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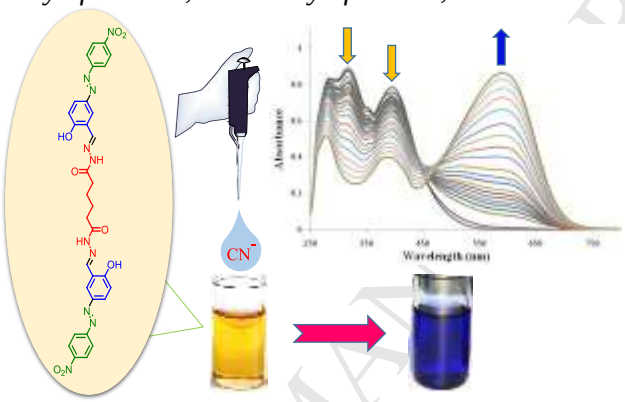
Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box 41335-1914, Rasht, Iran



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Synthesis of new bis-benzylidene-hydrazides as a sensitive chromogenic sensor for naked-eye detection of CN^- and AcO^- ions

Ammar Sheykhi-Estalkhjani[a], Nosrat O. Mahmoodi[a,*], Asieh Yahyazadeh[a,*] and Meysam Pasandideh Nadamani[a]

[a] *Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box 41335-1914, Rasht, Iran*

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ABSTRACT

Some new bis-benzylidene-hydrazides were synthesized via a condensation reaction of the corresponding azo dyes with adipic acid dihydrazide. All compounds because of the three possible stereoisomers showed four sets of signals in NMR. The anion recognition studies exhibited that the nitro bis-benzylidene-hydrazide derivative acts as a highly sensitive and selective chromogenic sensor for naked-eye detection of CN^- and AcO^- ions, with a distinct color change from yellow to blue and yellow to purple, respectively. The limit of detection (LOD) was found for **1d** toward CN^- to be 1.1 μM. The result of the Job's plot indicated stoichiometry of binding between chemosensor and anions is found to be 1:2.

1. Introduction

The anions play essential roles in medical diagnostics, physiology, industrial and environmental processes. Among the various anions, CN^- is one of the most worried anions, because it could be absorbed through lungs, gastrointestinal tract and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death.[1–3] In spite of its extreme toxicity, today cyanide is still extensively used in the gold and silver mining industry, plastic manufacturing, electroplating and resin industry.[4–6] To detect CN^-, several methods have been developed by means of different experimental procedures and detection techniques, for example chromatography, voltammetric, spectrophotography, potentiometric, electrochemical, optical methods and flow injection analysis technique.[7–18] Colorimetric methods have been actively studied in recent years because of conveniently and easily monitor target ions with the naked eye, quick response rates and at relatively low costs.[19–28] In the light of the above mentioned facts, it is necessary to design of molecules that can recognize, respond to, or sense anions selectively through visible, electrochemical and optical responses.

Over the last decade, chromogenic chemosensors based on a new azophenol-create colorimetric sensor shows a selective detection for specifically identify anions.[29–33] The advantage of these sensors is real-time monitoring, rapidity and no sophisticated technical equipment is required to perform these measurements and being naked eye visible.

In consideration of these characteristics, and in continuation of our previous works,[34–38] The synthesis, characterization and sensing properties of some new colorimetric bis-benzylidene-hydrazide receptors **1a-1h** for visual detection of CN^- and AcO^- ions was described (Scheme 1). The sensing processes can be realized by naked-eye detection, with a color change from yellow to blue and yellow to purple in presence of CN^- and AcO^- ions, respectively.

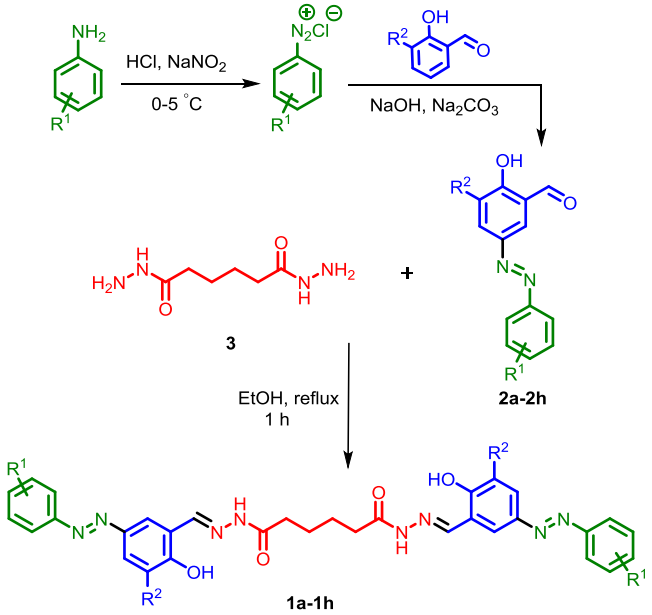
2. Results and discussion

2.1. Synthesis and Spectral studies

Our approach involves, the convenient one-pot, multi-component synthesis of bis-benzylidene-hydrazide receptors (**1a-1h**) through a condensation reaction of one equivalent of adipic acid dihydrazide (**3**) and two equivalents of premade azo-aldehyde dyes (**2a-2h**) as shown in Scheme 1. The azo-aldehyde dye precursors (**2a-2h**) separately were synthesized by reaction of *o*-vanillin or salicylaldehyde with benzene diazonium chloride salts that in sequence made by diazotization of corresponding aniline derivatives. The structure of products has been well characterized by FT-IR, UV-Vis, NMR spectroscopies and elemental analyses (see Table 1 and supporting data). The NMR spectra of (**1a-1h**) were recorded in DMSO at 25 °C. All of the

* Corresponding authors. E-mail addresses: mahmoodi@guilan.ac.ir (N. O. Mahmoodi), Tel: +981333320912; yahyazadeh@guilan.ac.ir (A. Yahyazadeh)

synthesized compounds showed four sets of signals in ^{1}H NMR duo to the three possible stereoisomers syn/syn, syn/anti (or anti/syn) and anti/anti with respect to the amide bonds.[39] The two syn/anti or anti/syn isomers are actually the same isomer with two set of signals attribute to syn- and anti-moieties separately. Fig. 1 designates the structures of the stereoisomers of bis-benzylidene-hydrazide **1a** interpreted base on the FT-IR and NMR spectra.



1a) R^1 = H, R^2 = H
1b) R^1 = 4-Me, R^2 = H
1c) R^1 = 4-Et, R^2 = H
1d) R^1 = 4-NO_2, R^2 = H
1e) R^1 = H, R^2 = OMe
1f) R^1 = 4-Et, R^2 = OMe
1g) R^1 = 4-Cl, R^2 = OMe
1h) R^1 = 4-Br, R^2 = OMe

Scheme 1. Synthesis of bis-benzylidene-hydrazides

Table 1. The properties of target bis-benzylidene-hydrazide receptors **1a-1h**

Product	Picture	λ_{max}(nm) (DMSO)	mp (°C)	Yield[a] (%)
1a		295, 387	296-297 dec	82
1b		287, 337, 370	291-292 dec	80
1c		315, 350, 378	297-298	83
1d		285, 317, 396	306-307 dec	77
1e		306, 356, 380	277-278	84
1f		288, 379	247-248	88
1g		308, 383	276-277	70
1h		309, 357, 387	273-274	75

[a] Isolated yields.

