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Colorimetric probes based on bioactive organic dyes for selective sensing of cyanide and fluoride ions

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ABSTRACT

Eight novel bioactive azo dyes containing thiazolidinone (TZD) derivatives (1O–4S) were designed and synthesized for antibacterial assays and colorimetric sensing of anions. Synthesized compounds were evaluated for their antibacterial activities using the disc diffusion technique. Majority of the compounds showed potent antibacterial activities against the tested bacterial strains in the zone assay. Moderate antibacterial activities were also exhibited in the minimum inhibitory concentration (MIC) assay. In addition, the synthesized compounds were evaluated for their colorimetric sensing of anions. In contrast to dyes with electron donating groups (EDGs), 4O having electron withdrawing groups (EWGs) showed highly selective colorimetric sensing of CN^- ions. Binding interaction of 4O with CN^- ions provides a remarkable colorimetric response from yellow to blue ($\Delta\lambda = 186$ nm), enabling naked-eye sensing without any spectroscopic instrumentation. Furthermore, the limit of detection (LOD) for 4O towards CN^- was found to be 0.74 μM.

1. Introduction

Azo dyes are the most attractive of the known classes of organic dyes, due to their various applications in various fields, including the food industry, textile dying, cosmetics, pigments and paints, high technology materials, biological–medical studies, optical storage capacity, optical switching and recently, as colorimetric probes [1–5]. The success of azo colorants is due to the simplicity of their synthesis, to the many possibilities presented by variation of the diazo compounds and coupling components, the generally high molar extinction coefficient as well as to the good light and wet fastness properties [1,6]. In addition to the original applications of dyes, the introduction of a bioactive moiety, such as thiazolidinones, into the backbone of the synthesized dyes potentiates their application as food colorants, drugs, cosmetics, medicinal compounds and other biomolecules. Thiazolidine and its derivatives as bioactive heterocycles play an outstanding role in medicinal chemistry and they have been extensively used as scaffolds for drug development. Thiazolidinones show a wide variety of biological activities such as antifungal, antibacterial, antiviral, antitumor, and antidiabetic potentials [7–11].

On the other hand, due to the important roles of the anions in biological, environmental, and industrial processes, the detection assays for anions is a growing field and has attracted much interest in molecular recognition studies. In addition, there is interest in finding better and more efficient ways of detecting anions that can be potentially harmful to the environment or human health. In particular, the selective sensing of cyanide and/or fluoride has gained attention due to their significance in clinical treatment and physiological systems as well as environmental processes [12–14]. For example, cyanide ions are important in many chemical processes, such as electroplating, plastics manufacturing, gold and silver extraction, tanning, and metallurgy. In addition, cyanide is known as a toxic anion, due to its effects on numerous body functions, including the vascular, visual, and central nervous systems. On the other hand, the petrochemical industry, gold mining, metal electroplating, photography and steel manufacturing, are responsible for cyanide pollution [15–17].

Several detection methods, including atomic absorption, electrochemical, voltammetric, and potentiometric methods, as well as ion-exchange chromatography have been explored [18–21]. Particularly, colorimetric sensors are desired and widely used due to their advantages such as cost-effectiveness, rapid, real time-monitoring, lack of equipment required and being naked eye detectable [22]. Therefore, developing colorimetric chemosensors has emerged as an area of mounting importance. Many studies concerning colorimetric sensors based on azo dyes have been reported [23]. However, there are very few reports on the synthesis of

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azo receptors containing a bioactive moiety. Taking these results into consideration, we now report the synthesis, characterization, antibacterial and anion sensing properties of eight new bioactive azo dyes containing thiazolidinones.

2. Experimental

2.1. Material and apparatus

All chemicals used in this study were obtained from Sigma–Aldrich and Merck Chemical companies and were used without further purification. All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer (Japan). The Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a FT-NMR (400 MHz) Brucker apparatus spectrometer (Germany), and the chemical shifts are expressed in δ ppm using TMS as an internal standard and J values are given in Hz. The visible spectra were measured using a Pharmacia Biotech Spectrophotometer (United States). The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates (Merck Chemical Company, Germany).

2.2. General procedure for the synthesis of dyes 1–4

The diazonium salts from aniline derivatives were prepared in good yield according to methods previously described [24]. After completion of diazotization reaction, in a second flask, salicylaldehyde was dissolved in water containing sodium hydroxide and sodium carbonate and cooled to 0 °C in an ice bath. The diazonium solution was slowly added to the phenolate solution in basic medium by adjusting the pH at 7.5–8.5 over 30–45 min. The resulting solution was stirred for 1–2 h in an ice bath and then allowed to reach room temperature. The precipitate was collected and washed several times with cool water after the solution was acidified (pH 5.5–6.5) by addition of diluted HCl. The precipitate was finally recrystallized in EtOH/H_2O to afford desired dyes 1–4.

