

# 8-Hydroxyquinoline based push-pull azo dye: Novel colorimetric chemosensor for anion detection



Ömer Arslan<sup>a</sup>, Burcu Aydinler<sup>a</sup>, Ergin Yalçın<sup>a</sup>, Banu Babür<sup>a</sup>, Nurgül Seferoğlu<sup>b</sup>, Zeynel Seferoğlu<sup>a,\*</sup>

<sup>a</sup> Gazi University, Department of Chemistry, 06500, Ankara, Turkey

<sup>b</sup> Gazi University, Advanced Technology Department, Inst. Sci. & Technol., Ankara, Turkey

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## ABSTRACT

A novel colorimetric chemosensor based on push-pull dye (**8HQA**) was synthesized and characterized by using IR, <sup>1</sup>H/<sup>13</sup>C NMR and HRMS for the purpose of recognition of anions and cations in DMSO. The absorption maxima of the chemosensor were determined in different solvents. The selectivity and sensitivity of **8HQA** to anions were determined with spectrophotometric and <sup>1</sup>H NMR titration techniques. The selectivity of **8HQA** for studied anions (CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) was determined in DMSO. There is no selectivity between competing anions such as CN<sup>-</sup>, F<sup>-</sup>, AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> at the stoichiometric ratio of 1:1 in UV-vis titrations experiments however, it was observed different color changes upon addition of CN<sup>-</sup>, F<sup>-</sup>, AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> to the DMSO solution. In addition, the chemosensor showed no colorimetric response for the following anions; Cl<sup>-</sup>, I<sup>-</sup> and HSO<sub>4</sub><sup>-</sup> in DMSO. The colorimetric sensing ability of **8HQA** was studied in the presence of chloride salts of different cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Sn<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>. Upon the addition of 4 equiv of each of the cations showed bathochromic shifts except for Ca<sup>2+</sup> and Cu<sup>2+</sup>. Interestingly, no selectivity was observed in interaction with metal cations. In addition, the molecular and electronic structures of **8HQA**, as well as the molecular complexes of **8HQA**, formed with the anions, were obtained theoretically and confirmed by DFT and TD-DFT calculations.

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## 1. Introduction

In recent years, sensing and recognition of anions, cations and biomolecules have become a highly hot topic of interest to scientist whose research studies on supramolecular and organic chemistry [1–25]. The anions like F<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> are quite significant in human health [26–28]. In addition, metals and their ions especially toxic metals such as Hg<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> play an important role in many biological and environmental processes. Therefore, determination of anions and cations in real sample is quite important with simpler, faster and cheaper methods than conventional techniques. Till now, the determination of anions and cations can be achieved by several analytical methods using spectroscopic techniques. However, simpler methods for practical applications of detection of any analyte of interest are desirable. Colorimetric and fluorimetric chemosensors can be alternative

techniques instead of the traditional analytical methods for determination of anions and cations in real sample. Therefore, the development of chromogenic chemosensors for anions and cations recognition has become an attractive research field and synthesis of new additional chemosensor is still required. Recently, we reported syntheses and spectroscopic properties of 8-hydroxyquinoline based carbocyclic and heterocyclic azo dyes [29–31]. Here, we developed a 8-hydroxyquinoline based push-pull azo dye as chemosensor containing dicyanovinylene as an electron acceptor group at the 4-position of phenyldiazanyl moiety, and the OH group in the quinoline heterocyclic moiety acts as a H-bond donor site. The structure of the chemosensor (**8HQA**) was characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS techniques. The effect of solvents with different polarities on the UV-vis absorption spectra of **8HQA** were investigated. In addition, the anion recognition properties of the receptor of **8HQA** towards the anions CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> were studied experimentally by colorimetric response, UV-Vis, and <sup>1</sup>H NMR spectroscopic titration methods. The nature of the interactions between **8HQA** and the anions were investigated by the quantum mechanical calculations at the level of

\* Corresponding author.