As shown in Fig. 1 & Fig. 2, each of the two hydrogens marked with green and orange colors shows four sets of signals. Two signals of the same intensity (with an area under each peak approximately equal to 1.79) are related to syn and anti conformers of structure **1a′**. The syn/anti isomer was found to be the predominant conformer, followed by the syn/syn and anti/anti conformers, respectively. In fact, there are two equal conformers of **1a′**-s/a (22.4%) and **1a′**-a/s (22.4%) with total amount of (44.8%) and two other isomers **1a**-s/s (40.1%) and **1a″**-a/a (15.1%). The presence of 1a, 1a′ and 1a″ stereoisomers confirmed by interpretation of ^{1}H and ^{13}C NMR and presented in experimental section.

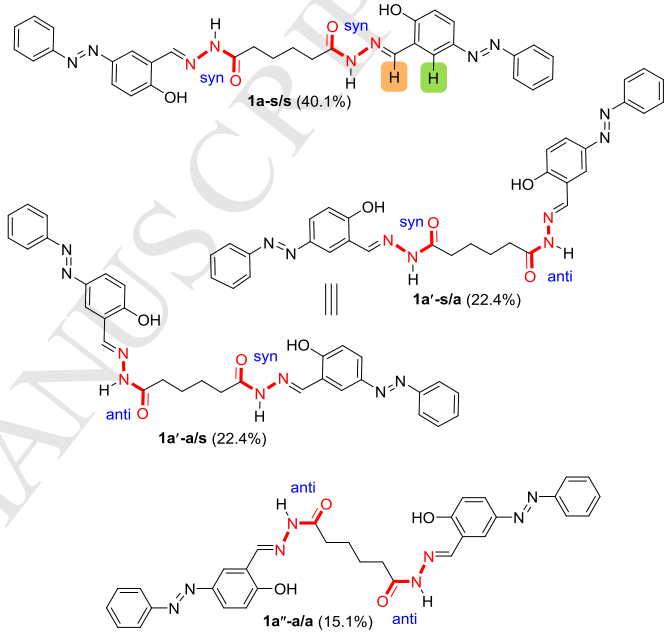


Fig. 1. Structures of three stereoisomers of bis-benzylidene-hydrazide **1a**

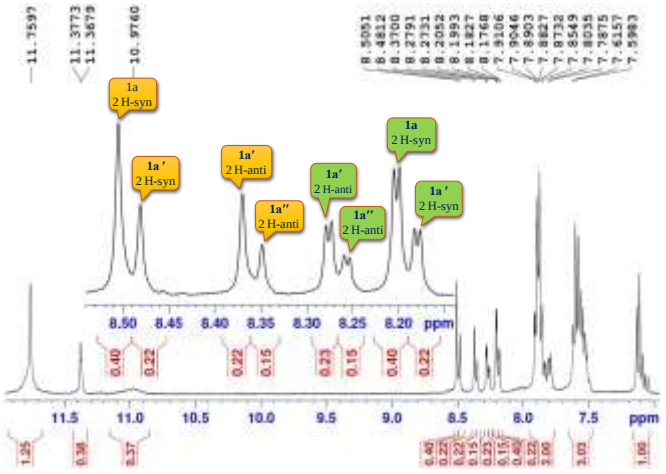


Fig. 2. ^{1}HNMR spectra of compound **1a**; four sets of signals related to three stereoisomers **1a**:**1a′**: **1a″** with a ratio of 40.1: 44.8: 15.1%

2.2. Colorimetric sensing of CN^- and AcO^-

The electronic absorption spectra of bis-benzylidene-hydrazide receptors (**1a-1h**), were measured in DMSO at a 3 $\times 10^{-5}$ M concentration, the results are summarized in Table 1. The electronic absorption spectra of **1a-1h** display mainly two bands with different shoulders (Fig. 3). The first UV band located at 285-317 nm can be assigned to the moderate energy $\pi \rightarrow \pi^*$ transition of the aromatic rings and the second band at 370-396

nm is due to low energy $\pi \rightarrow \pi^*$ transition.[40] Compound **1f** in DMSO display a broadband at 432-550 nm assigned to an $n \rightarrow \pi^*$ electronic transition of azo-aromatic chromophore and intramolecular charge transfer interaction.

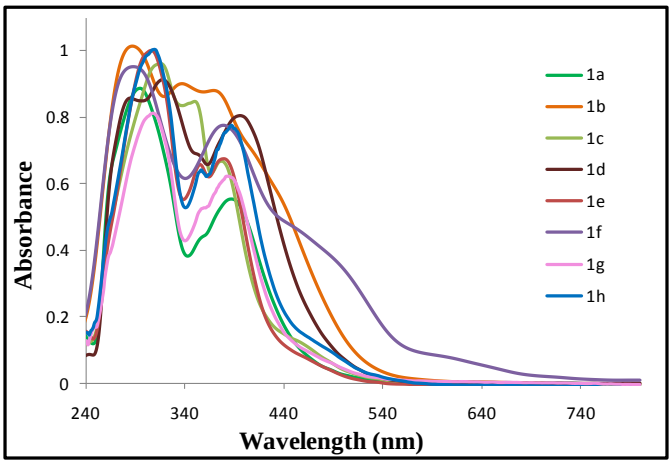


Fig. 3. Absorption spectra character of **1a-1h** in DMSO

As an initial test, we surveyed sensitivity of receptors **1a-1h** towards anions upon addition of 10 equivalents of various anions, including CO_3^{2-}, NO_2^-, AcO^-, NO_3^-, CN^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HCO_3^- and S^{2-} in DMSO/H_2O (9/1). Receptor **1d** showed superb sensitivity to CN^- and AcO^- among these anions. The sensitivity of receptor **1d** is attributed to increase of its anion stability due to the electron-withdrawing power of the *p*-nitro group substituents that powerfully extended the π-conjugation length. As shown in Fig. 4, receptor **1d** upon addition of CN^- and AcO^-, compared to other anions that display a remarkable and immediate colorimetric response from yellow to blue and yellow to purple, respectively.

Fig. 4. The color change observed by naked-eye of receptor **1d** (3×10^{-5} M) upon addition of 10 equiv. of various ions in DMSO/H_2O (9/1)

Furthermore, UV-Vis absorption spectral responses of receptor **1d** (3×10^{-5} M in DMSO/H_2O (9/1)) upon addition of 10 equiv. of different anions were also investigated (Fig. 5). Addition of CN^- and AcO^- ions had an intense effect on the electronic spectrum of **1d** and induced a new absorption peak appeared at 591 and 515 nm, respectively. However, when other anions were added no significant change was observed.

