J. Braz. Chem. Soc., Vol. 23, No. 8, 1488-1500, 2012.
Printed in Brazil - ©2012 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Anionic Chromogenic Chemosensors Highly Selective for Fluoride or Cyanide Based on 4-(4-Nitrobenzylideneamine)phenol

*Celso R. Nicoleti, Vanderléia G. Marini, Lizandra M. Zimmermann and Vanderlei G. Machado**

Departamento de Química, Universidade Federal de Santa Catarina (UFSC), 88040-900 Florianópolis-SC, Brazil

O composto 4-(4-nitrobenzilidenoamino)fenol foi utilizado em duas estratégias que permitem uma detecção altamente seletiva de F^- e CN^-. Primeiramente, observou-se que o composto em acetonitrila age como um quimiossensor cromogênico devido ao fato de que ânions básicos levam ao seu desprotonamento (solução incolor), resultando numa solução colorida contendo fenolato. A detecção seletiva de CN^- sobre F^- foi obtida adicionando-se 1,4% de água ao sistema: a água solvata preferencialmente o F^-, enquanto o CN^- fica relativamente livre para desprotonar o composto fenólico. Outra estratégia envolveu um ensaio de competição do fenolato e do analito pelo calix[4]pirrol em acetonitrila, um receptor altamente seletivo para F^-. O fenolato e o calix[4]pirrol formam um complexo por ligação de hidrogênio, com mudança na cor do meio. Dentre diversos ânions, somente o F^- foi capaz de restaurar a cor original correspondendo ao fenolato, pelo fato do ânion deslocá-lo do sítio de complexação.

4-(4-Nitrobenzylideneamine)phenol was used in two strategies allowing the highly selective detection of F^- and CN^-. Firstly, the compound in acetonitrile acts as a chromogenic chemosensor based on the idea that more basic anions cause its deprotonation (colorless solution), generating a colored solution containing phenolate. The discrimination of CN^- over F^- was obtained by adding 1.4% water to acetonitrile: water preferentially solvates F^-, leaving the CN^- free to deprotonate the compound. Another strategy involved an assay comprised of the competition between phenolate dye and the analyte for calix[4]pyrrole in acetonitrile, a receptor highly selective for F^-. Phenolate and calix[4]pyrrole form a hydrogen-bonded complex, which changes the color of the medium. On the addition of various anions, only F^- was able to restore the original color corresponding to phenolate in solution due to the fact that the anion dislodges phenolate from the complexation site.

Keywords: anionic chromogenic chemosensor, displacement assay, naked-eye detection, anion sensing, calix[4]pyrrole

Introduction

The fact that anions play a fundamental role in many chemical and biological processes has led to increased attention being focused on the field of the recognition and detection of anionic species.[1] Much effort is being spent on the design of chemosensors able to perform the selective visual detection of anions and also the quantification of such species.[1] In research concerned with anion sensing, many studies have been directed toward the development of chemosensors for the fluoride anion[2] due to the role it plays in many diseases, in industry and in environmental pollution.[3] Another interesting anion in terms of detection is CN^-, which is lethal in very small amounts due to its ability to strongly bind to the active site of cytochrome-oxidase, leading to the inhibition of the mitochondrial electron transport chain, and to a decrease in the oxidative metabolism.[4] CN^- has many applications in metallurgy, fishing, mining and in the fabrication of polymers.[4] Some fruit seeds and roots release CN^- through hydrolysis.[5] In addition, many chemical warfare compounds, such as sarin, soman and tabun,[6] deliver F^- and CN^- through hydrolysis[7] and this is important in relation to developing chemosensors for the detection of these neurotoxic agents.[8]

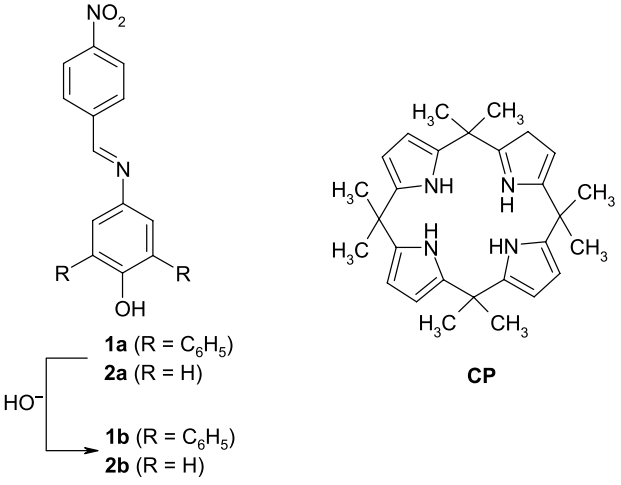
For the development of anionic chemosensors, a very simple strategy uses the design of molecules that change color, following an alteration in their molecular structure due to the presence of anions in the medium.

*e-mail: vanderlei.machado@ufsc.br

The selectivity of a chemosensor for an anionic species is related to its differential ability to interact with the receptor site in the chemosensor, for instance, through intermolecular hydrogen bonding (HB). In this context, Steiner[9] considered all HB as incipient proton transfer and that in strong HB this process can be found in a very advanced state. Phenol groups are commonly used in the molecular structure of these types of chemosensors.[10–14] The connection of the phenol donor group to an acceptor group through a conjugated bridge creates an interesting feature since the deprotonation of the compound generates a colored conjugated base. The acidity of the chemosensor can be improved by combining the effect of the medium polarity with modifications in the molecular structure of the compound.[12,13] A set of protonated dyes with phenol donor groups in their molecular structures has been studied by our group as simple anionic chromogenic chemosensors based on acid-base strategy.[11–14] One of these dyes is 4-(4-nitrobenzylideneamine)-2,6-diphenylphenol, compound **1a**, which was recently used to selectively detect CN^- in the presence of several anionic species in acetonitrile with very small amounts of water.[14] The colorless solutions of **1a** in acetonitrile are turned blue with the addition of basic species due to the formation of **1b**. From the various anionic species added to the solutions of **1a**, only CN^-, F^- and, with less intensity, CH_3COO^- and $H_2PO_4^-$ led to colored solutions. With the addition of up to 2.4% (v/v) of water, from all anions studied, only CN^- caused a detectable alteration in the color of the solution.[14]

In other type of strategy, involving displacement assays, a receptor is specially conceived to interact with a dye (or a chromogenic reagent) forming a complex, which causes an optical change in the system. The presence of the analyte causes a competition scenario that can lead to the dye being displaced from its initial complex, causing a perceptible change in the optical signal of the system.[15] This strategy has been successfully used in the development of assays for many types of analytes.[15,16] Many receptor molecules exhibiting the capability to recognize anions have been synthesized in recent years and their design comprises the use of hydrogen bonds alone or in conjugation with electrostatic forces to generate binding sites for anionic species. Among the most popular anion receptors, a very interesting example is *meso*-octamethylporphyrinogen, more commonly known as *meso*-octamethylcalix[4]pyrrole (**CP**). This receptor was originally discovered by Baeyer[17] in 1886 but only recently its anion binding properties were recognized.[18] The main advantages of its use in anion recognition and sensing are its easy and quick synthesis,[19–23] associated with the fact that functionalized anion sensors can be designed by means of the integration of the calix[4]pyrrole with different signaling subunits.[24,25] An interesting example of a colorimetric chemosensor was discovered by Gale *et al.*[25] and involved an efficient displacement assay. The addition of **CP** made a yellow *p*-nitrophenolate solution in dichloromethane colorless and the solution changed back to yellow after adding the fluoride anion, which is able to strongly bind at the receptor site, displacing *p*-nitrophenolate.[25] This finding inspired the study of a displacement assay based on the interaction of **CP** with 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one, a dye known as Brooker's merocyanine (**BM**), in acetonitrile.[26] A solution of **BM** in acetonitrile is colored and the addition of **CP** changes the color in the solution due to the formation of hydrogen-bonded **CP-BM** species. Finally, the original color of the solution can be easily restored with the addition of an adequate anion able to selectively bind to **CP** and, in this manner, displacing the free dye.[26]

In this work, 4-(4-nitrobenzylideneamino)phenol (compound **2a**) is employed in two strategies aimed at the detection of anions in solution. Firstly, **2a** is used as an anionic chromogenic chemosensor in acetonitrile and in acetonitrile-water mixtures in the presence of various anions, utilizing an acid-base approach. Another study is performed to show the potential of **2b** to detect anions in acetonitrile by means of a displacement assay that uses **CP** as an anionic receptor.



Scheme 1.

Experimental

General

All chemicals used were high-purity commercial reagents. The deionized water used in the measurements

was boiled and bubbled with nitrogen and kept in a nitrogen atmosphere to avoid the presence of carbon dioxide. Acetonitrile (Sigma-Aldrich, HPLC grade) was dried with calcium hydride, distilled and stored over molecular sieves (Sigma-Aldrich, 4 Å) as previously described.[27] Karl-Fischer titrations were performed with this solvent and demonstrated the presence of water in a concentration of 7.11×10^{-3} mol L^{-1} (0.016%). *Tetra-n*-butylammonium hydroxide was purchased from Sigma-Aldrich. All anions (HSO_4^-, $H_2PO_4^-$, NO_3^-, CN^-, CH_3COO^-, F^-, Cl^-, Br^- and I^-) were used as *tetra-n*-butylammonium salts with purity greater than 97-99%. The anions were purchased from Fluka (F^-, > 97%; Cl^-, > 98%; NO_3^-, > 97%; $H_2PO_4^-$, > 97%), Vetec (Br^-, > 99%; I^-, > 99%; HSO_4^-, > 99%) and Sigma-Aldrich (CH_3COO^-, > 97%) and were dried over phosphorous pentoxide under vacuum before use. Karl-Fischer experiments were performed for the following *tetra-n*-butylammonium salts in order to determine the content of water in each salt: CN^- (0.12% water), F^- (1.13% water), $H_2PO_4^-$ (0.11% water) and CH_3COO^- (0.07% water).