E-mail address: [znseferoglu@gazi.edu.tr](mailto:znseferoglu@gazi.edu.tr) (Z. Seferoğlu).

density functional theory (DFT and TD-DFT). In addition, the interactions between **8HQ**A and the cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) were also investigated by UV-Vis and naked-eye. Based on our study, we were surprised to find that no significant selectivity was observed towards cations.

## 2. Experimental

### 2.1. Materials and instrumentation

The chemicals used in the syntheses of all compounds were obtained from Sigma-Aldrich Chemical Company (USA) and were used without further purification. All solvents used were of analytical grade. The solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin layer chromatography (TLC), using Merck silica gel (60 F254) plates (0.25 mm) and visualized under Ultraviolet light (UV). FT-IR (ATR) spectra were recorded on Perkin-Elmer Spectrum 100 FT-IR spectrophotometer ( $\nu$ , are in  $\text{cm}^{-1}$ ). NMR spectra were recorded on a Bruker Avance 300 Ultra-Shield in DMSO- $d_6$ . Chemical shifts are expressed in  $\delta$  units (ppm). Ultraviolet–Visible (UV-vis) absorption spectra were recorded on Shimadzu Corporation, Kyoto Japan UV-1800 240V spectrophotometer (Gazi University Department of Chemistry, Turkey). Mass spectra were recorded on Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments; in  $m/z$  (rel. %) (Gazi University Laboratories, Department Pharmacological Sciences). Chemical shifts are expressed in  $\delta$  units (ppm) with tetramethylsilane (TMS) as the internal reference. Coupling constant ( $J$ ) is given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; triplet, t, multiplet, m. The melting points were measured on Electrothermal IA9200 apparatus and uncorrected. Thermal analyses were performed with a Shimadzu DTG-60H system, up to 600 °C ( $10\text{ }^\circ\text{C min}^{-1}$ ) under a dynamic nitrogen atmosphere ( $15\text{ mL min}^{-1}$ ). Typically, aliquots of a freshly prepared standard solutions of the alkylammonium salt of the anions ( $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{AcO}^-$ ,  $\text{HSO}_4^-$  and  $\text{H}_2\text{PO}_4^-$ ) and of chloride salt of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) were added, and their various UV-vis spectra were recorded.  $^1\text{H}$  NMR titrations for anions were carried out in DMSO- $d_6$  solution.

### 2.2. Synthetic procedures

2-(1-(4-aminophenyl)ethylidene)malononitrile (**1**) was synthesized by using literature method [32].

### 2.3. The synthesis of (E)-2-(1-(4-((8-hydroxyquinolin-5-yl)diazenyl)phenyl)ethylidene)malononitrile (**8HQ**A)

2 mmol 2-(1-(4-aminophenyl)ethylidene)malononitrile (**1**) was dissolved in hot glacial acetic acid-propionic acid mixture (2:1, 9.0 mL) and was rapidly cooled in an ice/salt bath to  $-5\text{ }^\circ\text{C}$ . The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulphuric acid (prepared from sodium nitrite (0.15 g) and