In other efforts, the superior selectivity of **1d** as a colorimetric chemosensor for the detection of CN^- in the presence of various competing anions was considered as illustrated in Fig. 4b. In the presence of other excess anions (10 equiv.), premade sensor **1d** (1 equiv.) and CN^- (10 equiv.), the absorption intensity of final solution was exhibited. The UV-Vis spectra revealed that the presence of other interfering anions up to 10 equiv. had no effect on the absorbance intensity of CN^-, with the exception of AcO^- (Fig. 5b). A similar competition test (same as above) was repeated for AcO^- (10 equiv.), premade sensor **1d** (1 equiv.) in the presence of other anions (10 equiv.), the UV-Vis spectra revealed that the presence of other interfering anions had no effect on the absorbance intensity of AcO^- (Fig. 5c). However, these experiments illustrated that the intraction of AcO^- is slightly greater than CN^- verses **1d**.

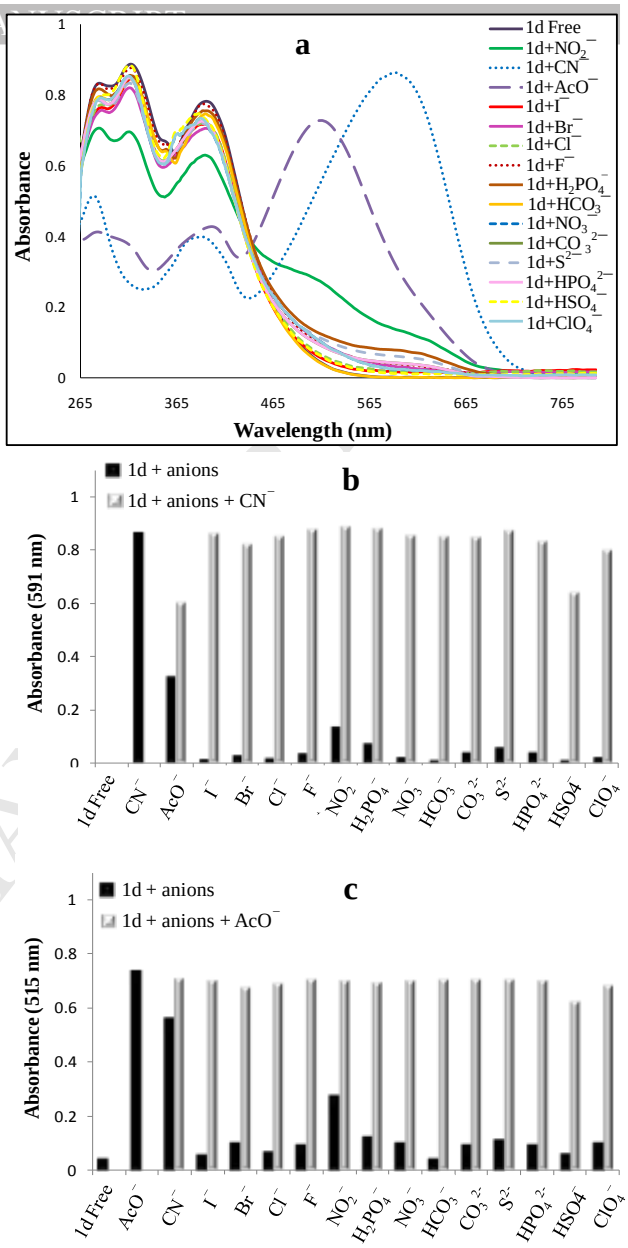


Fig. 5. a) UV-Vis absorption spectra of **1d** (3×10^{-5} M) in the presence of 10 equiv. of various anions in DMSO/H_2O (9/1). Effect of competitive anions (10 equiv.) on the interaction of; b) **1d**/CN^- (10 equiv.) and c) **1d**/AcO^- (10 equiv.)

The effect of pH on the host-guest binding affinity of receptor **1d** was considered. The absorption band of receptor **1d** at 591 nm was recognized to the formation of the **1d**-CN complex under various pH conditions. As revealed in Fig. 6, in pH less than 4, the color of the solution remained unchanged (yellow) and no absorption band was appeared at 591 nm. This phenomenon confirms that the complex **1d**-CN was not prepared. As the pH rose from 4 to 12, the absorption band at 591 nm intensified rapidly and the color of the solution turned to dark blue. The result confirmed that **1d** is a very sensitive sensor especially at basic pH and this will encompass the development of new pH-selective sensor.

The UV-Vis absorption spectral responses of **1d** in DMSO/H_2O (9/1) upon gradual addition of 10 equivalents of CN^- and AcO^- ions were investigated Fig. 7 & Fig. 8. Free **1d** indicated absorptions at 285, 317 and 396 nm. Upon gradual addition of CN^- to **1d**, these absorptions slightly decreased and a

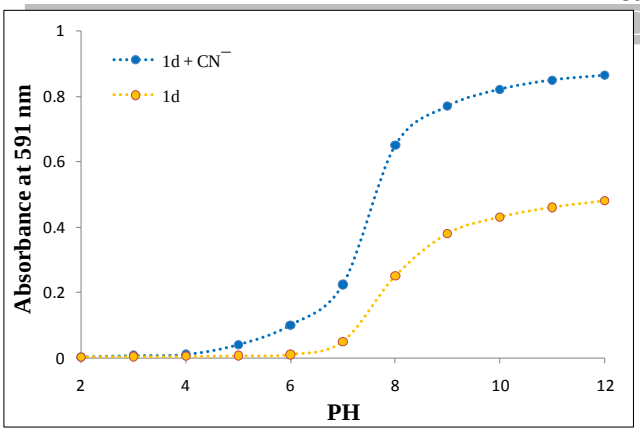


Fig. 6. Effect of pH on the UV-Vis spectra of sensor **1d** (3×10^{-5} M) and **1d** containing CN^- ion at 591 nm

new emerged remarkably growth centered at 591 nm and the intensity was steadily enhanced until the amount of CN^- reached 10 equivalents with simultaneously decreasing of the peaks at 285, 317 and 396 nm. Meanwhile, the color of the solution changed from yellow to blue, allowing naked-eye detection of CN^-. These changes can be attributed to the increase of intramolecular charge transfer (ICT) due to the strong interaction between CN^- ion with hydroxyl groups of receptor **1d** and the deprotonation effect. In other efforts, the absorption spectral changes of **1d** upon gradual addition of AcO^- ion were also

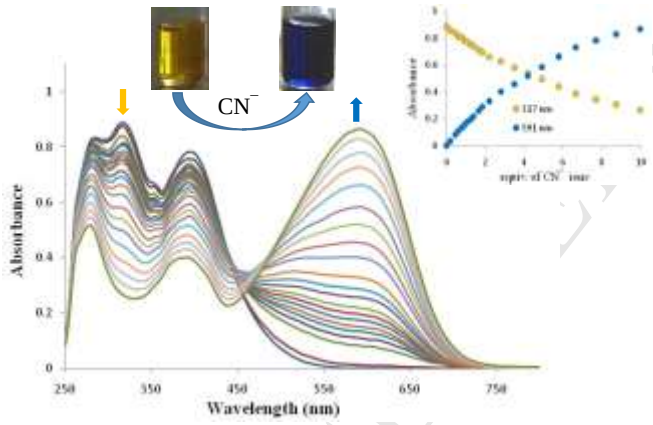


Fig. 7. UV-Vis absorption spectra of sensor **1d** (3×10^{-5} M in DMSO/H_2O (9/1)) upon addition of CN^- (0-10 equiv.). Inset showing the binding isotherm at selected wavelengths

