Synthesis, characterization and ion sensing properties of a new colorimetric chemosensor based on an hydrazone moiety

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Abstract: The new hydrazone derivative **3** was obtained in moderate yield by condensation of an heterocyclic aldehyde with hydrazine in ethanol, heated at reflux. The new compound was characterized by the usual spectroscopic techniques and a detailed photophysical study was undertaken. The evaluation of the compound as a colorimetric chemosensor was carried out by performing spectrophotometric titrations in acetonitrile and acetonitrile/water in the presence of relevant organic and inorganic anions, and transition metal cations.

Keywords: Synthesis; Colorimetric sensors; Hydrazone derivatives; “Naked eye detection”; Cyanide; Aqueous medium.

1. Introduction

The recognition and detection of ionic species has aroused great interest due to their important roles in many biological and environmental processes. Colorimetric chemosensors are molecules that allow naked-eye detection of ionic species without resource to any instrumentation, offering qualitative and quantitative information and are considered as one of the most effective analytical method for environmental monitoring, particularly in the detection of metal ions whose presence in the environment has serious consequences.[1]

Research of sensors with good sensitivity and good selectivity in aqueous medium has been of great interest. Chemosensors soluble in aqueous media are very interesting, because of the importance in revealing a number of biological processes, disease states and environmental pollutions.[2]

Hydrazone derivatives are versatile compounds with several applications such as in medicinal chemistry due to their vast biological activity and as optical (colorimetric and fluorimetric) sensing of anions and metal cations. Other applications in materials science include molecular switches, OLEDs, etc.[3,4]

In this communication, we report the synthesis of one hydrazone derivative, functionalized with an heterocyclic moiety, in order to evaluate its photophysical properties and chemosensory ability. The new derivative was characterized by the usual techniques and a detailed photophysical study was undertaken. The evaluation of the novel compound as a colorimetric chemosensor was carried out by performing titrations in acetonitrile and acetonitrile/water in the presence of relevant organic and inorganic anions, and of alkaline, alkaline-earth and transition metal cations.

2. Experimental

2.1. Procedure for the synthesis of hydrazone 3

Equal amounts (1 mmol) of 8-hydroxy-quinoline-2-carbaldehyde **1** and 2,4-dinitrophenylhydrazine **2** were dissolved in 10 mL of EtOH at 50 ^{o}C and the solution was heated at reflux during 24 h. After cooling, the pure compound precipitated as a solid, which was collected by filtration.

Compound **3** was obtained as a yellow solid (53 mg, 60 %). Mp > 300 ºC. IR (KBr): ν = 3411, 3281, 3104, 2855, 2361, 1983, 1744, 1619, 1604, 1564, 1506, 1278, 1235, 1198, 1168, 1133, 1097, 1056, 940, 915, 829, 763, 736 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.14 (dd, *J* = 7.2 and 1.2 Hz, 1H, H-7), 7.41 (dd, *J* = 8.4 and 1.6 Hz, 1H, H-5), 7.47 (t, *J* = 7.6 Hz, 1H, H-6), 8.15 (d, *J* = 4.4 Hz, 1H, H-4), 8.19 (d, *J* = 3.2 Hz, 1H, H-3), 8.34 (d, *J* = 8.4 Hz, 1H, H-6'), 8.39 (dd, *J* = 9.6 and 2.8 Hz, 1H, H-5'), 8.77 (s, 1H, N=CH), 8.85 (d, *J* = 2.8 Hz, 1H, H-3'), 9.39 (br s, 1H, OH), 11.77 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 111.61 (C-7), 116.82 (C-4), 117.46 (C-5), 117.77 (C-3), 122.22 (C-3'), 128.05 (C-6), 128.41 (C-4a), 129.16 (C-5'), 130.34 (C-2'), 136.17 (C-6'), 137.74 (C-4'), 137.89 (C-8), 143.79 (C-1'), 148.29 (N=C), 150.81 (C-2), 152.90 (C-8a) ppm. MS (ESI) *m/z* (%): 354 ([M]$^+$, 100). HRMS: (ESI) *m/z* (%) for $C_{16}H_{12}N_5O_5$; calcd 354.08242; found 354.08329.

