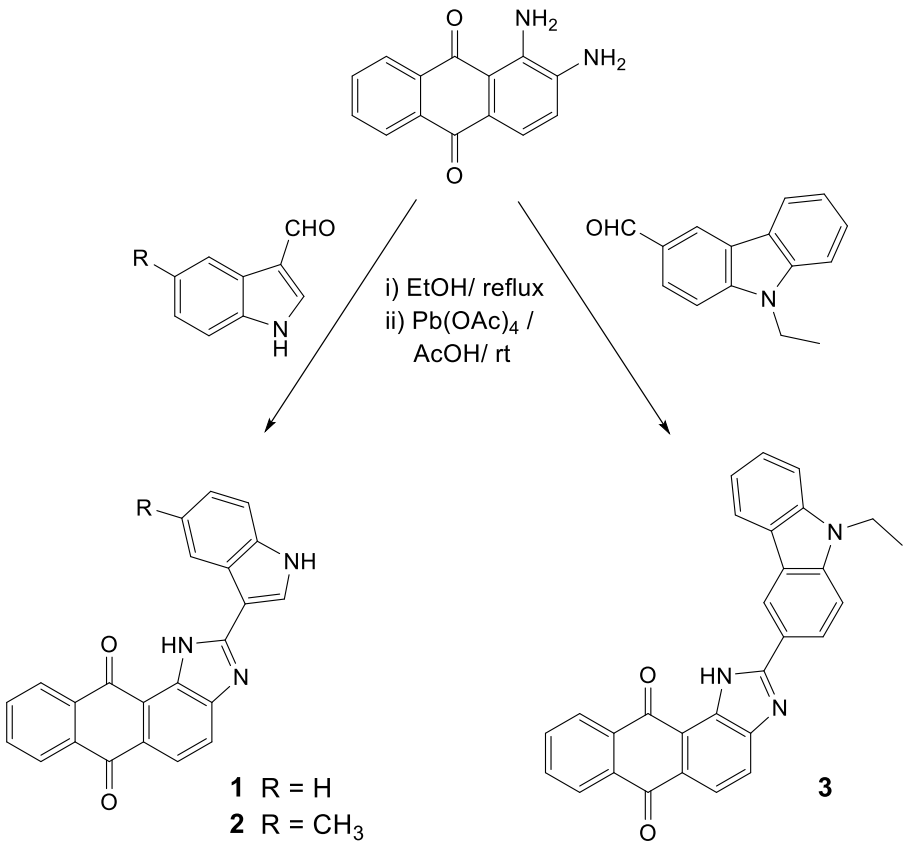
Figure 4. Spectrophotometric (A) and spectrofluorimetric (B) titration of compound **1** in acetonitrile with a standard solution of $[(Bu)_4N]F$ (T=298 K, [**1**] = 1×10^{-5} M, $\lambda_{\mathbf{1}exc}$ = 480 nm). In inset (A) is represented the absorption at 450 nm and 500 nm.

Figure 5. Spectrophotometric titration of compound **3** in acetonitrile with a standard solution of $[(Bu)_4N]CN$ (T=298 K, [**3**] = 1×10^{-5} M). In the inset is represented the absorption at 450 nm and 490 nm.

Figure 6. Spectrophotometric titrations of compounds **1-3** with $[(Bu)_4N]CN$ (A, B and C, respectively) in acetonitrile/H_2O (97:3, v/v) ([**1-3**] =2.0×10^{-5} M, T= 298K). The insets represent the maximums of absorption and emission bands.

Figure 7. Partial ^1H NMR spectra of compound **3** (3.0 x 10^{-2} M) in DMSO-d_6 in (a) the absence and the presence of (b) 0.5, (c) 1.0, and (d) 3.0 equiv of $[(Bu)_4N]F$.

Figure 8. Partial ^1H NMR spectra of compound **3** (3.0 x 10^{-2} M) in acetone-d_6 in (a) the absence and the presence of (b) 0.5, (c) 1.5, and (d) 3.0 equiv of $[(Bu)_4N]CN$.