Instrumentation

UV-Vis experiments were carried out on a Varian Cary Bio 50 and HP 8452A spectrophotometers equipped with a thermostated bath and all measurements were performed at 25 °C, employing a 1-cm quartz cuvette. The maximum wavelengths (λ_{max}) of the UV-Vis spectra were calculated from the first derivative of the absorption spectrum. Melting points were obtained on a Kofler hot stage and were uncorrected. The nuclear magnetic resonance (NMR) spectra were recorded on a Varian AS-400 spectrometer. Chemical shifts were recorded in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet and bs = broad singlet), integration and coupling constants (Hz). Infrared (IR) spectra were obtained on a Shimadzu model Prestige-21 spectrophotometer, with KBr pellets.

Synthesis of the compounds

Compound **1a** was synthesized and purified as described in the literature.[14]

Synthesis of **2a**

This compound was synthesized following a procedure adapted from the literature.[28] 4-Nitrobenzaldehyde (1.51 g; 10 mmol) and 4-aminophenol (1.09 g; 10 mmol) were stirred in ethanol (20 mL) in a round-bottomed flask. At the beginning the reaction, the mixture was slowly heated to ensure the solubilization of the reactants and then two drops of acetic acid were added. The color of the solution changed from yellow to dark orange. The reaction mixture was stirred at room temperature for 2 h and then left to stand overnight. The resulting solid was filtered, washed with cold ethanol, recrystallized from methanol and dried; yield 52%; mp 168.8 °C (176 °C);[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (s, 1H), 6.90 (d, 2H, *J* 8.4 Hz) 7.26 (d, 2H, *J* 8.4 Hz), 8.06 (d, 2H, *J* 8.6 Hz), 8.32 (d, 2H, *J* 8.6 Hz), 8.57 (s, 1H); IR (KBr) ν_{max}/cm^{-1} 3446 (O–H), 1597 (C=N), 1508, 1338 (N=O), 1450 (C=C).

Synthesis of **CP**

This compound was prepared through the adaptation of procedures described in the literature.[21,22] A solution of 3.1 mL (44.7 mmol) of freshly distilled pyrrole in anhydrous ethanol was added to a three-necked flask coupled to a reflux condenser. This system was placed in an ice bath and over a period of 10 min, 0.2 mL (1.87 mmol) of triflic acid was added dropwise to the stirred solution. A volume of 3.3 mL (44.7 mmol) of acetone was then added. At the end of the addition, a white solid precipitated and the stirring was stopped. The reaction mixture was left at room temperature for 1 h and the white solid was then crushed in ethanol and filtered under vacuum. The product was three times recrystallized in a 1:1 (v/v) ethanol:acetone mixture; yield 2.50 g, 47.5%; mp 298 °C (296 °C);[21] ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.51 (s, 24H), 5.68 (d, 8H, *J* 2.2 Hz), 9.26 (bs, 4H, NH); IR (KBr) ν_{max}/cm^{-1} 3444 (N–H), 2973, 2932, 2869 (C–H), 1578, 1506, 1448, 1414 (C–C and C–N).

pKa value for **2a** in aqueous solution

A solution of **2a** was prepared in a concentration of 4×10^{-3} mol L^{-1} in $CHCl_3$, and stored in glass flasks closed with rubber stoppers to avoid the evaporation of the solvent. An aliquot of the solution, sufficient to give a concentration of the compound of 1×10^{-5} mol L^{-1}, was collected with a microsyringe and placed in a flask. After the evaporation of the solvent, water at pH 2.22 (adjusted with 0.1 mol L^{-1} HCl) was added and the UV-Vis spectrum of the compound was recorded at 25 °C. The pH of the solution was measured and the UV-Vis spectrum was obtained after each addition of a small amount of 0.1 mol L^{-1} KOH until pH 10-12.

UV-Vis study of **2a** with the anions

A solution of **2a** was prepared in acetonitrile in a concentration of 5.0×10^{-5} mol L^{-1}. This solution was then

used to prepare the solution of each anion in a concentration of 6.0×10^{-4} mol L^{-1}, using 5 mL volumetric flasks. Subsequently, these solutions were transferred to cuvettes hermetically closed with rubber stoppers in order to minimize the evaporation of the solvent and to avoid the entrance of water to the system, and the UV-Vis spectra were obtained.

The experiments involving acetonitrile-water mixtures were carried out using the following procedure. Solutions of **2a** containing each anion were prepared in acetonitrile, as described in the previous paragraph. Small volumes of water were then added to each system, giving a positive response, that is, a change in the color of the acetonitrile. The UV-Vis spectra were obtained in order to evaluate whether this amount was sufficient to allow selective detection with the naked eye. The absorbance values were collected for the λ_{max} values verified for each mixture.

Titration of **2a** with the anions

Titration experiments in acetonitrile were performed with the preparation of the solution of **2a**, as previously described. This solution was used to prepare the stock anion solutions in flasks that were closed with rubber stoppers and the titrations were carried out by adding small amounts (2-50 μL) of the salt solution with a microsyringe to closed quartz cuvettes containing the solution of **2a**. The UV-Vis spectra were obtained after each addition and the absorbance values were collected at 547.0 nm. Titration experiments were also performed in acetonitrile-water systems, using the minimum water content which allowed selective detection of the anion, defined in the previous UV-Vis studies.

The experiment for the stoichiometry determination was performed in acetonitrile with the method of continuous variations (Job's method). This plot was obtained considering the formation of **2b** produced from **2a** and CN^-. Thus, this study was performed at 25 °C using stock solutions in the experiment with concentrations of 6.0×10^{-5} mol L^{-1} for **2a** and 7.0×10^{-5} mol L^{-1} for CN^- and the absorbance values were read at λ_{max} = 547.0 nm.

UV-Vis studies on the interaction of **CP** with **2b**

The following procedure was used for the study of the interaction of **CP** with **2b**. A 2.94×10^{-2} mol L^{-1} stock solution of **2a** was prepared in anhydrous ethanol. From this stock solution, 34 μL were transferred to a 25 mL volumetric flask. After the evaporation of the ethanol, the probe was dissolved in acetonitrile, resulting in a solution with a final concentration of 4.0×10^{-5} mol L^{-1}. In order to fully deprotonate the compound, 20 μL of a 0.2 mol L^{-1} *tetra-n*-butylammonium hydroxide (Sigma-Aldrich) methanolic solution were added. This very small amount of added methanol did not interfere with the UV-Vis band of **2b**. This solution was used in the preparation of a stock solution of 2.0×10^{-3} mol L^{-1} **CP**. Small aliquots of this last solution were added to a quartz cuvette thermostated at 25 °C, closed with a rubber septum and containing 1 mL of the solution of **2b**. UV-Vis spectra were obtained after each addition of the **CP** solution and the absorbance values were registered at 456.0 nm. A similar experiment was performed in order to study the interaction of **1b** with **CP**. In this case, the stock solutions contained 4.0×10^{-5} and 4.0×10^{-4} mol L^{-1} of **1b** and **CP**, respectively. All experiments were carried out in duplicate and the reproducibility of the data was confirmed.

UV-Vis studies on the interaction of **CP-2b** with the anions

A solution of **2b** (4.0×10^{-5} mol L^{-1}) in acetonitrile was prepared as described above. This solution was used in the preparation of the **CP**-**2b** complex, with a **CP** concentration of 1.2×10^{-4} mol L^{-1}. This **CP**-**2b** solution was used to prepare solutions of each anion with a concentration of 6.0×10^{-4} mol L^{-1} and UV-Vis spectra were obtained.

For the titrations, stock solutions containing F^- (1.5×10^{-3} mol L^{-1}) and HSO_4^- (2.0×10^{-3} mol L^{-1}) were prepared from the initial **CP**-**2b** solution. Small amounts of the stock solution of each anion were added to a quartz cuvette thermostated at 25 °C, closed with a rubber septum and containing 1 mL of the **CP**-**2b** solution. UV-Vis spectra were collected after each addition of the anion and the absorbance values were registered at 547.0 nm for F^- and at 372.0 nm for HSO_4^-. All experiments were carried out in duplicate and the reproducibility of the data was confirmed.

Titration of **2b** with HSO_4^-

A solution of **2b** was prepared in acetonitrile in a concentration of 4.0×10^{-5} mol L^{-1}, after which the compound was deprotonated (see above). This solution was used to make a 2.0×10^{-3} mol L^{-1} stock solution containing the anion. Subsequently, small aliquots of the anion stock solution were added to a quartz cuvette thermostated at 25 °C, closed with a rubber septum and containing 1 mL of the **2b** solution. UV-Vis spectra were obtained after each addition of the anion and the absorbance values were registered at 372.0 nm.

Calculations

The binding constants were calculated using the Origin 6.1 program.