2.2. Optical studies and spectrophotometric titrations of compound 3

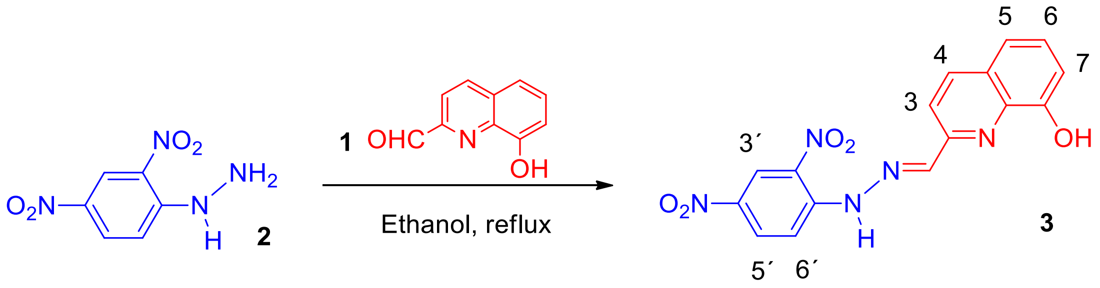
UV–visible absorption spectra (200–700 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Fluorescence spectra were collected using a FluoroMax-4 spectrofluorometer. The relative fluorescence quantum yields were determined by using 10^{-6} M solution of quinine sulphate in sulfuric acid as standard (Φ_F = 0.54).[5] Organic solvents used in the spectroscopic studies were of spectroscopic grade. Solutions of the hydrazone derivative **3** (*ca.* 1.0 × 10^{-5} M) and of the ions under study (ca. 1.0 × 10^{-2} and 1.0 × 10^{-3} M) were prepared in UV-grade acetonitrile or acetonitrile/water (95:5). Titrations of compound **3** in the presence of relevant organic and inorganic anions (AcO^-, F^-, Cl^-, Br^-, CN^-, NO_3^-, BzO^-, $H_2PO_4^-$, HSO_4^-), and transition metal cations (Cu^{2+}, Cd^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+}) was performed by the sequential addition of the ion stock solution to the hydrazone solution, in a 10-mm path length quartz cuvette and absorption emission spectra were measured by excitation at the wavelength of maximum absorption for the compound, with a 2-nm slit.

3. Results and discussion

3.1. Synthesis and characterization

The new hydrazone **3** was synthesized in 60 % yield, by condensation of 8-hydroxy-quinoline-2-carbaldehyde **1** with 2,4-dinitrophenylhydrazine **2** in ethanol at reflux

(Scheme 1). The new hydrazone was completely characterized by the usual spectroscopic techniques.



Scheme. Synthesis of hydrazone **3**.

The absorption and emission spectra of compound **3** were measured in acetonitrile solutions and showed intense lowest energy charge-transfer absorption band in the UV-visible region (λ_{max} (nm) = 382 nm; log ε of 4.57). On the other hand, no emission was observed for this compound due to the presence of the strong electron acceptor nitro group, which is a well-known quencher of the fluorescence. The absence of fluorescence is explained by the fact that the high rate of $S_1 \rightarrow S_0$ internal conversion that is related to the considerable charge-transfer character of the excited state, as a result of the strong electron-withdrawing ability of the nitro group.[6]

3.2 Spectrophotometric titrations and chemosensing studies for hydrazone 3 with anions and metallic ions

Evaluation of the new compound **3** (10^{-5} M) as a colorimetric chemosensor was carried out in ACN and ACN/H_2O solutions, in the presence of several ions (AcO^-, F^-, Cl^-, Br^-, CN^-, NO_3^-, BzO^-, $H_2PO_4^-$, HSO_4^-, Cu^{2+}, Cd^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+}) with biological, environmental and analytical relevance.