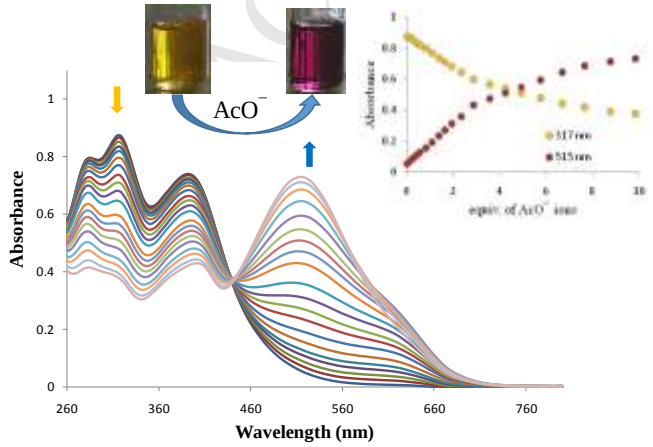


Fig. 8. UV-Vis absorption spectra of sensor **1d** (3×10^{-5} M in DMSO/H_2O (9/1)) upon addition of AcO^- (0-10 equiv.). Inset showing the binding isotherm at selected wavelengths

examined, which was roughly the same as the observed changes upon the addition of CN^- (Fig. 8). The difference between AcO^- and CN^- is the color change of solution from yellow to purple for AcO^- and yellow to dark blue for CN^-, respectively. As well, upon the addition of CN^-, the bathochromic shift and higher intensity of new absorption peak in comparison to AcO^- were observed (See Figs. 7 and 8).

The result of the Job's plot of UV-Vis titration of **1d** with CN^- indicate that the stoichiometric ratio inferred to be 1:2 (Fig. 9). The same result was confirmed by ^{1}H NMR titration obtained from average integration of the singlet signals of the OH and NH protons related to **1d** verses **1d** + 2 equiv. CN^- at δ 11.04-11.99 ppm (Fig. 10). Furthermore, the ^{1}H NMR spectra revealed that the chemosensor recognition of CN^- rely on the H-bonds, this deprotonation evidently directed to color change.

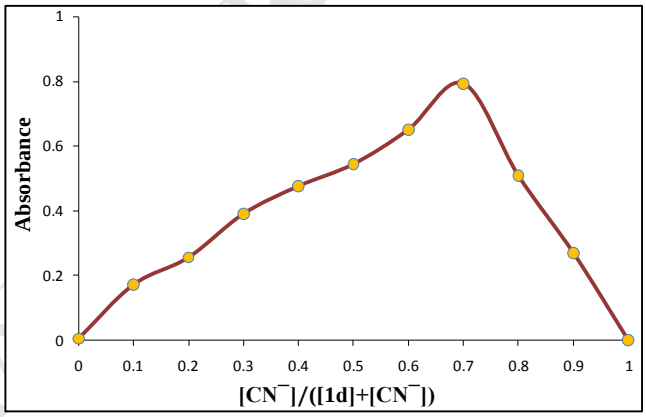


Fig. 9. Job's plot for stoichiometry of binding between receptor **1d** with CN^- in DMSO/H_2O (9/1) (λ = 591 nm)

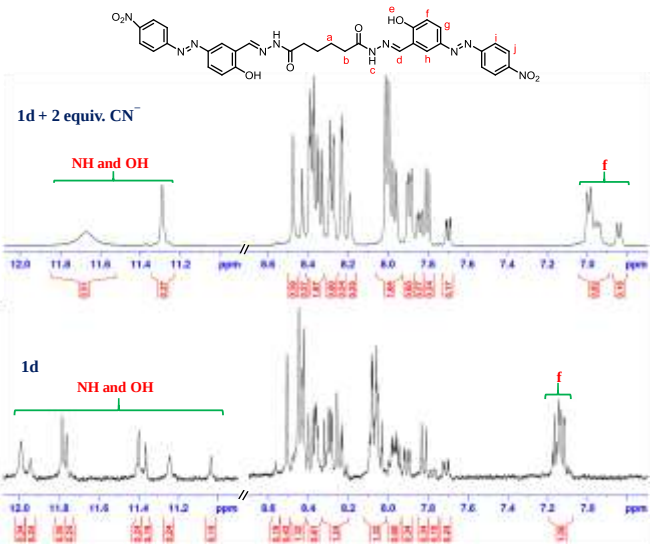


Fig. 10. Partial ^{1}H NMR spectra of **1d** and **1d** + 2 equiv. CN^- in DMSO-d_6

The world health organization (WHO) has set the maximum safe concentration for cyanide in drinking water at 1.9 μM. The limit of detection (LOD) was evaluated with the equation LOD = 3σ/s and was found for **1d** toward CN^- to be 1.1 μM which is lower than the maximum value of cyanide permitted by WHO in drinking water (see supporting data).

2.3. Antibacterial activity

The *In vitro* antibacterial activity of compounds **1a**–**1h** was evaluated against Gram-negative and Gram-positive bacteria including: *Micrococcus luteus* (*M. luteus*), *Staphylococcus*

aureus (*S. aureus*), *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*Ps. aeruginosa*) by zone inhibition method. Tetracycline and Ampicillin were used as standard drugs and DMSO was used as a solvent. The concentration of compounds was 1 mg/mL in DMSO. The Results are shown in Table 2 that the compound importance antibacterial activity against *Micrococcus luteus* is: **1b** > **1f** > **1a** > **1c** > **1d** = **1h** > **1e** = **1g**. Compound **1b** indicate higher antibacterial activity than standard drugs. Compounds **1c** and **1h** showed similar antibacterial activity as ampicillin. Whereas, none of the compounds had antibacterial activity verses *Ps. aeruginosa*.

Table 2. Antibacterial assay of **1a-1h** as a zone of inhibition (mm)

Compound	Antibacterial activity (mm)			
	M. luteus	*S. aureus*	*E. coli*	*Ps. aeruginosa*
1a	20	10	-	-
1b	28	16	4	-
1c	18	8	8	-
1d	16	4	-	-
1e	10	-	-	-
1f	24	4	8	-
1g	10	-	-	-
1h	16	8	-	-
Tetracycline	25	21	21	19
Ampicillin	27	22	8	0

3. Conclusion

Here, some new bis-benzylidene-hydrazide derivatives were successfully synthesized via a simple reaction between adipic acid dihydrazide and azo-coupled to o-vanillin or salicylaldehyde precursors. The anion recognition studies exhibited that **1d** acts as a highly sensitive and selective chromogenic sensor for naked-eye detection of CN^- and AcO^- ions. Upon the addition of CN^- and AcO^- ions, the solution was changed immediately from yellow to blue and yellow to purple, respectively. In addition, the ^{1}H NMR spectra revealed chemosensor recognition of CN^- via H-bonds, this deprotonation evidently directed to color change. For **1d** toward CN^-, the LOD was found to be 1.1 μM .The Job's plot titration of **1d** toward CN^- indicated a stoichiometry of binding between sensor and anions to be 1:2.