Results and Discussion

An anionic chromogenic chemosensor based on an acid-base strategy

Figure 1 shows the behavior of solutions of **2a** in acetonitrile in the presence of various anions. Solutions of this compound are colorless and become violet upon deprotonation using *tetra-n*-butylammonium hydroxide. When several anions (HSO_4^-, $H_2PO_4^-$, NO_3^-, CN^-, CH_3COO^-, F^-, Cl^-, Br^- and I^-) are individually added to solutions of **2a**, only F^- and CN^- are responsible for the appearance of a violet color in the solutions, typical of solutions of **2b**. In addition, CH_3COO^- and to a lesser extent $H_2PO_4^-$ cause changes in the color of **2a** solutions (to yellow), suggesting that these less basic anions interact with the protonated compound through HB. Figure 1 also shows that the addition of small water volumes to the solutions of **2a** changes the capability of the anions to color the solutions: with the addition of 1.4% of water only CN^- causes the deprotonation of **2a**. It has been recently demonstrated that the selectivity of chromogenic chemosensors in solution toward CN^- in the presence of other anions can be obtained with the addition of small amounts of water to organic solvents.[12–14,29,30] This is explained by the fact that the hydration energies of F^- (–465 kJ mol^{-1}), CH_3COO^- (–365 kJ mol^{-1}) and $H_2PO_4^-$ (–465 kJ mol^{-1}) are high in comparison with that obtained for CN^- (–295 kJ mol^{-1}).[31] The strong hydration of the anions makes them less able to act as a base. Since CN^- is less hydrated with the addition of water, this more basic species (in comparison with the others) is consequently more efficient in the abstraction of the proton of **2a**.

Figure 2 shows the UV-Vis spectra of **2a** in acetonitrile in the absence and in the presence of added anions. This compound in acetonitrile has a band with a maximum at 372.0 nm (ε_{max} = 1.63 × 10^4 L mol^{-1} cm^{-1}) and this band, under deprotonation, disappears simultaneously with the appearance of another band with a maximum at 547.0 nm (ε_{max} = 2.08 × 10^4 L mol^{-1} cm^{-1}). In the same manner, as can be observed, in the presence of the anions used in this study, in a concentration almost 12 times greater than that of **2a**, only F^-, CN^-, CH_3COO^- and $H_2PO_4^-$ led to the appearance of bands in the visible region. F^- and CN^- are responsible for the appearance of the band at 547.0 nm, corresponding to the formation of **2b**. In addition, the spectrum of **2a** with F^- almost coincides with that of **2b** (formed by the addition of hydroxide to the solution of **2a** in acetonitrile). CH_3COO^- and $H_2PO_4^-$ interact with the compound to form complexes through HB, which explains the appearance of a band at close to 400 nm. Thus, analysis of the spectral effect of each anion gives the following decreasing order: $F^- > CN^- > CH_3COO^- > H_2PO_4^-$. All other anions used were unable to deprotonate the compound in solution or to cause the appearance of an intermediate band typical of hydrogen-bonded species.

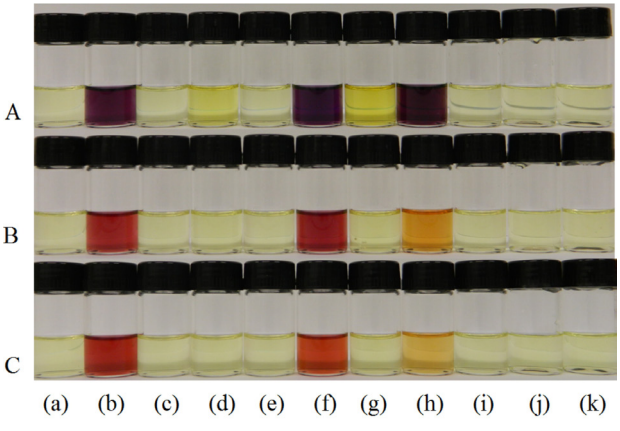


Figure 1. Solutions of (a) **2a**, (b) **2b** and **2a** in the presence of (c) HSO_4^-, (d) $H_2PO_4^-$, (e) NO_3^-, (f) CN^-, (g) CH_3COO^-, (h) F^-, (i) Cl^-, (j) Br^- and (k) I^- as *tetra-n*-butylammonium salts in acetonitrile (A) and acetonitrile with 1.0 (B) and 1.4% (C) of water. The concentration of each anion was 6.0 × 10^{-4} mol L^{-1} and of **2a** was 5.0 × 10^{-5} mol L^{-1}.

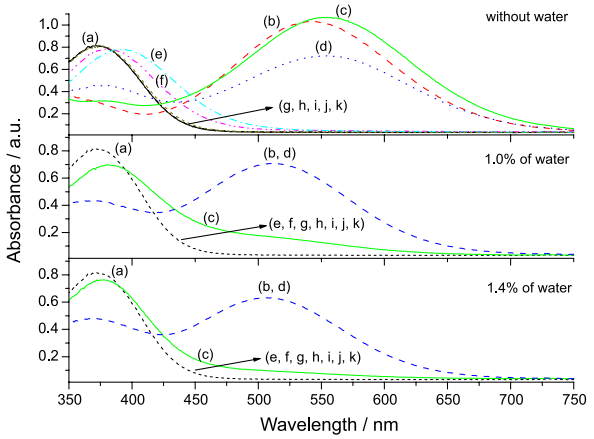


Figure 2. UV-Vis spectra for solutions of (a) **2a**, (b) **2b** and **2a** in the presence of (c) F^-, (d) CN^-, (e) CH_3COO^- and (f) $H_2PO_4^-$ in acetonitrile and acetonitrile with 1.0 and 1.4% (v/v) of water. For concentrations of **2a** and the anions, see Figure 1.

The pKa value for **2a** in water was determined as 10.57 ± 0.01. However, it would be of interest to estimate the acidity of this compound in acetonitrile. A list of pKa values for various phenols in acetonitrile was obtained from the literature.[32,33] The data were plotted as a function of the pKa for these phenols in water (see Supplementary Information (SI) section) and a linear correlation was observed (r^2 > 0.99). The equation obtained (pKa (CH_3CN) = 1.68 pKa (water) + 9.80) was used to estimate (employing the pKa experimentally determined in water) the pKa value for **2a** in acetonitrile, which is equal to 27.6. The use of the pKa for Reichardt's

pyridiniophenolate in water (8.6) in the same equation gives a value of 24.2, which is comparable to the value experimentally obtained by Coleman and Murray[33] in acetonitrile (22.1). The pKa values for HBr, H_2SO_4 and HCl in acetonitrile are 6.6, 8.7 and 10.6, respectively,[34] being of very small magnitude in comparison to the pKa of **2a**, showing that the anions Br^-, HSO_4^- and Cl^- are not sufficiently basic to interact with **2a**. Due to the practical difficulties associated with the titration of acids in acetonitrile,[35,36] the pKa values for compounds such as HCN and HF are not available in the literature. These values can be only estimated from a plot of the pKa values for various acids in acetonitrile as a function of the corresponding pKa values in dimethylsulfoxide (DMSO)[37] (see SI section). This approach led to values of 25.2 for HF and 23.1 for HCN. The pKa value experimentally determined for acetic acid in acetonitrile of 22.3[38] (the value calculated using the approach shown in the SI section is 22.5) is below the pKa values for HF and HCN. Although these calculations can be seen as a simplification, they match the observed order for the effect of the anions on the UV-Vis spectrum of **2a**. In addition, the experimental data are in good agreement with those obtained in a recent study carried out in DMSO, in which 2,4-dinitrodiphenylamine was used as the chemosensor, and the spectral effect of each anion followed the decreasing order: $F^- > CN^- > CH_3COO^- > H_2PO_4^-$.[30] This is the same order observed in this study and it was also observed that the pKa values for the conjugated acids of the anions that interact with the compound exactly match the capability of the anions to abstract the proton of the NH group in that chemosensor.[30]

Figure 2 also shows the influence of the addition of small volumes of water on the UV-Vis spectrum of **2a** in the presence of the anions. It can be observed that with the addition of 1.4% (v/v) of water to the system, only CN^- could fully deprotonate the compound, while practically no effect was observed with the other anions. In addition, the highest absorbance values for **2a** in acetonitrile were obtained in the presence of F^-, but a different behavior for this compound emerged with the addition of very small amounts of water, with a very high selectivity for CN^- being obtained, in comparison with the other anions. Another interesting feature observed in these experiments is that with the addition of 1.0 and 1.4% (v/v) of water to the solutions of **2b** in acetonitrile hypsochromic shifts of 41 and 46 nm, respectively, were observed in the position of the UV-Vis band. Therefore, **2b** exhibits a significant negative solvatochromism, and in mixtures of acetonitrile with very small volumes of water, the dye is preferentially solvated by water, through HB involving water molecules and the phenolate moiety of **2b**. These results are consistent with data reported in the literature for dyes with a phenolate group in their structure.[14,39]

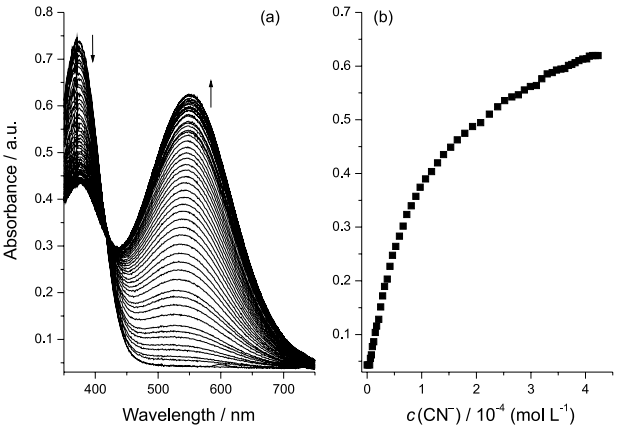


Figure 3. (a) Influence of the addition of increasing amounts of CN^- on the UV-Vis spectra of **2a** (5.0×10^{-5} mol L^{-1}) in acetonitrile at 25 °C. The final concentration of CN^- was 4.18×10^{-4} mol L^{-1}; (b) curve of the variation in the absorbance at 547.0 nm of **2a** with the addition of increasing amounts of CN^-.