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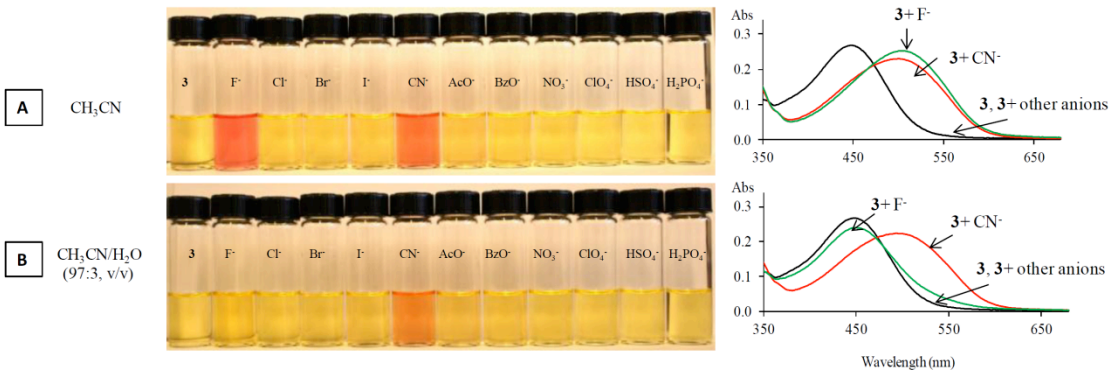

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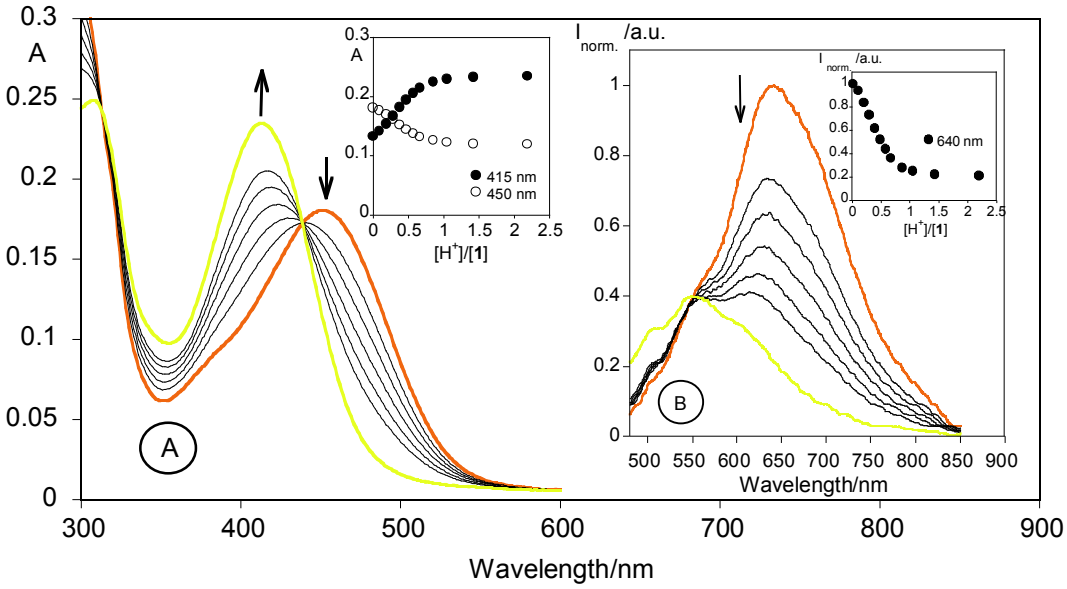