4. Experimental section

4.1. Materials and apparatus

Adipic acid dihydrazide (**3**) was purchased from Merck and used without further purification. The azo dyes (**2a-2h**) used as a precursor were synthesized according to our previously reported procedures.[35] Melting points were measured by electrothermal 9100s apparatus and were uncorrected. The FT-IR spectra were recorded on a Bruker Vector 22 in the region of 400–4000 cm^{-1} in KBr pellets. The absorption spectra of bis-benzylidene-hydrazides were measured by Shimadzu UV-2100 spectrophotometer in the range 200–800 nm (DMSO/H_2O (9:1), c = 3 × 10^{-5} M, cell path length 1 cm). ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance 400 MHz spectrometer using DMSO-d_6 as solvent. The CHN analyses were performed on a Vario-ELIII elemental analyzer. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95, EI: 70 eV, R:10000.

*4.2. General procedure for the synthesis of bis-benzylidene-hydrazides **1a-1h***

Azo dye, **2a-2h**, (2 mmol) was dissolved in absolute EtOH (10-15 ml) and the solution was stirred vigorously for 10 min at reflux condition. Then adipic dihydrazide acid **3** (0.174 g, 1 mmol) was added and the mixture stirred at reflux condition. The progress of the reaction was monitored by TLC (EtOAc:*n*-hexane, 1:3). The reaction was completed after 1 h and the product was collected by filtration, washed with EtOH and recrystallized from DMF/H_2O.

*4.2.1. N′¹,N′⁶-bis((E)-2-hydroxy-5-((E)-phenyldiazenyl)benzylidene)adipohydrazide (**1a**)*

Yield: 82%, mp 296-297 °C; FT-IR (KBr, υ/cm^{-1}): 3450 (O–H), 3201 (N–H), 3051 (aromatic C–H), 2941 (aliphatic C–H), 1664 (C=O), 1615 (C=N), 1545 (C=C), 1484 (N=N), 1275 (C-O). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): syn/syn isomer, 40.1%: 11.76 (s, 4H, H_e and H_c), 8.51 (s, 2H, H_d), 8.20 (d, *J* = 2.4 Hz, 2H, H_h), 7.91-7.78 (m, 6H, H_g, H_i), 7.61-7.49 (m, 6H, H_k, H_l), 7.13-7.04 (m, 2H, H_f), 2.34-2.29 (m, 4H, H_b), 1.73-1.66 (m, 4H, H_a); syn/anti and/or anti/syn isomers, 44.8%: 11.76 (s, 2H, H_e or H_c), 11.38 (s, 1H, H_e or H_c), 10.98 (br, 1H, H_e or H_c), 8.48 (s, 1H, $H_{d\ (syn)}$), 8.37 (s, 1H, $H_{d\ (anti)}$), 8.28 (d, *J* = 2.8 Hz, 1H, $H_{h\ (anti)}$), 8.18 (d, *J* = 2.4 Hz, 1H, $H_{h\ (syn)}$), 7.91-7.78 (m, 6H, H_g, H_i), 7.61-7.49 (m, 6H, H_k, H_l), 7.13-7.04 (m, 2H, H_f), 2.73-2.70 (m, 2H, $H_{b\ (anti)}$), 2.34-2.29 (m, 2H, $H_{b\ (syn)}$), 1.73-1.66 (m, 8H, H_a); anti/anti isomer, 15.1%: 11.37 (s, 2H, H_e or H_c), 10.98 (br, 2H, H_e or H_c), 8.35 (s, 2H, H_d), 8.26 (d, *J* = 2.8 Hz, 2H, H_h), 7.91-7.78 (m, 6H, H_g, H_i), 7.61-7.49 (m, 6H, H_k, H_l), 7.13-7.04 (m, 2H, H_f), 2.73-2.70 (m, 4H, H_b), 1.73-1.66 (m, 4H, H_a). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 174.47, 174.39, 169.03, 168.99, 160.57, 159.77, 152.48, 145.62, 145.54, 145.14, 139.74, 131.33, 131.26, 129.86, 129.74, 126.24, 124.89, 123.84, 122.76, 122.54, 121.45, 120.13, 117.68, 117.42, 34.43, 34.31, 32.40, 32.18, 25.25, 25.13, 24.56, 24.32. Anal. Calcd. For $C_{32}H_{30}N_8O_4$ (%): C, 65.07; H, 5.12; N, 18.97. Found: C, 65.14; H, 5.08; N, 18.91. HRMS-ESI (*m/z*) calcd. for $C_{32}H_{31}N_8O_4$ $[M + H]^+$ 591.2463, found 591.2467.

*4.2.2. N′¹,N′⁶-bis((E)-2-hydroxy-5-((E)-p-tolyldiazenyl)benzylidene)adipohydrazide (**1b**)*

Yield: 80%, mp 291-292 °C; FT-IR (KBr, υ/cm^{-1}): 3447 (O–H), 3202 (N–H), 3066 (aromatic C–H), 2955 (aliphatic C–H), 1668 (C=O), 1617 (C=N), 1558 (C=C), 1489 (N=N), 1274 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, 39.1%: 11.75 (s, 2H, H_e or H_c), 11.74 (s, 2H, H_e or H_c), 8.50 (s, 2H, H_d), 8.17 (d, *J* = 2.4 Hz, 2H, H_h), 7.88-7.69 (m, 6H, H_g, H_i), 7.40-7.32 (m, 4H, H_k), 7.12-7.04 (m, 2H, H_f), 2.33-2.29 (m, 4H, H_b), 2.41 (s, 6H, H_l), 1.74-1.65 (m, 4H, H_a); syn/anti and/or anti/syn isomers, 47.4%: 11.75 (s, 1H, H_e or H_c), 11.74 (s, 1H, H_e or H_c), 11.37 (s, 1H, H_e or H_c), 10.93 (s, 1H, H_e or H_c), 8.47 (s, 1H, $H_{d\ (syn)}$), 8.36 (s, 1H, $H_{d\ (anti)}$), 8.26 (d, *J* = 2.8 Hz, 1H, $H_{h\ (anti)}$), 8.15 (d, *J* = 2.4 Hz, 1H, $H_{h\ (syn)}$), 7.88-7.69 (m, 6H, H_g, H_i), 7.40-7.32 (m, 4H, H_k), 7.12-7.04 (m, 2H, H_f), 2.73-2.69 (m, 2H, $H_{b\ (anti)}$), 2.33-2.29 (m, 2H, $H_{b\ (syn)}$), 2.41 (s, 3H, $H_{l\ (syn\ or\ anti)}$), 2.35 (s, 3H, $H_{l\ (syn\ or\ anti)}$), 1.74-1.65 (m, 3H, H_a); anti/anti isomer, 13.5%: 11.36 (s, 2H, H_e or H_c), 10.89 (s, 2H, H_e or H_c), 8.35 (s, 2H, H_d), 8.23 (d, *J* = 2.8 Hz, 2H, H_h), 7.88-7.69 (m, 6H, H_g, H_i), 7.40-7.32 (m, 4H, H_k), 7.12-7.04 (m, 2H, H_f), 2.73-2.69 (m, 4H, H_b), 2.39 (s, 6H, H_l), 1.74-1.65 (m, 4H, H_a). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 168.98, 160.30, 150.55, 145.56, 145.14, 141.50, 130.40, 126.17, 123.52, 122.77, 120.09, 117.65, 34.30, 25.12, 21.48. Anal. Calcd. For $C_{34}H_{34}N_8O_4$ (%): C, 66.01; H,

5.54; N, 18.11. Found: C, 65.95; H, 5.50; N, 18.18. HRMS-ESI (*m/z*) calcd. for $C_{34}H_{35}N_8O_4$ [M + H]$^+$ 619.2776, found 619.2781.