Compound **2a** was titrated in acetonitrile with CN^- and the experiment was monitored through the analysis of the UV-Vis spectra (Figure 3a). With the addition of the anion, the band related to compound **2a** at 372.0 nm has a reduced intensity. Simultaneously, the band with λ_{max} at 547.0 nm (related to **2b**) has increased intensity, while an isosbestic point occurs at 413.0 nm. A plot of the absorbance values at 547.0 nm as a function of $c(CN^-)$ (Figure 3b) shows a behavior typical of a 1:1 **2a**:CN^- stoichiometry. The experimental data were fitted with the use of equation 1,[12-14,40,41] where *Abs* is the absorbance value after each addition of the anion, Abs_0 is the initial absorbance without anion added, Abs_{11} is the maximum absorbance value obtained by addition of the anion considering 1:1 **2a**:anion stoichiometry, $c(A^-)$ is the anion concentration in each addition, and K_{11} is the binding constant.

$$Abs = [Abs_o + Abs_{11}\, K_{11}\, c(A^-)]/[1 + K_{11}\, c(A^-)] \quad (1)$$

With the use of equation 1, a value of $K_{11} = (8.54 \pm 0.21) \times 10^3$ L mol^{-1} (standard deviation, SD = 5.0×10^{-5}) was obtained. The Job's plot[40,42] for the system involving CN^- and **2a** in acetonitrile at 547.0 nm is shown in Figure 4, which confirms the 1:1 stoichiometry. The addition of water to the system leads to a reduction in the magnitude of the binding constant. The UV-Vis spectra for the titration of **2a** with CN^-, in acetonitrile with 1.4% (v/v) of water added, show that on the addition of the anion the band with λ_{max} at 372.0 nm disappears while the band related to the deprotonated dye (with λ_{max} at 504.0 nm)

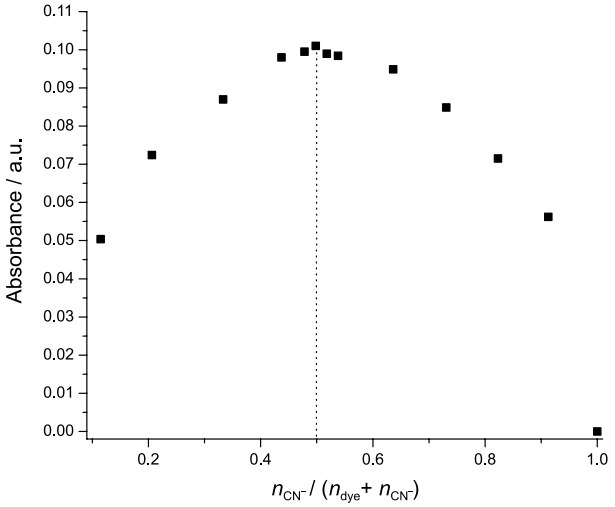


Figure 4. Job plot of **2a** with CN^- in acetonitrile (for details see Experimental section).

appears, an isosbestic point also occurring at 416.0 nm. The titration curve for this system reveals that the stoichiometry is also 1:1, with a value of $K_{11} = (2.93 \pm 0.03) \times 10^3$ L mol^{-1} (SD = 8.0×10^{-6}).

Figure 5a shows UV-Vis spectra for the titration of **2a** in acetonitrile using F^- as anion. The data show that with the addition of the anion, as observed in the case of the titration with CN^- in acetonitrile, the band with λ_{max} = 372.0 nm decreases in intensity while for the band with λ_{max} = 547.0 nm the intensity increases. However, no apparent isosbestic point is now observed: the spectra suggest that with the addition of the anion, firstly an increase in the absorbance values in the region between 400 and 450 nm occurs. This is better observed in Figure 5b, which details the first part of the titration, showing that the band with λ_{max} at 372.0 nm decreases with an increase in the absorbance in the range of 420.0-450.0 nm, an isosbestic point being observed at 403.0 nm. In the second part of the titration (Figure 5c), absorbance values at 420.0 nm decrease while the band related to the appearance of **2b** increases in intensity, with the occurrence of an isosbestic point at 465.0 nm. This behavior is typical of a situation in which the protonated chemosensor interacts firstly by means of HB with the anion. In the presence of an excess of the anion, the compound is deprotonated with the formation of a $[HA_2]^-$ complex.[12,13] This is corroborated by the fact that the experimental data used to obtain the titration curve could not be fitted using equation 1, but only with equation 2, which considers both 1:1 and 1:2 **2a**:anion stoichiometries.

$$Abs = \frac{Abs_o + Abs_{11}\, K_{11}\, c(A^-) + Abs_{12}\, K_{11}\, K_{12}\, (c(A^-))^2}{1 + K_{11}\, c(A^-) + Abs_{12}\, K_{11}\, K_{12}\, (c(A^-))^2} \quad (2)$$

In this equation, Abs_{12} is the maximum absorbance value obtained by addition of the anion considering 1:2 stoichiometry and K_{12} is the respective binding constant. The fitting of the experimental data using equation 2 gave $K_{11} = (4.86 \pm 1.24) \times 10^4$ L mol^{-1} and $K_{12} = (6.45 \pm 0.19) \times 10^3$ L mol^{-1} (SD = 1.4×10^{-5}).

The results obtained show three possible interactions for compound **2a** in acetonitrile, as presented in Scheme 2, depending on the basicity of the anion. If the anion is a strong base, the proton in the phenolic moiety of the compound is abstracted, and a violet solution is obtained. Another possibility discussed in some publications in the literature[43] involves firstly the formation of a complex between the anion and the protonated dye through HB, which weakens the H–O bond in the compound. The abstraction of the proton occurs with the addition of a second anion equivalent, leading to the formation of a $[HA_2]^-$ complex. The formation and stability of these species, for example $[HF_2]^-$, have been studied through

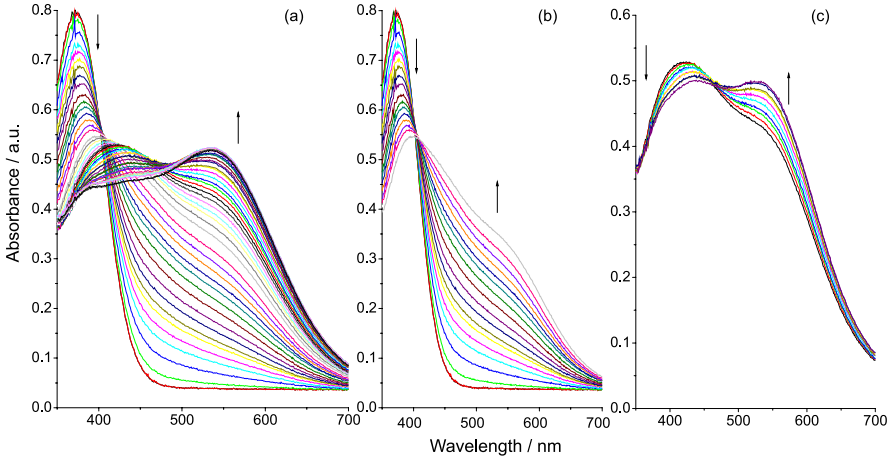
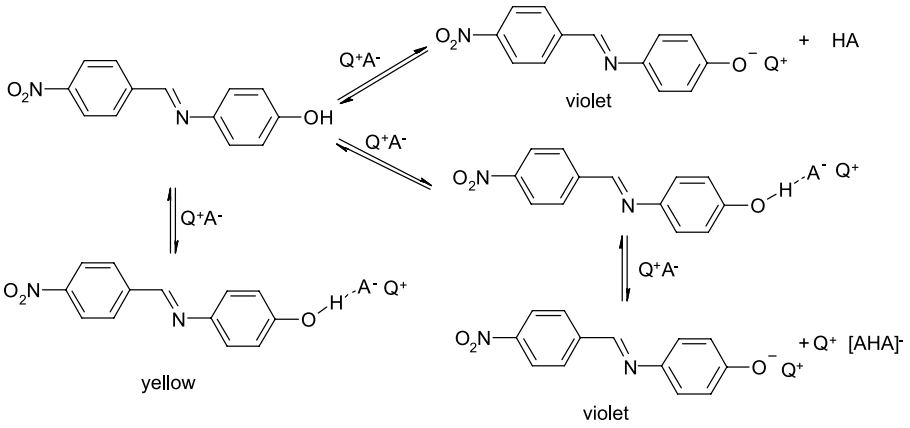


Figure 5. (a) Influence of the addition of increasing amounts of F^- on the UV-Vis spectra of **2a** (5.0×10^{-5} mol L^{-1}) in acetonitrile at 25 °C. The final concentration of F^- was 9.02×10^{-4} mol L^{-1}; (b) the first step of this titration from zero to 1.85×10^{-4} mol L^{-1} and (c) the last step from 3.58×10^{-4} mol L^{-1} to 6.11×10^{-4} mol L^{-1}.



