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Azo dyes featuring a pyrene unit: New selective chromogenic and fluorogenic chemodosimeters for Hg(II)

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ABSTRACT

Three new chemodosimeters **1**–**3** were prepared, and their chromogenic and fluorogenic behaviors toward various metal cations were investigated. Receptors **1**–**3** show exclusive response toward Hg^{2+} ion and also distinguish $Hg^{2+}$from other metal cations by different color changes in DMSO aqueous solution (DMSO/H_2O = 9/1). Among them, receptor **1** also exhibits a pronounced Hg^{2+}-induced fluorescence enhancement. Thus, the receptor **1** can be used as a colorimetric and fluorescent chemodosimeter for the determination of Hg^{2+} ion. The use of the test strip of the receptor **1** to detect Hg^{2+} was also reported.

1. Introduction

The development of artificial receptors for the sensing and recognition of transition and heavy metal ions has received considerable attention because they play important roles in living systems and have an extremely toxic impact on the environment [1–5]. Among them, Hg^{2+} ion is considered as one of the most dangerous cations for environment because it is widely distributed in air, water and soil. Mercury can accumulate in the human body and can affect a wide variety of diseases even in a low concentration, such as prenatal brain damage, serious cognitive and motion disorders and Minamata disease [6–8]. Therefore, it is highly desirable to develop selective and sensitive assays for Hg^{2+} ions.

In recent years, many efforts have been devoted to design various chemosensors specific for Hg^{2+} ion detection [9–32]. The most attractive approach focuses on the research of novel colorimetric and fluorescent Hg^{2+} ion sensors, which allow naked eyes detection of the change of color without resorting to the use of expensive instruments and fluorescent emission upon specific Hg^{2+} ion inducing reaction. Some selective chemodosimeters for the Hg^{2+} ion have been designed to adopt mercury-promoted desulfurization, leading to an irreversible chemical event between thioamide derivatives and Hg^{2+} ion [18–30]. However, most chemodosimeters developed so far have been related to their fluorescence changes upon metal ion introduction [25–30]. As we know, chemodosimeters inducing both color changes and fluorescence changes are still rather rare [27,33].

In this context, each chemodosimeter proposed contains a pyrene unit and an azobenzene moiety, in which the thiourea group is responsible for the Hg^{2+} recognition leading to unique color change and fluorescence enhancement. The pyrene subunit is versatile and frequently employed for the construction of important chemosensor having efficient fluorogenic behavior [34–36]. The azobenzene moiety herein is very useful because its color change is remarkably responsive to an electronic effect of substrate species in the event of the Hg^{2+} ion-induced chemodosimetric desulfurization. In this paper, we report the syntheses of three chemodosimeters (**1**–**3**) and their photochemical elucidation of their selective color and fluorescence changes toward Hg^{2+} cation. To the best of our knowledge, **1** is a rare example of azobenzene based chemodosimeter for Hg^{2+} ion.

2. Experimental

2.1. Synthesis

2.1.1. Materials and methods

All cations, in the form of nitrate salts, were purchased from Sigma or Aldrich chemical company, stored in desiccators under

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vacuum containing self-indicating silica. Solvents were purified prior to use and stored under nitrogen. Dimethyl sulfoxide were dried with calcium hydride and distilled in reduced pressure. The reagents, 4-isothiocyanate-4′-trifluoromethylazobenzene (**7**), 4-isothiocyanate-4′-nitroazobenzene (**8**), 4-isothiocyanatoazobenzene (**9**), 4-isocyanate-4′-trifluoromethylazobenzene (**10**), 4-isocyanate-4′-nitroazobenzene (**11**) and 4-isocyanatoazobenzene (**12**) were prepared by the literature procedures [37–44]. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. UV–vis spectra were measured on a Cary 300 spectrophotometer. Fluorescence spectra were performed on HITACHI F-4500 fluorescence spectrophotometer.

*2.1.2. Synthesis of 1-(4-(4-trifluoromethylphenyldiazenyl) phenyl)-3-(pyren-1-yl)thiourea (**1**)*