*4.2.3. N′¹,N′⁶-bis((E)-5-((E)-(4-ethylphenyl) diazenyl)-2-hydroxybenzylidene)adipohydrazide (**1c**)*

Yield: 83%, mp 297-298 °C; FT-IR (KBr, υ/cm^{-1}): 3449(O–H), 3259 (N–H), 3055 (aromatic C–H), 2963-2870 (aliphatic C–H), 1657 (C=O), 1617 (C=N), 1550 (C=C), 1484 (N=N), 1274 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, 39.5%: 11.76-11.74 (m, 4H, H_e or H_c), 8.50 (s, 2H, H_d), 8.17 (d, *J* = 2.4 Hz, 2H, H_h), 7.89-7.71 (m, 6H, H_i, H_g), 7.43-7.34 (m, 4H, H_k), 7.12-7.04 (m, 2H, H_f), 2.74-2.62 (m, 4H, H_l), 2.35-2.29 (m, 4H, H_b), 1.74-1.65 (m, 4H, H_a), 1.24 (t, *J* = 7.6 Hz, 6H, H_m); syn/anti and/or anti/syn isomers, 48%: 11.76-11.74 (m, 2H, H_e or H_c), 11.37 (s, 1H, H_e or H_c), 10.92 (br, 1H, H_e or H_c), 8.48 (s, 1H, $H_{d\ (syn)}$), 8.36 (s, 1H, $H_{d\ (anti)}$), 8.26 (d, *J* = 2.4 Hz, 1H, $H_{h\ (anti)}$), 8.16 (d, *J* = 2.4 Hz, 1H, $H_{h\ (syn)}$), 7.89-7.71 (m, 6H, H_i, H_g), 7.43-7.34 (m, 4H, H_k), 7.12-7.04 (m, 2H, H_f), 2.74-2.62 (m, 6H, H_l, $H_{b\ (anti)}$), 2.35-2.29 (m, 2H, $H_{b\ (syn)}$), 1.74-1.65 (m, 4H, H_a), 1.24 (t, *J* = 7.6 Hz, 3H, $H_{m\ (syn\ or\ anti)}$), 1.18 (t, *J* = 7.6 Hz, 3H, $H_{m\ (syn\ or\ anti)}$); anti/anti isomer, 12.5%: 11.37 (s, 2H, H_e or H_c), 10.92 (br, 2H, H_e or H_c), 8.35 (s, 2H, H_d), 8.23 (d, *J* = 2.4 Hz, 2H, H_h), 7.89-7.71 (m, 6H, H_i, H_g), 7.43-7.34 (m, 4H, H_k), 7.12-7.04 (m, 2H, H_f), 2.74-2.62 (m, 8H, H_l, H_b), 1.74-1.65 (m, 4H, H_a), 1.24 (t, *J* = 7.6 Hz, 6H, H_m). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 174.46, 174.43, 169.02, 168.97, 160.32, 159.50, 150.76, 150.69, 147.61, 147.52, 145.65, 145.59, 145.21, 139.78, 139.70, 129.20, 129.16, 129.06, 126.11, 125.01, 124.80, 123.64, 122.85, 122.25, 122.01, 121.47, 121.40, 120.10, 117.65, 117.37, 34.39, 34.30, 32.40, 32.26, 28.52, 28.47, 25.28, 25.12, 24.58, 24.39, 15.82, 15.76. Anal. Calcd. For $C_{36}H_{38}N_8O_4$ (%): C, 66.86; H, 5.92; N, 17.33. Found: C, 66.95; H, 5.98; N, 17.29. HRMS-ESI (*m/z*) calcd. for $C_{36}H_{39}N_8O_4$ [M + H]$^+$ 647.3089, found 647.3093.

*4.2.4. N′¹,N′⁶-bis((E)-2-hydroxy-5-((E)-(4-nitrophenyl)diazenyl)benzylidene)adipohydrazide (**1d**)*

Yield: 77%, mp 306-307 °C; FT-IR (KBr, υ/cm^{-1}): 3447 (O–H), 3212 (N–H), 3053 (aromatic C–H), 2953 (aliphatic C–H), 1662 (C=O), 1613 (C=N), 1545 (C=C), 1517 (NO_2 asymmetric), 1483 (N=N), 1341 (NO_2 symmetric), 1284 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, 35.4%: 11.99 (s, 2H, $H_{c\ or}$ H_e), 11.79 (s, 2H, $H_{c\ or}$ H_e), 8.56-8.20 (m, 8H, H_d, H_h, H_k), 8.10-7.70 (m, 6H, H_g, H_i), 7.18-7.10 (m, 2H, H_f), 2.36-2.30 (m, 4H, H_b), 1.77-1.68 (m, 4H, H_a); syn/anti and/or anti/syn isomers, 47.9%: 11.94 (s, 1H, $H_{c\ (syn)\ or}$ $H_{e\ (syn)}$), 11.76 (s, 1H, $H_{c\ (syn)\ or}$ $H_{e\ (syn)}$), 11.40 (s, 1H, $H_{c\ (anti)\ or}$ $H_{e\ (anti)}$), 11.24 (s, 1H, $H_{c\ (anti)\ or}$ $H_{e\ (anti)}$), 8.56-8.20 (m, 8H, H_d, H_h, H_k), 8.10-7.70 (m, 6H, H_g, H_i), 7.18-7.10 (m, 2H, H_f), 2.75-2.68 (m, 2H, $H_{b\ (anti)}$), 2.36-2.30 (m, 2H, $H_{b\ (syn)}$), 1.77-1.68 (m, 4H, H_a); anti/anti isomer, 16.7%: 11.36 (s, 2H, $H_{c\ or}$ H_e), 11.03 (s, 2H, $H_{c\ or}$ H_e), 8.56-8.20 (m, 8H, H_d, H_h, H_k), 8.10-7.70 (m, 6H, H_g, H_i), 7.18-7.10 (m, 2H, H_f), 2.75-2.68 (m, 4H, H_b), 1.77-1.68 (m, 4H, H_a). The product shows low solubility in any appropriate solvents to allow for structural characterization using ^{13}C NMR. Anal. Calcd. For $C_{32}H_{28}N_{10}O_8$ (%): C, 56.47; H, 4.15; N, 20.58. Found: C, 56.55; H, 4.11; N, 20.51. HRMS-ESI (*m/z*) calcd. for $C_{32}H_{29}N_{10}O_8$ [M + H]$^+$ 681.2164, found 681.2161.