Scheme 2. Possible interactions of **2a** with the anions.

theoretical calculations.[44] The addition of water to the medium leads to a reduction in the magnitude of the binding constant due to the fact that it interacts with the anion, lowering its ability to act as a base. With less basic anions, such CH_3COO^- and $H_2PO_4^-$, hydrogen-bonded complexes of **2a** and the anion are formed, as indicated by the yellow coloration obtained in solution.

The titration of **2a** with the anions revealed a 1:1 **2a**:anion stoichiometry for CN^- and both 1:1 and 1:2 stoichiometries for F^-. A previous study carried out with compound **1a** in acetonitrile led to both 1:1 and 1:2 stoichiometries for CN^- and 1:2 **1a**:anion stoichiometry for F^-.[14] Recently, Reichardt's pyridiniophenolate and Brooker's merocyanine, compounds with the pyridinium cation as an acceptor center in their molecular structure, were studied in their protonated form as anionic chemosensors in acetonitrile and in trichloromethane.[12,13] Titrations with basic anions led to a 1:3 chemosensor:anion stoichiometry, which was attributed to the formation of a complex between the pyridinium group and the anion, of an electrostatic nature, prior to the interaction of the anion with the phenol moiety in the compound.[12,13] Since the pyridinium group is absent from the molecular structure of **1a** and **2a**, these results represent important evidence to support the model suggested for the interaction of anionic species with protonated merocyanines.

An anionic chromogenic chemosensor based on a displacement assay

Compound **2a** deprotonated in acetonitrile gives a violet color to the solution. If the receptor **CP** is added to the solution of the dye formed (**2b**), the color of the solution immediately changes to pale-yellow. This is due to the formation of a complex between **CP** and **2b** through HB involving the oxygen in the phenolate group of the dye and the NH groups of **CP**.[25,26] Figure 6a shows a set of UV-Vis spectra for the titration of **2b** in acetonitrile with small amounts of **CP**. While the intensity of the band with λ_{max} at 547.0 nm for the dye is reduced with the addition of **CP**, other band related to the complex formed between **CP** and **2b** appears simultaneously with

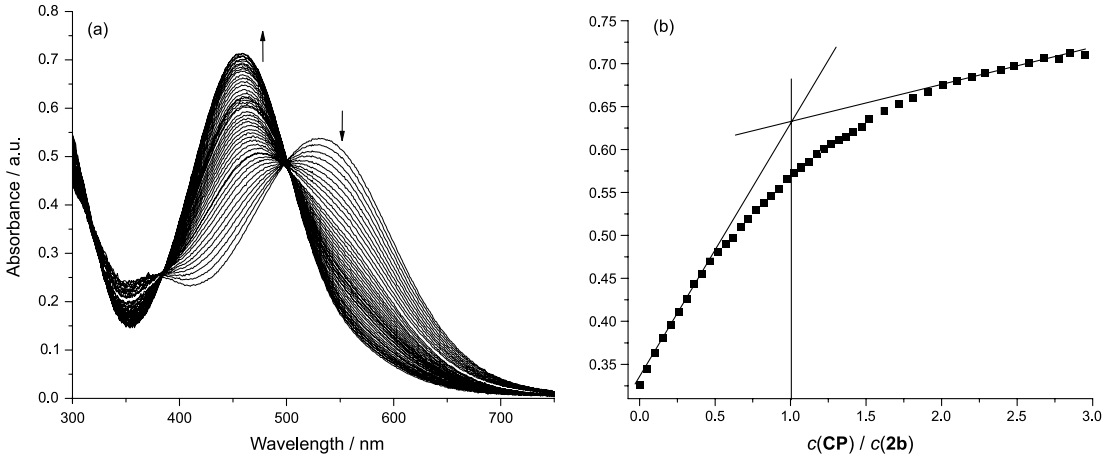


Figure 6. (a) UV-Vis spectra of **2b** (4.0×10^{-5} mol L^{-1}) in acetonitrile at 25 ºC after addition of increasing amounts of **CP**. The final concentration of **CP** was 1.2×10^{-4} mol L^{-1}; (b) mole-ratio plot for the interaction of **CP** with **2b**.

λ_{max} at 456.0 nm. An isosbestic point occurs at 500.0 nm, suggesting equilibrium between the species in solution. The absorbance values were obtained at 456.0 nm for each *c*(**CP**), giving the mol-ratio plot shown in Figure 6b, which clearly shows a 1:1 **CP**-**2b** stoichiometry. The addition of very small amounts of water to **CP**-**2b** in acetonitrile disrupts the complex due to the ability of water to strongly interact with **CP** and **2b** through hydrogen bonding. In addition, if **1b** is titrated with **CP** in acetonitrile, no changes occur in the UV-Vis spectrum of the dye presumably because the phenyl groups on the 2,6-positions are responsible for a steric blocking that hinders the HB between the NH groups on **CP** and the oxygen in the phenolate group.

Figure 7a shows the treatment of the data using the Benesi-Hildebrand equation (equation 3), which was used in order to estimate the initial values of $\Delta\varepsilon_{11}$ and K_{11} to be subsequently used in the non-linear fit.[40,45,46] In this equation, *b* is the path length, *c*(**2b**) is the dye concentration, $\Delta\varepsilon_{11}$ is difference in the molar absorptivity values for the complex and free dye and K_{11} is the binding constant for a 1:1 complex formation. ΔA is the change in absorbance at 547.0 nm for the solution containing the dye when the **CP** concentration changes from zero to *c*(**CP**). The fit of the experimental data gives $K_{11} = 1.85 \times 10^4$ L mol^{-1} ($r^2 = 0.999$, SD = 4.4×10^{-3}). Figure 7b shows the titration curve for **2b** with **CP**, which was used to give the binding constant for **CP**-**2b**, applying equation 4,[40,45] providing $K_{11} = (1.85 \pm 0.06) \times 10^4$ L mol^{-1} (SD = 2.0×10^{-5}):

$$b/\Delta A = 1/c(\mathbf{2b})\ K_{11}\ \Delta\varepsilon_{11}\ c(\mathbf{CP}) + 1/c(\mathbf{2b})\ \Delta\varepsilon_{11} \quad (3)$$

$$\Delta A/b = (\mathbf{2b})\ K_{11}\ \Delta\varepsilon_{11}\ c(\mathbf{CP})/[1 + K_{11}\ c(\mathbf{CP})] \quad (4)$$

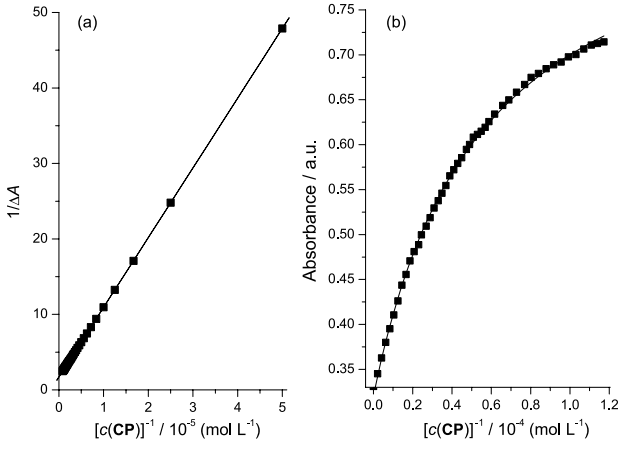


Figure 7. (a) Benesi-Hildebrand treatment for the titration of **2b** and **CP** in acetonitrile at 25 ºC, fitted using equation 3; (b) titration curve of **2b** and **CP** in acetonitrile at 25 ºC. Absorbance values were collected at 456.0 nm and the data were fitted using equation 2.

Figure 8A shows the effect of the individual addition of different anions (F^-, Cl^-, Br^-, I^-, CN^-, $H_2PO_4^-$, HSO_4^- and NO_3^-) as *tetra*-*n*-butylammonium salts to the **CP**-**2b** solution. Interestingly, only F^- causes the reappearance of the violet color and in addition HSO_4^- makes the **CP**-**2b** solution colorless, allowing the visual detection of these anions, distinguishing them from between the other species studied. Figure 8B shows the UV-Vis spectra for the **CP**-**2b** solutions in the presence of each anion. The spectra show two types of spectral effects: one caused by F^- (followed in a much lesser extent by Cl^-), involving a reduction in the absorbance at 456.0 nm (related to **CP**-**2b**) with the simultaneous reappearance of the band of **2b** at 547.0 nm. The data show that F^- strongly binds to **CP** and