Under nitrogen, to a stirred solution of 1-aminopyrene (0.217 g, 1.0 mmol) in $CHCl_3/CH_3CN$ (3/1), 4-isothiocyanate-4′-trifluoromethylazobenzene (0.307 g, 1.0 mmol) in $CHCl_3$ (10 mL) was added at room temperature. After cooling, the resulting mixture was stirred and heated to reflux for 72 h. The solution was cooled and filtered. The residue was purified by recrystallization from CH_3CN to give **1** (0.36 g, 68%) as a yellow solid. Mp: 212–213 °C. FT-IR (KBr): 3447, 2986, 2899, 1644, 1434, 1399, 1317, 1061, 948, 698 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.55 (s, 1H), 10.32 (s, 1H), 8.33–8.30 (m, 3H), 8.25 (d, J = 3.2 Hz, 2H), 8.20 (s, 2H), 8.12–8.09 (m, 4H), 8.04 (d, J = 8.4 Hz, 2H), 7.96–7.91 (m, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): 181.6, 154.7, 148.3, 144.4, 133.2, 131.1, 131.0, 130.9, 130.7, 130.0, 128.7, 127.7, 127.2, 127.1, 127.0, 126.7, 126.0, 125.9, 125.7, 125.5, 125.0, 124.3, 124.0, 123.6, 123.4, 123.3, 123.1, 118.9, 113.9 ppm. FAB MS m/z = 525.1363 [M+H]$^+$, calc. for $C_{30}H_{20}N_4F_3S$ = 525.1363.

*2.1.3. Synthesis of 1-(4-(4-nitrophenyldiazenyl) phenyl)-3-(pyren-1-yl)thiourea (**2**)*

The preparation of **2** followed the above-mentioned procedure using 1-aminopyrene and 4-isothiocyanate-4′-nitroazobenzene in the same molar ratio. Yield: 0.38 g (71%). Mp: 190–192 °C. FT-IR (KBr): 3441, 2990, 2906, 1644, 1436, 1406, 1311, 1060, 955 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.59 (s, 1H), 10.40 (s, 1H), 8.42 (d, J = 9.2 Hz, 2H), 8.33–8.31 (m, 3H), 8.25 (d, J = 3.2 Hz, 2H), 8.21 (s, 2H), 8.13–8.04 (m, 4H), 7.99–7.94 (m, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): 181.6, 155.8, 148.6, 148.4, 144.8, 133.2, 131.1, 131.0, 128.1, 127.7, 127.1, 127.0, 126.7, 126.0, 125.8, 125.5, 125.0, 124.3, 123.7, 123.4, 123.1 ppm. FAB MS m/z = 501.1249 [M]$^+$, calc. for $C_{29}H_{19}N_5O_2S$ = 501.1262.

*2.1.4. Synthesis of 1-(4-phenyldiazenylphenyl)-3-(pyren-1-yl)thiourea (**3**)*

The preparation of **3** followed the above-mentioned procedure using 1-aminopyrene and 4-isothiocyanateazobenzene in the same molar ratio. Yield: 0.29 g (65%). Mp: 189–190 °C. FT-IR (KBr): 3452, 2996, 2904, 1644, 1440, 1409, 1306, 1052, 958, 712 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.50 (s, 1H), 10.25 (s, 1H), 8.33–8.07 (m, 9H), 7.89–7.86 (m, 5H), 7.60–7.52 (m, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): 181.6, 152.5, 143.4, 133.2, 131.1, 130.9, 130.0, 128.0, 127.7, 127.1, 127.0, 126.7, 126.0, 125.7, 125.5, 125.0, 124.3, 123.8, 123.5, 123.1, 122.9 ppm. FAB MS m/z = 457.1490 [M+H]$^+$, calc. for $C_{29}H_{21}N_4S$ = 457.1488.

*2.1.5. Synthesis of 1-(4-(4-trifluoromethylphenyldiazenyl) phenyl)-3-(pyren-1-yl)urea (**4**)*

The preparation of **4** followed the above-mentioned procedure using 1-aminopyrene and 4-isocyanate-4′-trifluoromethylazobenzene in the same molar ratio. Yield: 0.41 g (80%). Mp: 339–340 °C. FT-IR (KBr): 3383, 2997, 2911, 1650, 1437, 1407, 1314, 1015, 954, 706 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.65 (s, 1H), 9.34 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.36 (d, J = 9.2 Hz, 1H), 8.30–8.26 (m, 4H), 8.15–8.06 (m, 3H), 8.04–7.99 (m, 2H), 7.97–7.93 (m, 4H), 7.82 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): 154.7, 153.3, 147.1, 144.5, 132.9, 131.5, 131.0, 130.8, 130.4, 127.8, 127.6, 127.5, 127.1, 126.9, 126.4, 125.8, 125.6, 125.1, 124.9, 124.5, 123.3, 123.1, 122.2, 121.5, 121.0, 118.9, 118.7 ppm. FAB MS m/z = 509.1596 [M+H]$^+$, calc. for $C_{30}H_{20}N_4F_3O$ = 509.1591.