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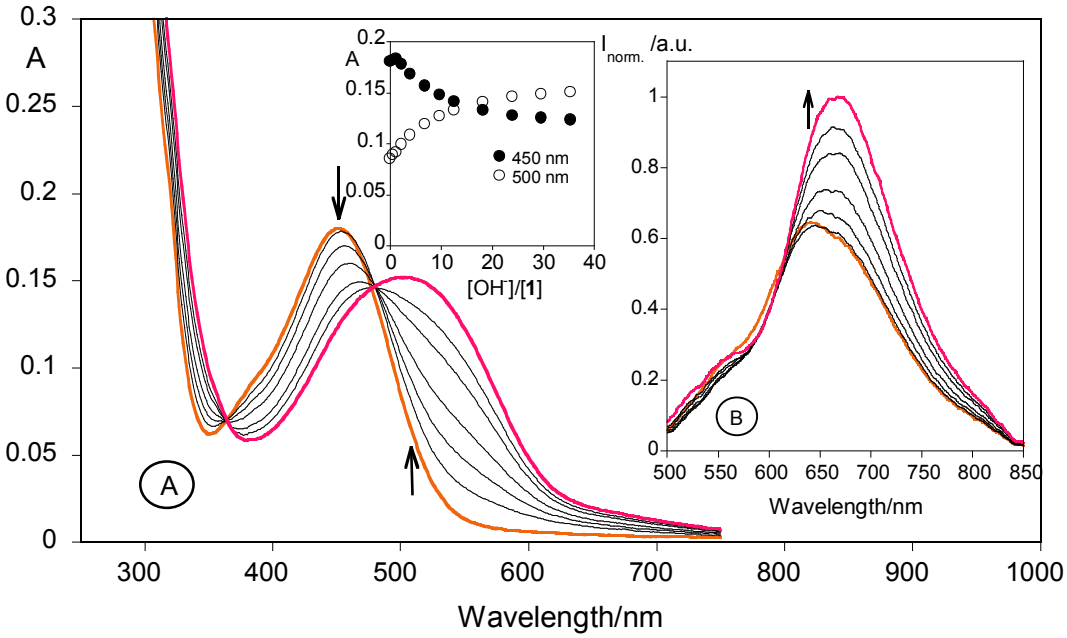

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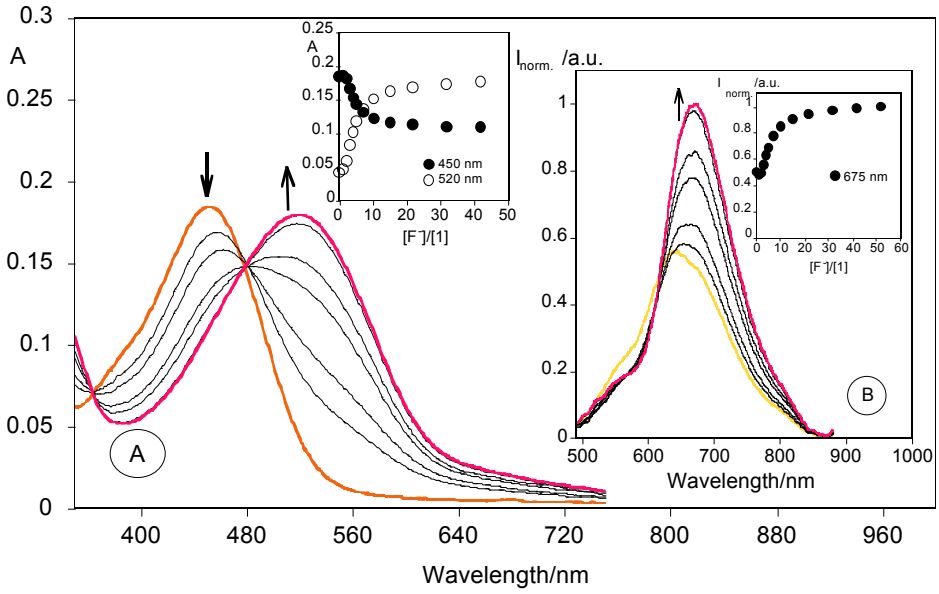