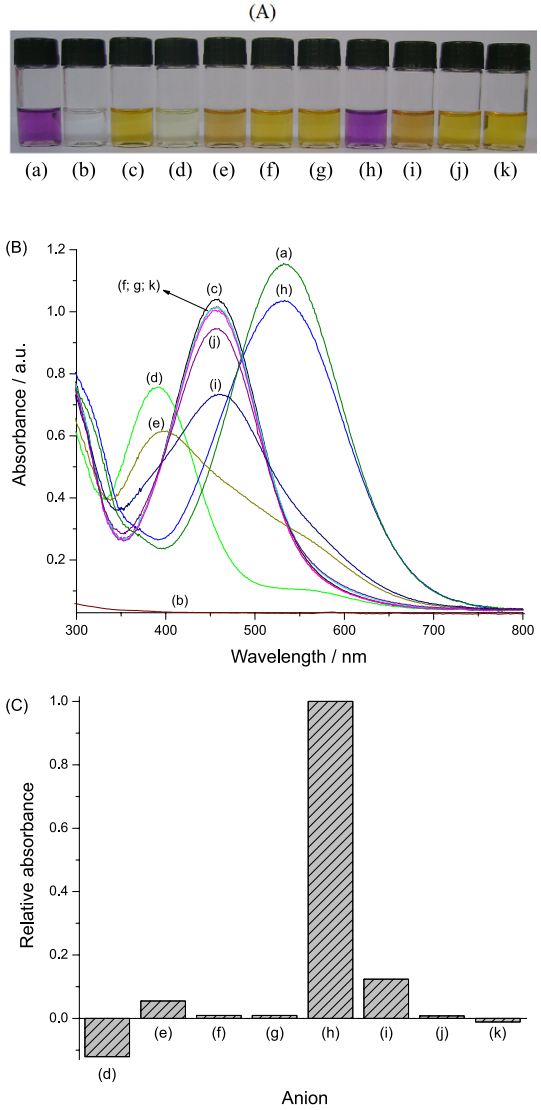


Figure 8. (A) Solutions in acetonitrile, (B) UV-Vis spectra and (C) relative absorbances of (a) **2b**, (b) **CP**, (c) **CP**-**2b**, and **CP**-**2b** in the presence of (d) HSO_4^-, (e) $H_2PO_4^-$, (f) NO_3^-, (g) CN^-, (h) F^-, (i) Cl^-, (j) Br^- and (k) I^- (*c*(anion) = 6.0×10^{-4} mol L^{-1}). The concentrations of **CP** and **2b** were 1.2×10^{-4} and 4.0×10^{-5} mol L^{-1}, respectively.

displaces **2b** from the receptor site, making the dye free to signal the presence of the analyte. HSO_4^- and to a minor extent $H_2PO_4^-$ are responsible for another spectral effect that is a reduction in the intensity of the band related to **CP**-**2b** simultaneously with the appearance of a band with λ_{max} at 372.0 nm. The latter coincides with the band observed for the solutions of **2a** in acetonitrile, meaning that HSO_4^- is sufficiently acidic to protonate **2b**, which is responsible for breaking the **CP**-**2b** complex.

Figure 9a shows UV-Vis spectra corresponding to the titration of **CP**-**2b** in acetonitrile with increasing amounts of F^-. On addition of F^-, a reduction in the intensity of the **CP**-**2b** band at 456.0 nm occurs with the simultaneous appearance of the band for **2b** at λ_{max} = 547.0 nm, which indicates that **2b** is displaced from the binding site of **CP** by F^-. The titration curve in Figure 9b was obtained using the absorbance values at 547.0 nm as a function of $c(F^-)$. The sigmoidal profile of the curve is typical of that occurring in competition assays, revealing the competition of the anion for free **CP** and **CP**-**2b** in the solution. The treatment of the experimental data[40,47] allowed the binding constant for **CP** and F^- to be estimated 1.09×10^5 L mol^{-1}, which is a value comparable with that previously obtained by Schmidtchen[48] using calorimetric measurements.

The effect of the addition of HSO_4^- on the UV-Vis spectrum for **CP**-**2b** in acetonitrile at 25 ºC can be seen in Figure 10a, which shows a decrease in the band related to **CP**-**2b** at 456.0 nm with the simultaneous occurrence of the band related to the formation of the protonated dye (**2a**), with λ_{max} at 372.0 nm. Figure 10b represents the corresponding titration curve obtained from the absorbance values at 372.0 nm for each addition of the anion. The data could not be fitted using equations 2 and 3 and, in addition, no isosbestic point occurs in the set of UV-Vis spectra. Data suggest that HSO_4^- is sufficiently acid to protonate the dye. This finding was verified by carrying out the titration of the dye (**2b**) with the anion. Figure 11a shows the UV-Vis spectra for the titration of **2b** by HSO_4^- in acetonitrile at 25 ºC, and a decrease in the band related to **2b** with the simultaneous appearance of the band related to the formation of **2a** was observed. Figure 11b shows the corresponding titration curve, which was fitted using equation 3, giving $K_{11} = (5.32 \pm 0.09) \times 10^3$ L mol^{-1}

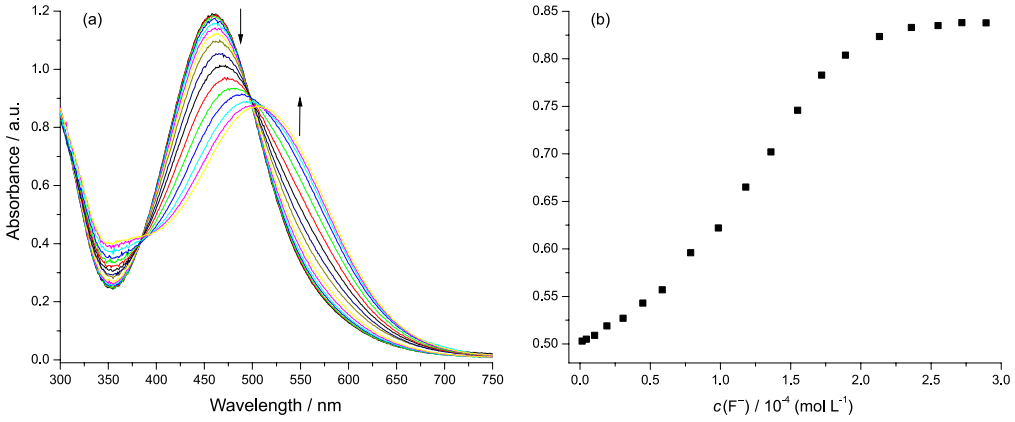


Figure 9. (a) UV-Vis spectra of **CP**-**2b** in acetonitrile at 25 ºC after addition of increasing amounts of F^-; (b) titration curve of **CP**-**2b** with F^- in acetonitrile. Absorbance values were collected at 547.0 nm, c(**CP**) = 1.2×10^{-4} mol L^{-1} and c(**2b**) = 4.0×10^{-5} mol L^{-1}.

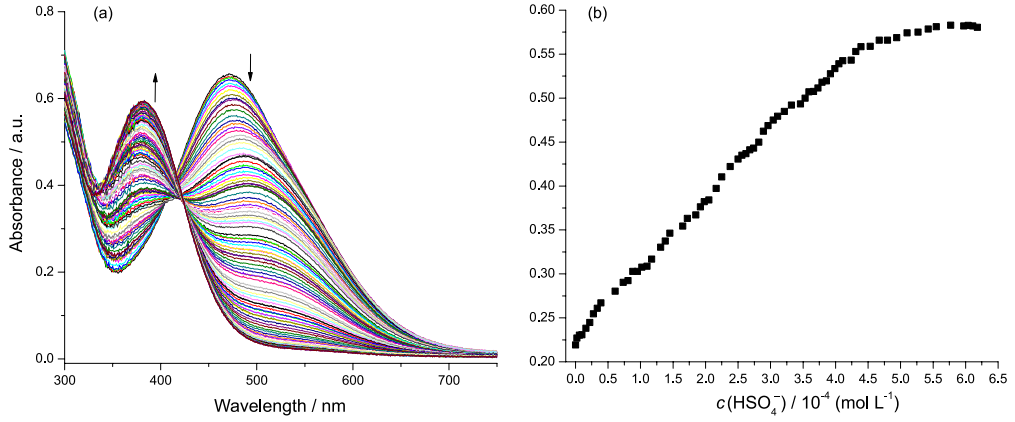


Figure 10. (a) UV-Vis spectra of **CP**-**2b** in acetonitrile at 25 ºC after addition of increasing amounts of HSO_4^-; (b) titration curve of **CP**-**2b** with HSO_4^- in acetonitrile. Absorbance values were collected at 372.0 nm, c(**CP**) = 1.2×10^{-4} mol L^{-1} and c(**2b**) = 4.0×10^{-5} mol L^{-1}.