*2.1.6. Synthesis of 1-(4-(4-nitrophenyldiazenyl)phenyl)-3-(pyren-1-yl)urea (**5**)*

The preparation of **5** followed the above-mentioned procedure using 1-aminopyrene and 4-isocyanate-4′-nitroazobenzene in the same molar ratio. Yield: 0.42 g (86%). Mp: 234–235 °C. FT-IR (KBr): 3527, 3355, 2359, 2250, 2124, 1653, 1052, 1008, 857 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.69 (s, 1H), 9.35 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.8 Hz, 1H), 8.36–8.33 (m, 1H), 8.30–8.28 (m, 4H), 8.15–8.08 (m, 2H), 8.06–7.97 (m, 6H) 7.83 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): 155.9, 153.2, 148.4, 147.2, 145.0, 132.9, 131.5, 131.0, 127.8, 127.6, 127.5, 126.9, 126.4, 125.8, 125.6, 125.4, 125.1, 124.9, 123.6, 122.2, 121.5, 121.0, 118.7 ppm. FAB MS m/z = 485.1567 [M+H]$^+$, calc. for $C_{29}H_{20}N_5O_3$ = 485.1568.

*2.1.7. Synthesis of 1-(4-phenyldiazenylphenyl)-3-(pyren-1-yl)urea (**6**)*

The preparation of **6** followed the above-mentioned procedure using 1-aminopyrene and 4-isocyanatoazobenzene in the same molar ratio. Yield: 0.18 g (40%). Mp: 293–294 °C. FT-IR (KBr): 3357, 2354, 2340, 2250, 2124, 1654, 1554, 1053, 1026, 802 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.57 (s, 1H), 9.30 (s, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 9.2 Hz, 1H), 8.30–8.25 (m, 4H), 8.15–8.04 (m, 3H), 7.94 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.60–7.50 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): 153.3, 152.5, 147.2, 143.6, 133.0, 131.5, 131.3, 131.0, 129.9, 127.8, 127.6, 127.4, 126.9, 126.4, 125.8, 125.6, 125.1, 124.9, 124.6, 122.7, 122.0, 121.6, 120.9, 118.7 ppm. FAB MS m/z = 441.1742 [M+H]$^+$, calc. for $C_{29}H_{21}N_4O$ = 441.1717.

*2.1.8. Isolation of 1-(4-(4-trifluoromethylphenyldiazenyl) phenyl)-3-(pyren-1-yl)urea (**4**)*

To a solution of **1** (0.05 g, 0.1 mmol) in $CHCl_3/CH_3CN$ (3/1) was slowly added $Hg(NO_3)_2{\cdot}H_2O$ (0.10 g, 0.3 mmol) in $CHCl_3$ (10 mL). The resulting mixture was stirred at room temperature for 30 min and then washed with saturated Na_2S solution and water, dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by column chromatography on SiO_2 using $CHCl_3/CH_3CN$/hexane = 2/1/1 as the eluent, to give **4** (0.05 g, 89%) as a yellow solid. Mp: 339–340 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.65 (s, 1H), 9.34 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.36 (d, J = 9.2 Hz, 1H), 8.30–8.26 (m, 4H), 8.15–8.06 (m, 3H), 8.04–7.99 (m, 2H), 7.97–7.93 (m, 4H), 7.82 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): 154.6, 153.3, 147.1, 144.5, 132.9, 131.5, 131.0, 130.8, 130.4, 127.8, 127.6, 127.4, 127.0, 126.9, 126.4, 125.8, 125.6, 125.1, 124.9, 124.5, 123.3, 123.0, 122.2, 121.5, 121.0, 118.9, 118.6 ppm. FAB MS m/z = 509.1598 [M+H]$^+$, calc. for $C_{30}H_{20}N_4F_3O$ = 509.1591.

The ^{1}H NMR, ^{13}C NMR and FAB MS spectral data are consistent with the above data.

*2.1.9. Isolation of 1-(4-(4-nitrophenyldiazenyl) phenyl)-3-(pyren-1-yl)urea (**5**)*

A similar procedure to isolate **5** was carried out using 1-(4-(4-nitrophenyldiazenyl)phenyl)-3-(pyren-1-yl)thiourea and $Hg(NO_3)_2$ in the same molar ratio. Yield: 0.04 g (91%). Mp: 234–235 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.69 (s, 1H), 9.35 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.8 Hz, 1H), 8.36–8.33 (m, 1H), 8.30–8.28 (m, 4H), 8.15–8.08 (m, 2H), 8.06–7.97 (m, 6H) 7.83 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): 155.8,