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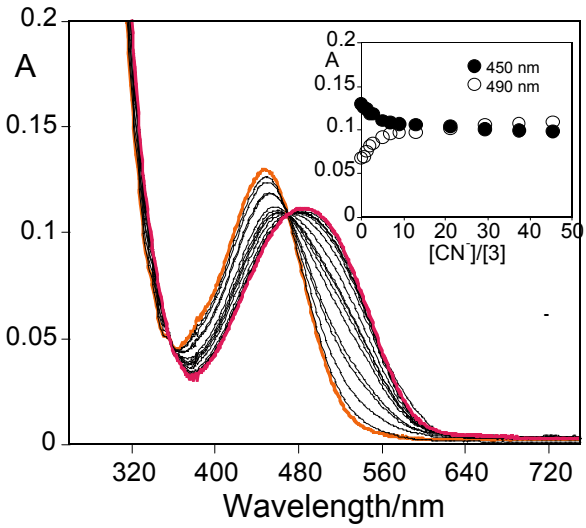

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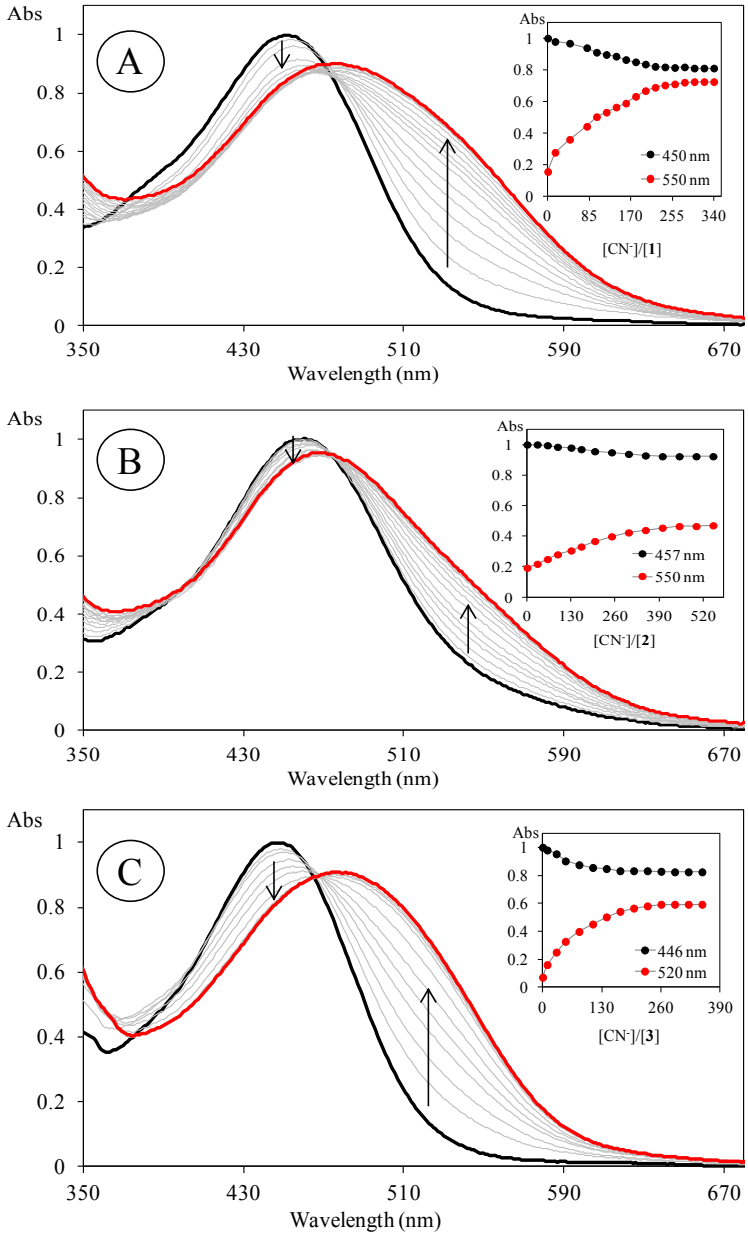