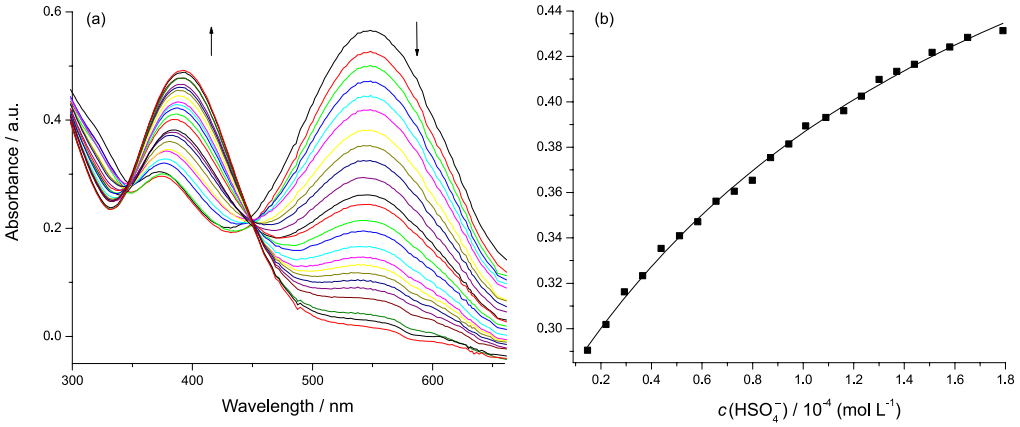
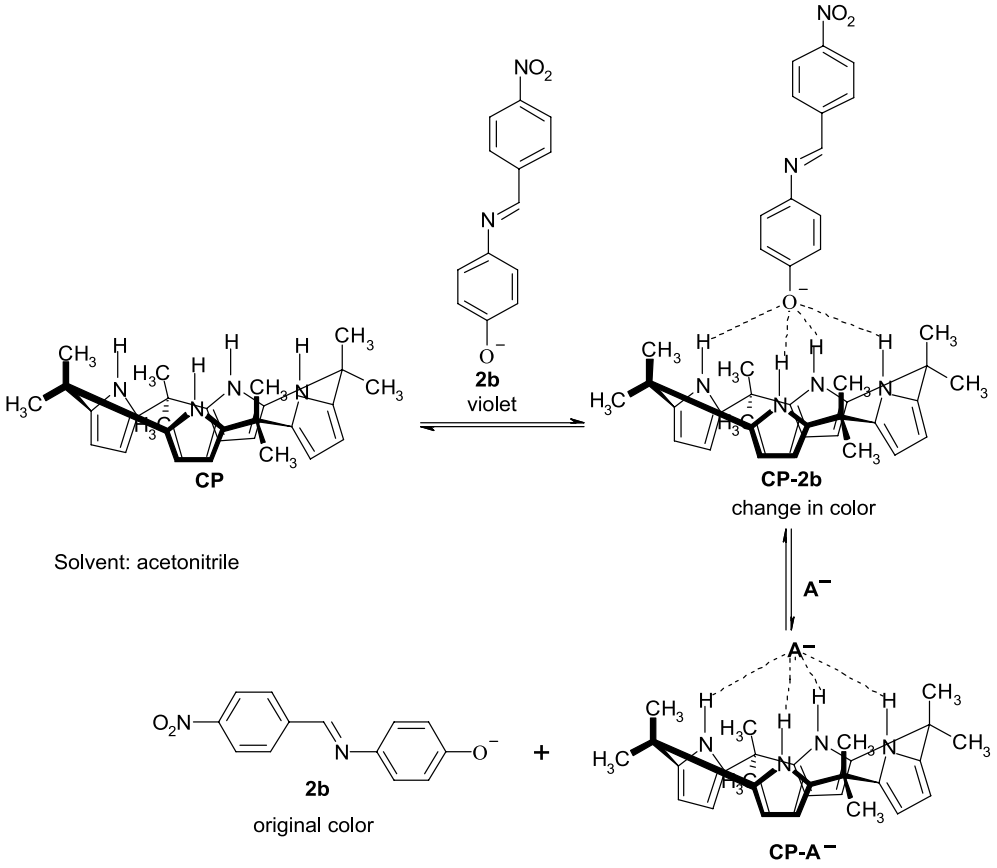


Figure 11. (a) UV-Vis spectra of **2b** (4.0×10^{-5} mol L^{-1}) in acetonitrile at 25 ºC after addition of increasing amounts of HSO_4^-; (b) titration curve of **2b** with HSO_4^- in acetonitrile, with the absorbance values collected at 372.0 nm.



Scheme 3. A chromogenic chemosensor based on a displacement assay.

(SD = 3.95×10^{-6}). The absence of an isosbestic point in Figure 10a and the fact that the corresponding titration curve could not be mathematically fitted indicate that the anion acts not only by protonating **2b** but is also able to interact with **CP** and **CP**-**2b**.

The displacement assay studied is summarized in the Scheme 3. The first step involves the formation of a 1:1 HB complex, formed by **CP** and **2b**. The addition of F^- to this complex causes the displacement of **2b** due to the formation of a strong hydrogen-bonded complex comprising **CP** and the anion. The change in the color of the solution, from orange to violet, which accompanies the addition of F^-, should be used for the visual detection of the anion.

Conclusions

It was demonstrated herein that compound **2a** can be used in solution for the highly selective detection of F^- or

CN^-, depending on the strategy used for anion sensing. In its protonated form, this compound behaves as an efficient anionic chromogenic chemosensor exploiting the differences in the basicity of the anions. A high selectivity of CN^- in relation to the other anions studied was obtained on addition of very small amounts of water to solutions of **2a** in acetonitrile. The preferential solvation through HB of $H_2PO_4^-$, CH_3COO^- and F^- occurs by water or hydrogen-bonded acetonitrile-water complexes, leaving the CN^- free to interact with the chemosensor.

It was also shown that if the compound is used in its deprotonated form it can be recognized by **CP**, which results in a change in the color of the system. Since F^- has a very high binding constant for **CP** in comparison with that of the dye, the anion is able to displace **2b** from the complexation site, which leaves the dye free to restore the original color of the solution. Another interesting feature is that with the addition of HSO_4^-, the solution becomes colorless because it protonates the dye. This allows, in principle, the use of **2b** in organic solvents for the selective detection of HSO_4^- in the presence of other anionic species.

Supplementary Information

The UV-Vis spectra, titration curves, association constant determined by displacement titration, results of studies on the stability of **2a** in acetonitrile, pKa determination for **2a** and pKa estimates in acetonitrile are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

The financial support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and UFSC are gratefully acknowledged.

References

1. For recent reviews, see for instance: Martínez-Mañez, R.; Sancenón, F.; *Chem. Rev.* **2003**, *103*, 4419; Suksai, C.; Tuntulani, T.; *Chem. Soc. Rev.* **2003**, *32*, 192; Suksai, C.; Tuntulani, T.; *Top. Curr. Chem.* **2005**, *255*, 163; Kubik, S.; Reyheller, C.; Stüwe, S.; *J. Inclusion Phenom. Macrocyclic Chem.* **2005**, *52*, 137; Callan, J. F.; de Silva, A. P.; Magri, D. C.; *Tetrahedron* **2005**, *61*, 8551; Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M.; *Coord. Chem. Rev*. **2006**, 250, 3094; Anslyn, E. V.; *J. Org. Chem*. **2007,** *72*, 687; Zimmermann-Dimer, L. M.; Machado, V. G.; *Quim. Nova* **2008**, *31*, 2134; Cho, D. G.; Sessler, J. L.; *Chem. Soc. Rev*. **2009**, *38*,1647; Gale, P.A.; *Chem. Soc. Rev*. **2010**, *39*, 3746; Moragues, M. E.; Martínez-Mañez, R.; Sancenón, F.; *Chem. Soc. Rev.* **2011**, *40*, 2593; Wenzel, M.; Hiscock, J. R.; Gale, P. A.; *Chem. Soc. Rev*. **2012**, *41*, 480.
2. For reviews, see for instance: Cametti, M.; Rissanen, K.; *Chem. Commun*. **2009**, 2809; Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbai, F. P.; *Chem. Rev*. **2010**, *110*, 3958.
3. Faibish, D.; Ott, S. M.; Boskey, A. L.; *Clin. Orthop. Relat. Res.* **2006**, 28; Ayoob, S.; Gupta, A. K.; *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 433; Miretzky, P.; Cirelli, A. F.; *J. Fluorine Chem.* **2011**, *132*, 231.
4. Lv, J.; Zhang, Z. J.; Li, J. D.; Luo, L. R.; *Forensic Sci. Int.* **2005**, *148*, 15 ; Nelson, L. ; *J. Emerg. Nurs.* **2006**, *32*, S8 ; Zelder, F. H.; Männel-Croisé, C.; *Chimia* **2009**, *63*, 58.
5. Agatemor, C.; *EJEAFChe.* **2009**, *8*, 189.
6. Dale, T. J.; Rebek, J.; *J. Am. Chem. Soc*. **2006**, *128*, 4500; Royo, S.; Martínez-Máñez, R.; Sancenón, F.; Costero, A. M.; Parra, M.; Gil, S.; *Chem. Commun.* **2007**, 4839; Burnworth, M.; Rowan, S. J.; Weder, C.; *Chem. Eur. J.* **2007**, *13*, 7828.
7. Yang, Y.-C.; Bakerand, J. A.; Ward, J. R.; *Chem. Rev.* **1992**, *92*, 1729.
8. See for instance: He, S.; Iacono, S. T.; Budy, S. M.; Dennis, A. E.; Smith Jr., D. W.; Smith, R. C.; *J. Mater. Chem.* **2008**, *18*, 1970; Dale, T. J.; Rebek, J.; *Angew. Chem., Int. Ed.* **2009**, *48*, 7850; Gotor, R.; Costero, A. M.; Gil, S.; Parra, M.; Martínez-Mañez, R.; Sancenón, F.; *Chem. Eur. J.* **2011**, *17*, 11994; Royo, S.; Costero, A. M.; Parra, M.; Gil, S.; Martínez–Mañez, R.; Sancenón, F.; *Chem. Eur. J.* **2011**, *17*, 6931.
9. Steiner, T.; *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem*., *Int. Ed*. **2002**, *41*, 48.
10. Lee, D. H.; Lee, K. H.; Hong, J.-I.; *Org. Lett.* **2001**, *3*, 5; Tong, H.; Zhou, G.; Wang, L.; Jing, X.; Wang, F.; Zhang, J.; *Tetrahedron Lett.* **2003**, *44*, 131; Zhang, X.; Guo, L.; Wu, F.-Y.; Jiang, Y.-B.; *Org. Lett.* **2003**, *5*, 2667; Zhang, X.; Shiraishi, Y.; Hirai, T. *Tetrahedron Lett*. **2007**, *48*, 8803.
11. Reis, D. C.; Machado, C.; Machado, V. G.; *Tetrahedron Lett*. **2006**, *47*, 9339.
12. Zimmermann-Dimer, L. M.; Machado, V. G.; *Dyes Pigm.* **2009**, *82*, 187.
13. Zimmermann-Dimer, L. M.; Reis, D. C.; Machado, C.; Machado, V. G.; *Tetrahedron* **2009**, *65*, 4239.
14. Marini, V. G.; Zimmermann, L. M.; Torri, E.; Machado, V. G.; *Arkivoc* **2010**, *xi*, 146.
15. For reviews, see: Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V.; *Acc. Chem. Res.* **2001**, *34*, 963; Nguyen, B. T.; Anslyn, E. V.; *Coord. Chem. Rev*. **2006**, *250*, 3118; Liu, K.; Su, X.; Huo, J.; *Mini-Rev. Org. Chem*. **2012**, *9*, 118.
16. For recent papers, see for instance: Comes, M.; Aznar, E.; Moraques, M.; Marcos, M. D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J.; Villaescusa, L. A.; Gil, L.; Amorós, P.; *Chem. Eur. J.* **2009**, *15*, 9024; Mullen, K. M.; Davis, J. J.; Beer, P. D.; *New J. Chem*. **2009**, *33*, 769; Carolan, J. V.; Butler, S. J.; Jolliffe, K. A.; *J. Org. Chem*. **2009**, *74*, 2992; Kim, S. Y.; Hong, J. I.;