Preliminary tests were carried out by addition of up to 50 equiv of each ion to the solution of hydrazone **3** in ACN and in aqueous mixture ACN/H_2O (95:5) (Table 1, Figure 1).

It was observed that compound **3** displayed a marked colour change, from pale yellow to dark pink, upon interaction with F^- and CN^-, from pale yellow to pink with AcO^-, BzO^- and $H_2PO_4^-$, from pale yellow to orange with Fe^{3+} and Hg^{2+}, from pale yellow to dark yellow with Fe^{2+}, Pd^{2+} and Ni^{2+} or from pale yellow to brown with Cu^{2+} in acetonitrile solution. Moreover, hydrazone **3** showed selectivity for the cyanide ion and for Pd^{2+}, Hg^{2+} and Cu^{2+} in aqueous mixture displaying a marked colour change, from pale yellow to pink in the presence of CN^{-}, from pale yellow to dark yellow in the presence of Pd^{2+} and Hg^{2+} or from pale yellow to pale brown upon interaction with Cu^{2+} (Figure 1).

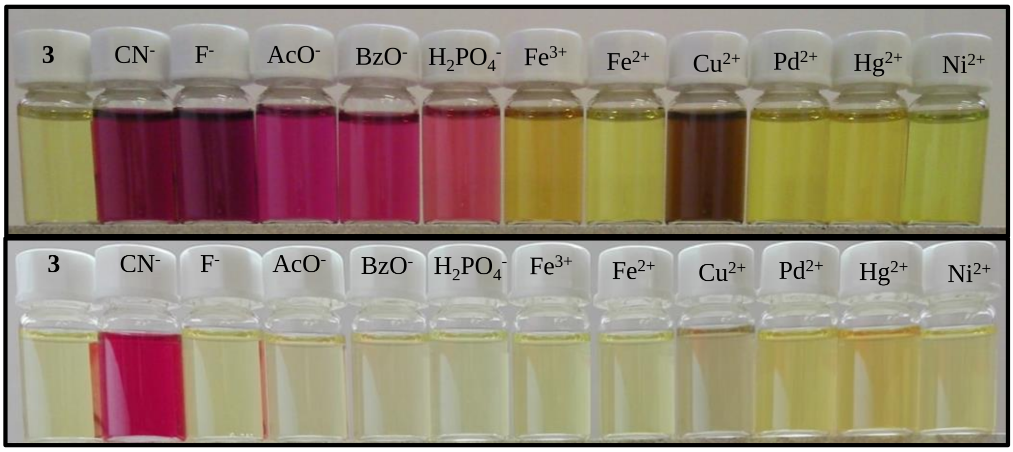


Figure 1: Colour changes of compound **3** (10^{-4} M in upon: ACN, down: ACN/H_2O (95:5)) in the presence of 50 equiv. of CN^{-}, F^{-}, AcO^{-}, BzO^{-}, $H_2PO_4^{-}$, Fe^{3+}, Fe^{2+}, Cu^{2+}, Pd^{2+}, Hg^{2+} and Ni^{2+} (in the form of tetrafluorborate or perchlorate salts).

Spectrophotometric titration of compound **3** in ACN with CN^{-} and F^{-} revealed the same trend in the UV-Vis spectra: the intensity of the longest wavelength absorption band at 379 nm decreased progressively upon addition of the anion, with the simultaneous growth of a new red-shifted absorption band located at 500 nm. In Figure 2 the spectrophotometric titrations of compound **3** with CN^{-} and F^{-} are shown, where the drastic effect of anion interactions with the receptor **3** are evident.