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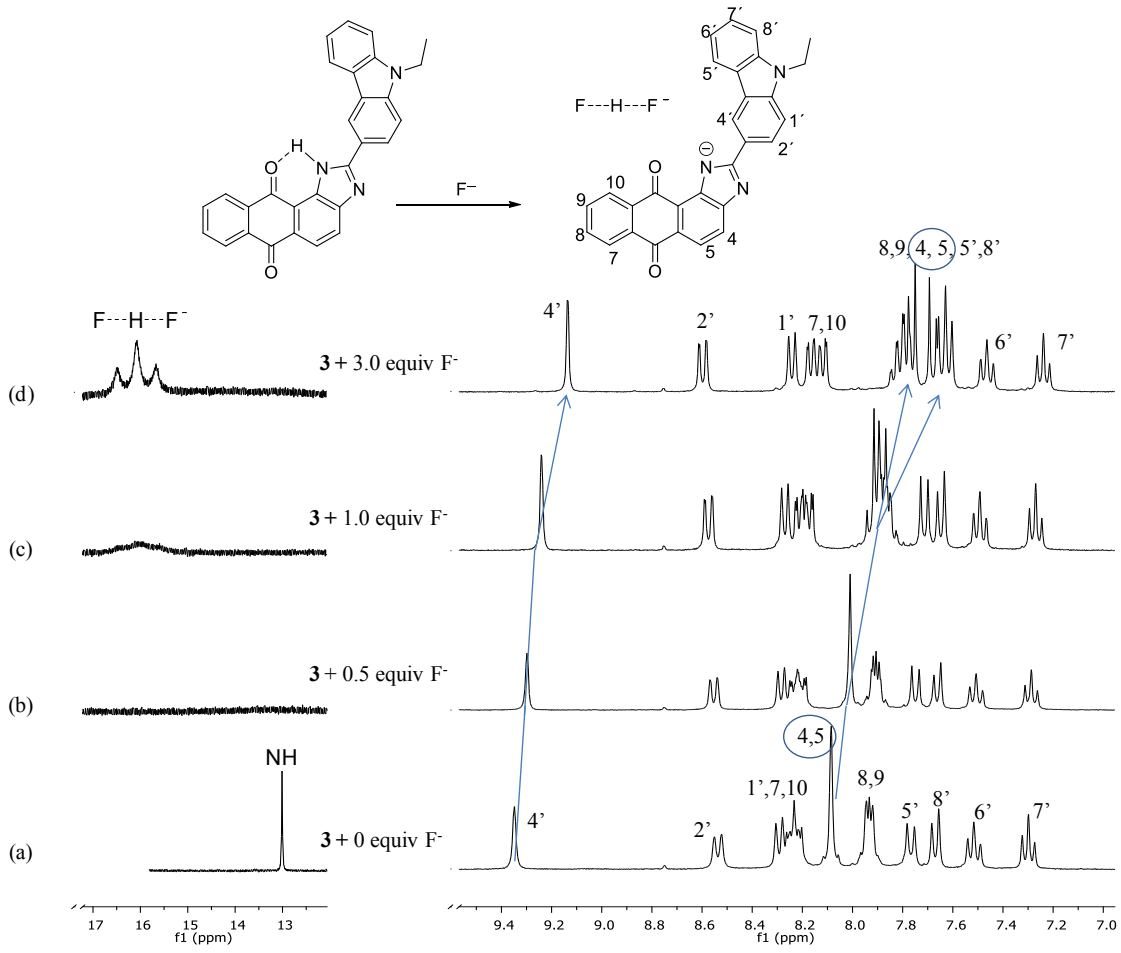