*4.2.5. N′¹,N′⁶-bis((E)-2-hydroxy-3-methoxy-5-((E)-phenyldiazenyl)benzylidene) adipohydrazide (**1e**)*

Yield: 84%, mp 277-278 °C; FT-IR (KBr, υ/cm^{-1}): 3450 (O–H), 3087 (aromatic C–H), 2991-2944 (aliphatic C–H), 1670 (C=O), 1581 (C=C), 1461(N=N), 1270 (C–O), 768, 691. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, 39.5%: 11.77 (s, 2H, $H_{c\ or}$ H_e), 11.57 (br, 2H, H_e), 8.51 (s, 2H, H_d), 7.90-7.79 (m, 6H, H_h, H_i), 7.62-7.50 (m, 8H, H_g, H_k, H_l), 3.96-3.91 (m, 6H, H_f), 2.77-2.70 (m, 2H, $H_{b\ (anti)}$), 2.34-2.30 (m, 2H, $H_{b\ (syn)}$), 1.74-1.66 (m, 4H, H_a); syn/anti and/or anti/syn isomers, 47.2%: 11.77 (s, 1H, $H_{c\ (syn)\ or}$ $H_{e\ (syn)}$), 11.57 (br, 1H, $H_{c\ (syn)\ or}$ $H_{e\ (syn)}$), 11.39 (m, 1H, $H_{c\ (anti)\ or}$ $H_{e\ (anti)}$), 10.36 (br, 1H, $H_{c\ (anti)\ or}$ $H_{e\ (anti)}$), 8.49 (s, 1H, $H_{d\ (syn)}$), 8.41 (s, 1H, $H_{d\ (anti)}$), 7.98 (d, *J* = 2.4 Hz, 1H, $H_{h\ (anti)}$), 7.90-7.79 (m, 5H, $H_{h\ (syn)}$, H_i), 7.62-7.50 (m, 7H, $H_{g\ (syn)}$, H_k, H_l), 7.48 (d, *J* = 2 Hz, 1H, $H_{g\ (anti)}$), 3.96-3.91 (m, 6H, H_f), 2.77-2.70 (m, 2H, $H_{b\ (anti)}$), 2.34-2.30 (m, 2H, $H_{b\ (syn)}$), 1.74-1.66 (m, 4H, H_a); anti/anti isomer, 13.3%: 11.38 (m, 2H, H_c), 10.36 (br, 2H, H_e), 8.39 (s, 2H, H_d), 7.96 (d, *J* = 2 Hz, 2H, H_h), 7.90-7.79 (m, 4H, H_i), 7.62-7.50 (m, 6H, H_k, H_l), 7.43 (d, *J* = 2.4 Hz, 2H, H_g), 3.96-3.91 (m, 6H, H_f), 2.77-2.70 (m, 4H, H_b), 1.74-1.66 (m, 4H, H_a). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 174.51, 174.41, 169.01, 168.96, 152.44, 152.34, 150.75, 149.77, 149.27, 145.31, 145.22, 145.11, 139.66, 139.55, 131.32, 129.90, 129.76, 122.77, 121.06, 119.54, 119.39, 118.07, 104.43, 102.70, 56.47, 56.41, 34.44, 34.31, 32.32, 32.11, 25.19, 25.11, 24.51, 24.30. Anal. Calcd. For $C_{34}H_{34}N_8O_6$ (%): C, 62.67; H, 5.26; N, 17.25. Found: C, 62.58; H, 5.18; N, 17.33. HRMS-ESI (*m/z*) calcd. for $C_{34}H_{35}N_8O_6$ [M + H]$^+$ 651.2674, found 651.2679.

*4.2.6. N′¹,N′⁶-bis((E)-5-((E)-(4-ethylphenyl) diazenyl)-2-hydroxy-3-methoxybenzylidene) adipohydrazide (**1f**)*

Yield: 88%, mp 247-248 °C; FT-IR (KBr, υ/cm^{-1}): 3416 (O–H), 3198 (N–H), 3056 (aromatic C–H), 2961-2870 (aliphatic C–H), 1670 (C=O), 1606 (C=N), 1547 (C=C), 1460 (N=N), 1267 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, 37.3%: 11.76 (s, 2H, H_c), 11.53 (br, 2H, H_e), 8.51 (s, 2H, H_d), 7.86-7.73 (m, 6H, H_h, H_i), 7.54 (d, *J* = 2.4 Hz, 2H, H_g), 7.44-7.34 (m, 4H, H_k), 3.96-3.91 (m, 6H, H_f), 2.75-2.63 (m, 4H, H_l), 2.36-2.30 (m, 4H, H_b), 1.76-1.66 (m, 4H, H_a), 1.25 (t, *J* = 7.6 Hz, 6H, H_m); syn/anti and/or anti/syn isomers, 48.5%: 11.76 (s, 1H, $H_{c\ (syn)\ or}$ $H_{e\ (syn)}$), 11.53 (br, 1H, $H_{c\ (syn)\ or}$ $H_{e\ (syn)}$),11.38 (s, 1H, $H_{c\ (anti)\ or}$ $H_{e\ (anti)}$), 10.30 (br, 1H, $H_{c\ (anti)\ or}$ $H_{e\ (anti)}$), 8.49 (s, 1H, $H_{d\ (syn)}$), 8.41 (s, 1H, $H_{d\ (anti)}$), 7.96 (d, *J* = 2.4 Hz, 1H, $H_{h\ (anti)}$), 7.86-7.73 (m, 5H, $H_{h\ (syn)}$, H_i), 7.52 (d, *J* = 2.4 Hz, 1H, $H_{g\ (syn)}$), 7.47 (d, *J* = 2.4 Hz, 1H, $H_{g\ (anti)}$), 7.44-7.34 (m, 4H, H_k), 3.96-3.91 (m, 6H, H_f), 2.75-2.63 (m, 6H, H_l, $H_{b\ (anti)}$), 2.36-2.30 (m, 2H, $H_{b\ (syn)}$), 1.76-1.66 (m, 4H, H_a), 1.25 (t, *J* = 7.6 Hz, 3H, H_m), 1.20 (t, *J* = 7.6 Hz, 3H, H_m); anti/anti isomer, 14.2%: 11.37 (s, 2H, H_c), 10.30 (br, 2H, H_e), 8.40 (s, 2H, H_d), 7.93 (d, *J* = 2.4 Hz, 2H, H_h), 7.85-7.73 (m, 4H, H_i), 7.44-7.34 (m, 6H, H_g, H_k), 3.96-3.91 (m, 6H, H_f), 2.75-2.63 (m, 8H, H_l, H_b), 1.76-1.66 (m, 4H, H_a), 1.25 (t, *J* = 7.6 Hz, 6H, H_m). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 174.48, 174.42, 168.98, 168.94, 150.71, 150.65, 150.45, 149.44, 149.24, 147.58, 147.52, 147.41, 145.37, 145.25, 145.15, 139.63, 129.22, 129.06, 122.87, 121.06, 119.50, 119.03, 117.65, 117.44, 104.51, 102.97, 102.76, 56.47, 56.41, 34.40, 34.30, 32.32, 32.18, 28.52, 25.22, 25.11, 24.52, 24.37, 15.81, 15.76. Anal. Calcd. For $C_{38}H_{42}N_8O_6$ (%): C, 64.57; H, 5.99; N, 15.85. Found: C, 64.51; H, 6.05; N, 15.97. HRMS-ESI (*m/z*) calcd. for $C_{38}H_{43}N_8O_6$ [M + H]$^+$ 707.3300, found 707.3304.