concentrated sulphuric acid (3 mL at  $50\text{ }^\circ\text{C}$ ). The mixture was stirred for an additional 2 h at  $0\text{ }^\circ\text{C}$ . Excess nitrous acid was consumed by the addition of urea. The resulting diazonium salt was cooled in salt/ice mixture. After diazotization was complete the diazo liquid was slowly added to vigorously stirred solution of 8-hydroxyquinoline (2 mmol) in potassium hydroxide (2 mmol in 4 mL methanol and 2 mL and water). The solution was stirred at  $0\text{--}5\text{ }^\circ\text{C}$  for 2 h. After 2 h, the pH of the reaction mixture was maintained at 4–6 by the addition of saturated sodium carbonate solution. The mixture was stirred for one hour at room temperature. After that, the resulting solid was filtered, washed with cold water and dried. Recrystallization from ethanol gave dark brown solid. Yield 50%; mp  $232\text{ }^\circ\text{C}$ ; FT-IR (ATR)  $\nu/\text{cm}^{-1}$  3249 (N-H), 2960 (C-H), 2218 ( $\text{C}\equiv\text{N}$ ), 1732 ( $\text{C}=\text{O}$ );  $^1\text{H}$ NMR (DMSO- $d_6$ , 300 MHz)  $\delta$  9.37 (d,  $J = 8.56\text{ Hz}$ , 1H),  $\delta$  9.00 (d, 2.60 Hz 1H),  $\delta$  8.14 (d,  $J = 8.53\text{ Hz}$ , 2H),  $\delta$  8.06 (d,  $J = 8.59\text{ Hz}$ , 1H),  $\delta$  7.92 (d,  $J = 8.53\text{ Hz}$ , 2H),  $\delta$  7.80 (m,  $J = 8.52\text{ Hz}$ , 1H),  $\delta$  7.26 (d,  $J = 8.56\text{ Hz}$ , 1H),  $\delta$  2.71 (s, 3H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz)  $\delta$  176.5, 159.1, 154.7, 149.6, 139.2, 138.3, 138, 132.4, 129.7, 129.3, 128.6, 128.3, 123.9, 123.1, 115.9, 113.8, 113.7, 112.3, 84.3, 24.7 ppm; HRMS (ESI,  $\text{CH}_3\text{CN}$ ) ( $\text{C}_{20}\text{H}_{14}\text{N}_5\text{O}$ ) found. 340.1200, calc.340.1198.

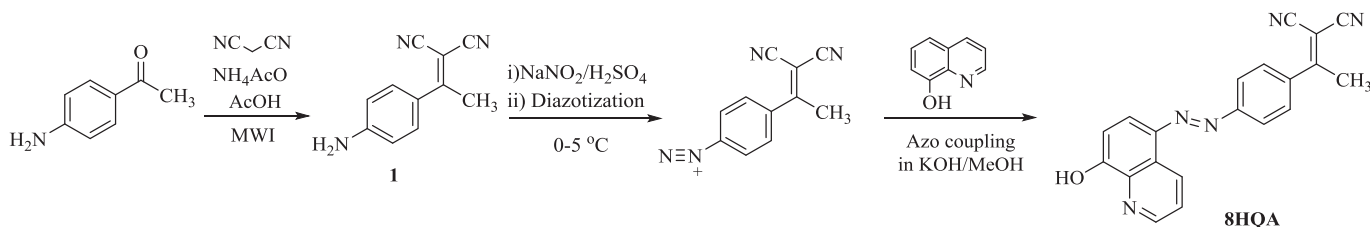
### 2.4. Computational methods

All calculations were carried out using the Gaussian09 program package [33]. The molecule geometry was optimized at HF/631 g with the rotations C8-C10-C13-C15 torsion angles by  $20^\circ$  intervals in the range of  $0\text{--}360^\circ$  to find the most possible conformation. Then, this conformation was taken as a starting geometry and re-optimized using B3LYP/631 + g(d,p) [34,35] in gas phase and different solvents. It is confirmed that no imaginary vibrational frequencies at the optimized geometries to indicate true minima of the potential energy surface. The absorption spectra of the molecule and its deprotonated forms were calculated by using the time-dependent density functional method (TD-DFT) and using self-consistent reaction field (SCRf) method, based on the polarizable continuum model (PCM) [36,37].

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthesis of **8HQ**A was performed by stepwise procedure as illustrated in Scheme 1 was synthesized using Microwave Irradiation Method (MWI) with excellent yield. In addition, **8HQ**A was prepared by coupling 8-hydroxyquinoline with diazotized **1** in nitrosyl sulphuric acid. The structure of **8HQ**A was confirmed by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS techniques. The spectral data were consistent with the proposed structure (Supplementary data, Figs. S1–S4). The prepared dye may show two possible tautomeric forms, namely azo form **A** and hydrazone **B** as shown in Scheme 2. After deprotonation of two tautomeric forms, it may be stable as common anion mesomeric structure **C** (Scheme 2). In some



Scheme 1. Synthesis of (E)-2-(1-(4-((8-hydroxyquinolin-5-yl)diazenyl)phenyl)ethylidene)malononitrile (**8HQ**A).

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