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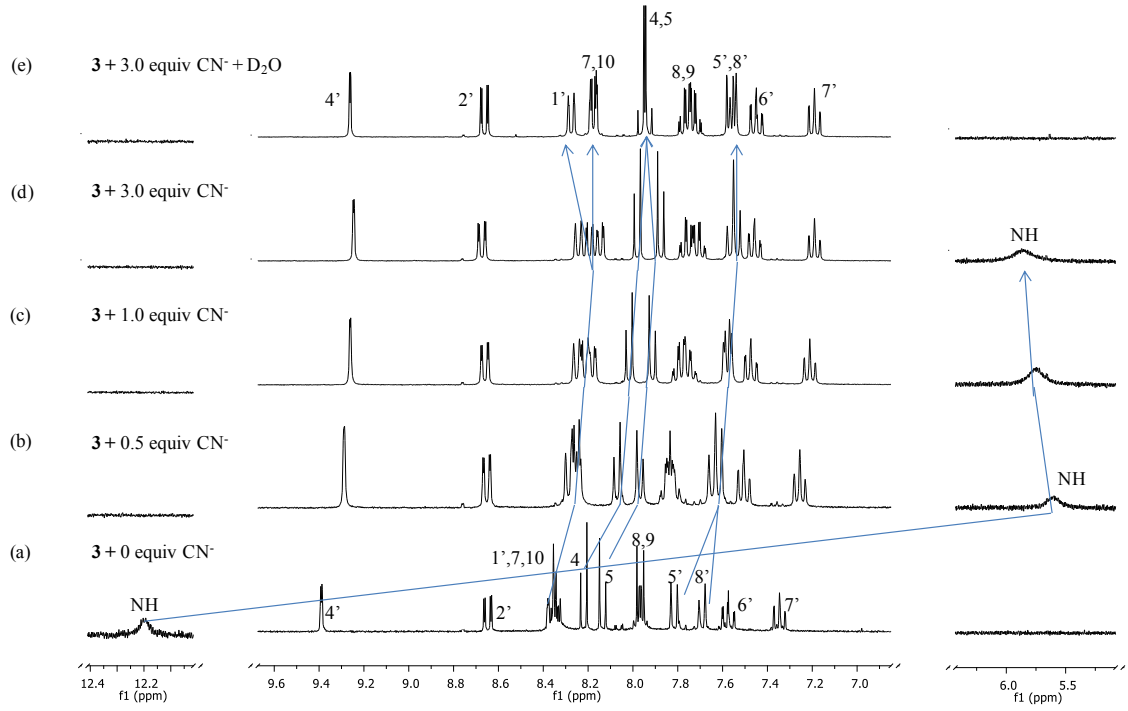

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Table 1. Yields and UV-visible absorption data for compounds **1-3** in acetonitrile.

Cpd	Yield (%)	NMR δ_H (ppm)	IR ν (cm^{-1})[c]	Absorption	
				λ_{abs} (nm)	log ε
1	95	12.93[a] 11.90[b]	3442	452	4.00
2	93	12.86[a] 11.78[b]	3427	456	4.10
3	81	12.94	3447	448	4.09

[a] For the N*H* of imidazo moiety in DMSO-d_6. [b] For the N*H* of indole moiety in DMSO-d_6. [c] For the NH stretching band.

Table 2. Association constants for compounds **1-3** in the presence of F^- and CN^- in acetonitrile and acetonitrile /H_2O (97:3, v/v). For all interactions, the stoichiometry suggested from Hyperquad software was 2:1 (L:A).

Compound	**Anion**	**log K_{ass}**	
		acetonitrile	**acetonitrile/H_2O (97:3)**
1	F^-	6.31 ± 0.08	[a]
	CN^-	6.80 ± 0.08	6.949 ± 0.005
2	F^-	6.34 ± 0.07	[a]
	CN^-	7.04 ± 0.09	6.263 ± 0.006
3	F^-	8.50 ± 0.07	[a]
	CN^-	8.96 ± 0.07	7.132 ± 0.004

[a] No reliable results were obtained.

Table 3. Limit of detection (LOD) and limit of quantification (LOQ) of compound **3** for fluoride and cyanide ion in acetonitrile and acetonitrile /H_2O (97:3, v/v).

Solvent	**LOD**	**LOQ**
CH_3CN	CN^- (3.31 μM) F^- (4.97 μM)	CN^- (9.68 μM) F^- (13.38 μM)
CH_3CN/H_2O (97:3, v/v)	CN^- (3.0 mM)	CN^- (12.0 mM)