1-(3-Formyl-4-hydroxyphenylazo)-4-methoxybenzene (**1**): yellow solid; yield 76%; m.p. 123–124 °C; FT-IR (KBr) ν cm^{-1}: 3410, 1646, 1598, 1580, 1500, 1278. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 2.46 (s, 3H, CH_3), 7.12 (*d*, 1H, J = 8.8 Hz, Ar–H), 7.22 (*d*, 2H, J = 8.0 Hz, Ar–H), 7.76 (*d*, 2H, J = 8.0 Hz, Ar–H), 8.06 (*d*, 1H, J = 8.4 Hz, Ar–H), 8.18 (*d*, 1H, J = 2.4 Hz, Ar–H), 10.36 (s, 1H, OH), 11.52 (broad singlet, 1H, CHO).

1-(3-Formyl-4-hydroxyphenylazo)-4-chlorobenzene (**2**): yellow solid; yield 81%; m.p. 174–176 °C; FT-IR (KBr) ν cm^{-1}: 3374, 1663, 1565, 1478, 1280. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.22 (*d*, 1H, J = 9.2 Hz, Ar–H), 7.66 (*d*, 2H, J = 6.8 Hz, Ar–H), 7.90 (*d*, 2H, J = 6.8 Hz, Ar–H), 8.12 (*d*, 1H, J = 2.4 Hz, Ar–H), 8.20 (*d*, 1H, J = 2.4 Hz, Ar–H), 10.38 (s, 1H, OH), 11.64 (broad singlet, 1H, CHO).

1-(3-Formyl-4-hydroxyphenylazo)-4-cyanobenzene (**3**): yellow solid; yield 88%; m.p. 203–205 °C; FT-IR (KBr) ν cm^{-1}: 3400, 2220, 1664, 1565, 1480, 1280. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.18 (*d*, 1H, J = 9.2 Hz, Ar-H), 7.72 (*d*, 2H, J = 8.4 Hz, Ar–H), 7.81 (*d*, 2H, J = 8.4 Hz, Ar–H), 8.13 (*dd*, 1H, J = 2.3 Hz, Ar–H), 8.28 (d, 1H, J = 2.3 Hz, Ar–H), 10.37 (s, 1H, OH), 11.61 (broad singlet, 1H, CHO).

1-(3-Formyl-4-hydroxyphenylazo)-4-nitrobenzene (**4**): yellow solid; yield 94%; m.p. 186–188 °C; FT-IR (KBr) ν cm^{-1}: 3400, 1660, 1600, 1510, 1474, 1320, 1280. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.24 (*d*, 1H, J = 9.2 Hz, Ar–H), 8.16 (*dd*, 1H, J = 2.4 Hz, Ar-H), 8.22 (*d*, 2H, J = 8.8 Hz, Ar–H), 8.33 (*d*, 1H, J = 2.4 Hz, Ar–H, Ar–H), 8.47 (*d*, 2H, J = 8.8 Hz, Ar–H), 10.19 (s, 1H, OH), 11.54 (s, 1H, CHO).

2.3. General synthesis of bioactive compounds (1O–4S)

A mixture of azo precursors (3 mmol) and thiazolidinone derivatives (3 mmol) with a catalytic quantity of piperidine was refluxed in absolute ethanol for 5–6 h and then cooled to 0 °C in an ice bath. After that HCl (0.5 M) and water are added and the precipitate is filtered and washed with water and petroleum ether (three times). The resulting product was isolated by recrystallization from EtOH/H_2O.

Compound 1O: yellow solid; yield: 62%; m. p. 181–183 °C; FT-IR (KBr) ν cm^{-1}: 3208, 1730, 1680, 1590, 1500, 1478. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 3.86 (s, 3H, OCH_3), 7.10–7.15 (*m*, 3H, Ar–H), 7.85 (*m*, 4H, Ar–H and C = CH), 8.03 (s, 1H, Ar–H), 10.38 (s, 1H, OH), 11.39 (s, 0.47H, NH, tautomeric form), 12.62 (s, 0.53H, OH, tautomeric form). ^{13}C NMR (DMSO-d_6, ppm): δ 56.0, 115.0, 117.1, 120.9, 122.8, 123.7, 124.8, 126.4, 126.9, 145.5, 146.4, 160.0, 162.1, 167.8, 168.2.

Compound 1S: yellow solid; yield: 50%; m. p. 146–148 °C; FT-IR (KBr) ν cm^{-1}: 2920, 1718, 1700, 1594, 1540, 1495. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 3.87 (s, 3H, OCH_3), 7.12 (*m*, 3H, Ar–H), 7.81–7.99 (*m*, 5H, Ar–H and C = CH), 10.24 (s, 1H, OH), 11.21 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ 55.8, 114.9, 117.2, 120.9, 122.6, 123.8, 124.3, 126.5, 127.1, 145.4, 146.5, 160.4, 1161.8, 168.6, 178.6.