Tetrahedron Lett. **2009**, *50*, 1951; Saeed, M. A.; Powell, D. R.; Hossain, M. A.; *Tetrahedron Lett*. **2010**, *51*, 4904; Gao, J.; Riis-Johannessen, T.; Scopelliti, R.; Qian, X. H.; Severin, K.; *Dalton Trans*. **2010**, *39*, 7114; Watchasit, S.; Kaowliew, A.; Suksai, C.; Tuntulani, T.; Ngeontae, W.; Pakawatchai, C.; *Tetrahedron Lett*. **2010**, *51*, 3398; He, X. A.; Zhang, Q.; Wang, W. T.; Lin, L. L.; Liu, X. H.; Feng, X. M.; *Org. Lett.* **2011**, 13, 804; Kim, S. H.; Hwang, I. J.; Gwon, S. Y.; Burkinshaw, S. M.; Son, Y. A.; *Dyes Pigm.* **2011**, *88*, 84; Tang, L. J.; Liu, M. H.; Li, F. F.; Nandhakumar, R.; *J. Fluoresc*. **2011**, *21*, 701.

17. Baeyer, A.; *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 2184.
18. Gale, P. A.; Sessler, J. L.; Král, V.; Lynch, V.; *J. Am. Chem. Soc.* **1996**, *118*, 5140.
19. Dennstedt, M.; Zimmermann, J.; *Chem. Ber.* **1887**, *20*, 850.
20. Dennstedt, M.; *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 1370.
21. Rothemund, P.; Gage, C. L.; *J. Am. Chem. Soc.* **1955**, *77*, 3340.
22. Brown, W. H.; Hutchinson, B. J.; MacKinnon, M. H.; *Can. J. Chem.* **1971**, *49*, 4017.
23. Sobral, A. J. F. N.; *J. Chem. Educ.* **2005**, *82*, 618; Shriver, J. A.; Westphal, S. G.; *J. Chem. Educ.* **2006**, *83*, 1330.
24. Sessler, J. L.; Gale, P. A.; Genge, J. W.; *Chem. Eur. J.* **1998**, *4*, 1095; Miyaji, H.; Anzenbacher Jr., P.; Sessler, J. L.; Bleasdale, E. R.; Gale, P. A.; *Chem. Commun.* **1999**, 1723; Miyaji, H.; Sato, W.; Sessler, J. L.; Lynch, V. M.; *Tetrahedron Lett.* **2000**, *41*, 1369; Gale, P. A.; Hursthouse, M. B.; Light, M. E.; Sessler, J. L.; Warriner, C. N.; Zimmerman, R. S.; *Tetrahedron Lett.* **2001**, *42*, 6759.
25. Gale, P. A.; Twyman, L. J.; Handlin, C. I.; Sessler, J. L.; *Chem. Commun.* **1999**, 1851.
26. Linn, M. M.; Poncio, D. C.; Machado, V. G.; *Tetrahedron Lett.* **2007**, *48*, 4547.
27. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R.; *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: London, 1989, p. 410.
28. Kaya, I.; Culhaoglu, S.; *Iran. Polym. J.* **2006**, *15*, 487.
29. Ros-Lis, J. V.; Martínez-Máñez, R.; Soto, J.; *Chem. Commun*. **2002**, 2248; Tomasulo, M.; Raymo, F. M.; *Org. Lett*. **2005**, *7*, 4633; Ros-Lis, J. V.; Martínez-Máñez, R.; Soto, J.; *Chem. Commun*. **2005**, 5260; Sun, Y.; Wang, G.; Guo, W.; *Tetrahedron* **2009**, *65*, 3480.
30. Marini, V. G.; Zimmermann, L. M.; Machado, V. G.; *Spectrochim. Acta, Part A* **2010**, *75*, 799.
31. Marcus, Y. *J. Chem. Soc., Faraday Trans*. **1991**, *87*, 2995; Dickins, R. S.; Parker, D. In Gloe, K., ed.; *Macrocyclic Chemistry: Current Trends and Future Perspectives*; Springer: Dordrecht, 2005, p. 121.
32. Jover, J.; Bosque, R.; Sales; J. *QSAR Comb. Sci.* **2007**, *26*, 385.
33. Coleman, C. A.; Murray, C. J; *J. Org. Chem.* **1992**, *57*, 3578.
34. Eckert, F.; Leito, I.; Kaljurand, I.; Kütt, A.; Klamt, A.; Diedenhofen, M.; *J. Comput. Chem.* **2009**, *30*, 799.
35. Coetzee, J. F.; *Prog. Phys. Org. Chem.* **1967**, *4*, 45.
36. Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I.A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I.; *J. Org. Chem*. **2011**, *76*, 391.
37. Bordwell, F. G.; *Acc. Chem. Res.* **1988**, *21*, 456.
38. Kolthoff, I. M.; Chantooni Jr., M. K.; Bhowmik, S.; *J. Am. Chem. Soc.* **1968**, *90*, 23; Kolthoff, I. M.; Chantooni Jr., M. K.; *J. Am. Chem. Soc*. **1975**, *97*, 1376.
39. Ortega, J.; Ràfols, C.; Bosch, E.; Rosés, M.; *J. Chem. Soc., Perkin Trans. 2* **1996**, 1497; Bosch, E.; Rosés, M.; Herodes, K.; Koppel, I.; Leito, I.; Koppel, I.; Taal, V.; *J. Phys. Org. Chem.* **1996**, *9*, 403; da Silva, D. C.; Ricken, I.; Silva, M. A. R.; Machado, V. G.; *J. Phys. Org. Chem*. **2002**, *15*, 420.
40. Connors, K. A.; *Binding Constants: the Measurement of Molecular Complex Stability*; Wiley Interscience: New York, 1987; Valeur, B.; Pouget, J.; Bourson, J.; Kaschke, M.; Ernsting, N. P.; *J. Phys. Chem.* **1992**, *96*, 6545.
41. Chen, Y.-L.; Xu, T.-K.; Shen, X.-H.; Gao, H.-C.; *J. Photochem. Photobiol., A* **2005**, *173*, 42.
42. Job, A.; *Liebigs Ann. Chem.* **1928**, *9*, 113.
43. Boiocchi, M.; Del Boca, L.; Gómez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E.; *J. Am. Chem. Soc.* **2004**, *126*, 16507; Amendola, V.; Boiocchi, M.; Fabbrizzi, L.; Palchetti, A.; *Chem. Eur. J.* **2005**, *11*, 120; Boiocchi, M.; Del Boca, L.; Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M.; Monzani, E.; *Chem. Eur. J.* **2005**, *11*, 3097; Wu, Y.; Peng, X.; Fan, J.; Gao, S.; Tian, M.; Zhao, J.; Sun, S.; *J. Org. Chem.* **2007**, *72*, 62; Gómez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E.; *Org. Biomol. Chem.* **2005**, *3*, 1495.
44. Gronert, S.; *J. Am. Chem. Soc.* **1993**, *115*, 10258.
45. Venturini, C. de G.; Andreaus, J.; Machado, V. G.; Machado, C.; *Org. Biomol. Chem.* **2005**, *3*, 1751.
46. Benesi, H. A.; Hildebrand, J. H.; *J. Am. Chem. Soc*. **1949**, *71*, 2703.
47. Zhong, Z. L.; Anlyn, E. V.; *J. Am. Chem. Soc.* **2002**, *124*, 9014; Kim, S. Y.; Hong, J.-I.; *Tetrahedron Lett.* **2009**, *50*, 1951.
48. Schmidtchen, F. P.; *Org. Lett.* **2002**, *4*, 431.

Submitted: April 16, 2012
Published online: July 12, 2012