*4.2.7. N′¹,N′⁶-bis((E)-5-((E)-(4-chlorophenyl) diazenyl)-2-hydroxy-3-methoxybenzylidene) adipohydrazide (**1g**)*

Yield: 70%, mp 276-277 °C; FT-IR (KBr, υ/cm^{-1}): 3441 (O–H), 3187 (N–H), 3044 (aromatic C–H), 2958 and 2930 (aliphatic C–H), 1657 (C=O), 1605 (C=N), 1539 (C=C), 1465 (N=N), 1268 (C–O), 751 (C-Cl). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, 34.6%: 11.72 (s, 2H, H_e), 11.33 (s, 2H, H_c), 8.48 (s, 2H, H_d), 7.87-7.74 (m, 6H, H_h, H_i), 7.62-7.35 (m, 6H, H_g, H_k), 3.90-3.86 (m, 6 H, H_f), 2.31-2.30 (m, 4H, H_b), 1.72-1.66 (m, 4H, H_a); syn/anti and/or anti/syn isomers, 47.7%: 11.72 (s, 2H, $H_{e\ or}$ H_c), 11.33 (s, 2H, $H_{e\ or}$ H_c), 8.45 (s, 1H, $H_{d\ (syn)}$), 8.39 (s, 1H, $H_{d\ (anti)}$), 7.95 (d, *J* = 7.2 Hz, 1H, $H_{h\ (anti)}$), 7.87-7.74 (m, 5H, $H_{h\ (syn)}$,

H_i), 7.62-7.35 (m, 6H, H_g, H_k), 3.90-3.86 (m, 6H, H_f), 2.73-2.68 (m, 2H, $H_{b\ (anti)}$), 2.31-2.30 (m, 2H, $H_{b\ (syn)}$), 1.72-1.66 (m, 4H, H_a); anti/anti isomer, 17.7%: 11.72 (s, 2H, H_e), 11.33 (s, 2H, H_c), 8.37 (s, 2H, H_d), 7.93 (d, J = 7.2 Hz, 2H, H_h), 7.87-7.74 (m, 4H, H_i), 7.62-7.35 (m, 6H, H_g, H_k), 3.90-3.86 (m, 6 H, H_f), 2.73-2.68 (m, 4H, H_b), 1.72-1.66 (m, 4H, H_a). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 173.96, 173.83, 168.50, 168.44, 150.62, 150.55, 150.43, 149.12, 148.96, 144.96, 143.95, 139.31, 139.08, 134.83, 134.76, 129.41, 129.23, 123.76, 120.52, 119.97, 119.92, 118.99, 118.44, 118.31, 103.43, 101.83, 101.74, 55.83, 55.78, 33.89, 33.76, 31.76, 31.60, 24.68, 24.60, 24.00, 23.80. Anal. Calcd. For $C_{34}H_{32}Cl_2N_8O_6$ (%): C, 56.75; H, 4.48; N, 15.57. Found: C, 56.83; H, 4.41; N, 15.66. HRMS-ESI (*m/z*) calcd. for $C_{34}H_{33}Cl_2N_8O_6$ $[M + H]^+$ 719.1895, found 719.1893.

*4.2.8. N′¹,N′⁶-bis((E)-5-((E)-(4-bromophenyl) diazenyl)-2-hydroxy-3-methoxybenzylidene) adipohydrazide (**1h**)*

Yield: 75%, mp 273-274 °C; FT-IR (KBr, υ/cm^{-1}): 3450 (O–H), 3189 (N–H), 3043 (aromatic C–H), 2928 (aliphatic C–H), 1656 (C=O), 1606 (C=N), 1539 (C=C), 1463(N=N), 1268(C–O). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): syn/syn isomer, : 11.76 (s, 2H, H_e), 11.38-11.37 (m, 2H, H_c), 8.50 (s, 2H, H_d), 7.89 (d, J = 2.4 Hz, 2H, H_h), 7.84-7.70 (m, 8H, H_i, H_k), 7.52 (d, J = 2.4 Hz, 2H, H_g), 3.93-3.89 (m, 6 H, H_f), 2.34-2.29 (m, 4H, H_b), 1.74-1.66 (m, 4H, H_a); syn/anti and/or anti/syn isomers, : 11.76 (s, 2H, $H_{e\ or}$ H_c), 11.38-11.37 (m, 2H, $H_{e\ or}$ H_c), 8.48 (s, 1H, $H_{d\ (syn)}$), 8.40 (s, 1H, $H_{d\ (anti)}$), 7.98 (d, J = 2.4 Hz, 1H, $H_{h\ (anti)}$), 7.86 (d, J = 2.4 Hz, 1H, $H_{h\ (syn)}$), 7.84-7.70 (m, 8H, H_i, H_k), 7.52(d, J = 2.4 Hz, 1H, $H_{g\ (syn)}$), 7.46 (d, J = 2.4 Hz, 1H, $H_{g\ (anti)}$), 3.93-3.89 (m, 6H, H_f), 2.75-2.69 (m, 2H, $H_{b\ (anti)}$), 2.34-2.29 (m, 2H, $H_{b\ (anti)}$), 1.74-1.66 (m, 4H, H_a); anti/anti isomer, : 11.76 (s, 2H, H_e), 11.38-11.37 (m, 2H, H_c), 8.38 (s, 2H, H_d), 7.95 (d, J = 2.4 Hz, 2H, H_h), 7.84-7.70 (m, 8H, H_i, H_k), 7.39 (d, J = 2.4 Hz, 2H, H_g), 3.93-3.89 (m, 6 H, H_f), 2.75-2.69 (m, 4H, H_b), 1.74-1.66 (m, 4H, H_a). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 174.51, 174.38, 169.00, 168.94, 151.33, 149.36, 145.26, 144.87, 139.60, 139.43, 132.89, 132.72, 124.61, 124.46, 121.08, 120.00, 119.52, 118.66, 104.18, 102.48, 102.32, 56.53, 56.38, 56.35, 34.43, 34.31, 32.27, 32.12, 25.18, 25.10, 24.50, 24.31. Anal. Calcd. For $C_{34}H_{32}Br_2N_8O_6$ (%): C, 50.51; H, 3.99; N, 13.86. Found: C, 50.59; H, 4.07; N, 13.82. HRMS-ESI (*m/z*) calcd. for $C_{34}H_{33}Br_2N_8O_6$ $[M + H]^+$ 807.0884, found 807.0890.

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Highlight

- Eight new bis-benzylidene-hydrazides synthesized and characterized.
- Chemosensor **1d** acts as highly sensitive chromogenic sensor for CN^- and AcO^- ions.
- Bis-benzylidene-hydrazides exhibit three stereoisomers: syn/syn, anti/syn and anti/anti isomers.
- The ^1H NMR spectra revealed chemosensor recognition of CN^- via H-bonds.
- The LOD for 1d toward CN^- found to be 1.1 μM.
- For nitro bis-benzylidene-hydrazide derivative + CN^- ratio of binding chemosensor: anion is ~ 1:2.