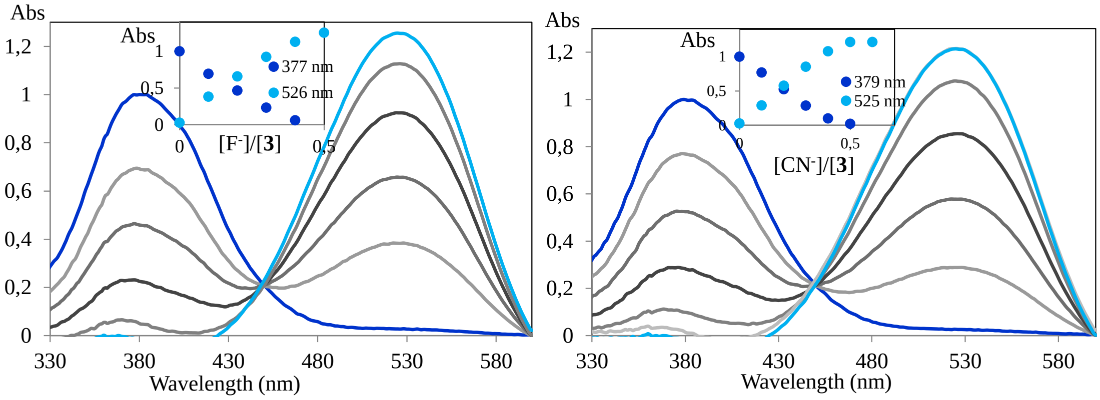


Figure 2. Spectrophotometric titration of **3** with addition of increasing amounts of CN^- and F^- in ACN. The inset represents the normalized absorption at 377 or 379 nm ([**3**] = $1x10^{-5}$ M, T = 298 K).

Designing selective chemosensors in aqueous medium is a very appealing topic, because there is a high demand for colorimetric chemosensors that can be applied in the detection of environmental and biomedical analytes. Therefore, spectrophotometric titrations of compound **3** in ACN/H_2O (95:5) showed that receptor **3** exhibited selectivity for the CN^- and for Pd^{2+}, Hg^{2+} and Cu^{2+}.

Compound **3** exhibited an absorption band at 383 nm which corresponds to a light yellow color in ACN/H_2O solution. Upon addition of increasing amount of CN^-, this band progressively decreased while a new absorption band appeared at 513 nm ($\Delta\lambda$ = 130 nm), proving that this compound is a colorimetric chemosensor that has a high selectivity for CN^-, through "naked eye" detection, showing a color change from light yellow to pink.

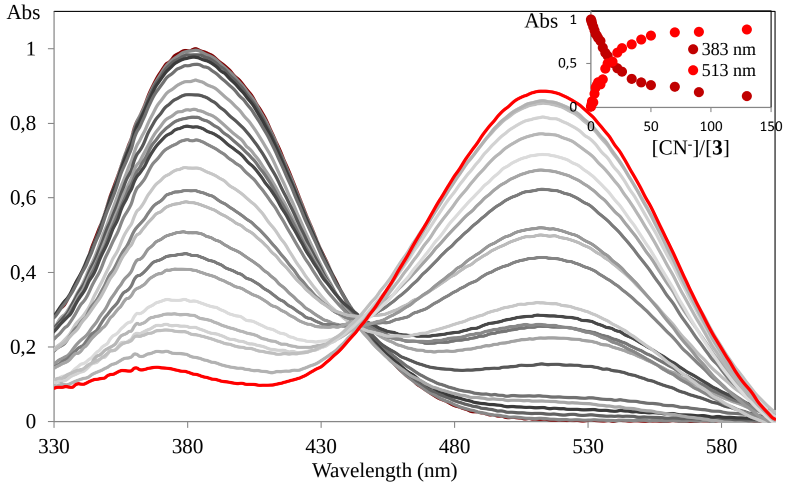


Figure 3: Spectrophotometric titrations of **3** with addition of increasing amounts of CN^- in ACN/H_2O (95:5). The inset represents the normalized emission ([**3**] = $1x10^{-5}$ M, T = 298 K).

4. Conclusions

The synthesis of a new hydrazone derivative **3** was achieved in good yield using a simple experimental procedure. The chemosensory ability was evaluated for several ions by spectrophotometric titrations in acetonitrile and acetonitrile/water (95:5) revealing that hydrazone **3** is a selective colorimetric chemosensor for CN^-, and for Cu^{2+}, Pd^{2+}, Hg^{2+} in aqueous medium.

Acknowledgements

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