Compound 2O: yellow solid; yield: 83%; m. p. 226–228 °C; FT-IR (KBr) ν cm^{-1}: 3409, 1712, 1696, 1588, 1478. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.15 (*d*, 1H, J = 9.2 Hz, Ar–H), 7.61 (*d*, 2H, J = 8.4 Hz, Ar–H), 7.85 (*d*, 2H, J = 8.8 Hz, Ar–H), 7.88 (s, 1H, Ar–H), 7.90 (*d*, 1H, J = 7.6 Hz, Ar–H), 8.01 (s, 1H, C = CH), 10.36 (s, 1H, OH), 12.12 (broad singlet, 1H, NH and OH, tautomeric forms). ^{13}C NMR (DMSO-d_6, ppm): δ 117.2, 121.1, 123.5, 124.0, 124.5, 126.2, 127.3, 129.9, 135.8, 145.3, 150.8, 160.9, 167.8, 168.2.

Compound 2S: yellow solid; yield: 65%; m. p. 205–207 °C; FT-IR (KBr) ν cm^{-1}: 3410, 1700, 1682, 1594, 1546, 1485. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.16 (d, 1H, J = 8.8 Hz, Ar–H), 7.66 (d, 2H, J = 8.8 Hz, Ar–H), 7.89 (*m*, 4H, Ar–H), 8.05 (s, 1H, C = CH), 10.36 (s, 1H, OH), 11.41 (broad singlet, 1H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ 117.1, 121.0, 123.7, 124.1, 124.4, 126.3, 127.3, 129.8, 135.7, 145.3, 151.0, 160.7, 171.5, 179.2.

Compound 3O: yellow solid; yield: 78%; m. p. 264–269 °C; FT-IR (KBr) ν cm^{-1}: 2920, 2220, 1718, 1700, 1590, 1556, 1506. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.18 (d, 1H, J = 6.8 Hz, Ar–H), 7.96–8.01 (*m*, 5H, Ar–H), 8.05 (*m*, 2H, Ar–H, C = CH), 10.38 (s, 1H, OH), 12.18 (broad singlet, 1H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ 113.1, 117.4, 118.9, 121.3, 123.5, 124.1, 124.5, 125.9, 127.7, 134.2, 145.4, 154.4, 161.7, 167.9, 168.2.

Compound 3S: yellow solid; yield: 76%; m. p. 200–202 °C; FT-IR (KBr) ν cm^{-1}: 3380, 2221, 1734, 1700, 1590, 1510, 1458. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.17 (d, 1H, J = 8.8 Hz, Ar–H), 7.87–7.93 (*m*, 2H, Ar–H, C = CH), 8.0 (*d*, 2H, J = 8.8 Hz, Ar–H), 8.06 (*d*, 2H, J = 8.4 Hz, Ar–H), 8.08 (*d*, 1H, J = 2.4 Hz, Ar–H), 10.38 (s, 1H, OH), 11.56 (broad singlet, 1H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ 113.0, 117.3, 119.0, 122.3, 123.5, 123.6, 125.2, 125.6, 129.5, 134.2, 145.5, 154.5, 161.4, 173.6, 179.8.

Compound 4O: yellow solid; yield: 91%; m. p. 230–232 °C; FT-IR (KBr) ν cm^{-1}: 2920, 1724, 1700, 1650, 1600, 1520, 1478. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.16 (*d*, 1H, J = 8.4 Hz, Ar–H), 7.88–7.93 (*m*, 3H, Ar–H and C = CH), 7.97 (*d*, 2H, J = 8.4 Hz, Ar–H), 8.36 (*d*, 2H, J = 8.4 Hz, Ar–H), 10.36 (s, 1H, OH), 12.26 (broad singlet, 1H, NH and OH, tautomeric forms). ^{13}C NMR (DMSO-d_6, ppm): δ 113.8, 117.8, 121.8, 123.5, 124.7, 125.0, 125.4, 127.5, 144.9, 148.1, 155.7, 163.3, 169.4, 170.1.

Compound 4S: yellow solid; yield: 94%; m. p. 209–211 °C; FT-IR (KBr) ν cm^{-1}: 2921, 1718, 1700, 1648, 1590, 1519, 1476. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, 298 K): δ 7.18 (*d*, 1H, J = 8.8 Hz, Ar–H), 7.92 (*m*, 2H, Ar–H, C = CH), 8.06 (*d*, 2H, J = 8.8 Hz, Ar–H), 8.1 (*d*, 1H,