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Colorimetric detection of cyanide with *N*-nitrophenyl benzamide derivatives

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A series of structurally simple *N*-nitrophenyl benzamide derivatives have been developed as chemosensors toward cyanide in aqueous environment by taking advantage of the cyanide's strong affinity toward the acyl carbonyl carbon. The high selectivity of these compounds toward CN^- makes it a practical system for monitoring CN^- concentrations in aqueous samples.

1. Introduction

Anion recognition is an area of growing interest in supramolecular chemistry due to its important role in a wide range of environmental, clinical, chemical, and biological applications, and considerable attention has been focused on the design of artificial receptors that are able to selectively recognize and sense anion species.[1] Among various anions, cyanide is one of the most concerned anions because it is being widely used in synthetic fibers, resins, herbicide, and the gold-extraction process.[2] Unfortunately, cyanide anion is extremely detrimental, and could be absorbed through lungs, gastrointestinal track, and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death.[3] According to the World Health Organization (WHO), only water with cyanide concentration lower than 1.9 μM is able to drink.[4] Thus, there exists a need for an efficient sensing system for cyanide to monitor cyanide concentration from contaminant sources.

Many of the cyanide anion receptors reported to date have relied on hydrogen-bonding motifs and, as a consequence, have generally displayed poor selectivities relative to other anions.[5] To overcome this limitation, reaction-based receptors, rationally designed cyanide anion indicators, have been developed recently.[6–13] This reaction-based recognition mode takes advantage of the particular feature of the cyanide ion: its nucleophilic character, and enables the recognition system with some characteristic features such as analyte-specific response and little competition from the aqueous media, which are highly desirable features for an efficient recognition and detection system. Based on this idea, nucleophilic addition of cyanide to oxazine,[6] pyrylium,[7] squarane,[8] trifluoroacetophenone,[9] acyltrazene,[10] acridinium,[11] salicylaldehyde,[12] and carboxamide[13] has been reported in recent few years, in which the interference by other anions, such as F^- and AcO^-, can be efficiently minimized.

Recently, we developed a structurally simple chemical system integrating both nitroaniline chromophore and activated amide functionality for cyanide sensing (Scheme 1). We were attracted to this system because (1) it can be obtained by simple synthetic procedures, (2) it contains an active amide carbonyl group as an electrophile[13] for the cyanide anion and a nitroaniline group as a latent chromogenic moiety, and (3) various control compounds, with other modifications of the skeleton, would be readily available, supplying a base for systematic studies toward recognition motifs for cyanide. It is expected that cyanide is detectable by nucleophilic attack toward the activated amide carbonyl function followed by fast proton transfer of the acidic amide hydrogen to the developing alkoxide anion of this compound.[12] The proton transfer may trigger the latent chromogenic nitroaniline group into an active state (its anionic state), thus resulting in the enhancement of the push–pull character of the intramolecular charge transfer (ICT) transition, which is possibly reflected in the new red-shifted absorption. Herein, we wish to report the design, synthesis of these probes, and their unique interaction mode with cyanide.

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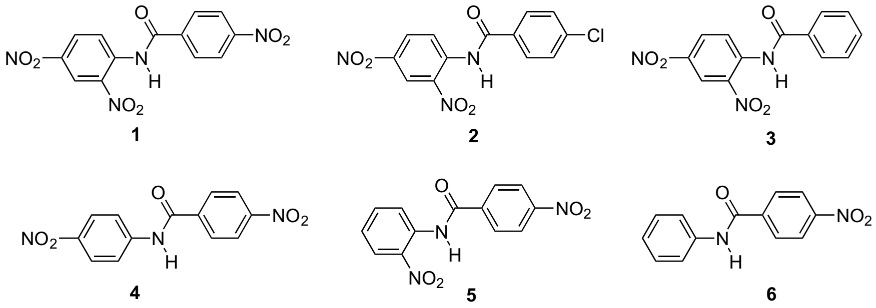


Scheme 1. The chemosensors evaluated in this study.

2. Results and discussion

2.1. Synthesis and crystal structure

The synthesis of these receptors is straightforward. Treatment of 4-substituted benzoyl chloride with corresponding aromatic amines in CH_2Cl_2 in the presence of triethylamine afforded the objective compounds (**1**–**5**). A control compound (**6**) was also synthesized according to the same procedures. All of the compounds were characterized by NMR, IR, and MS spectroscopy, and elemental analysis. Crystal of receptor **1** suitable for X-ray crystallography was also obtained on slow evaporation of MeOH solution of **1**. In an attempt to characterize the conformation, the crystal structure of **1** was determined by single crystal X-ray diffraction, as shown in Figure 1. The most interesting feature of the structure is the coplanarity of amide—2,4-dinitrophenyl unit, indicating the optimal conformation for ICT process resulting from the delocalization of electron on the nitrogen of amide group toward electron-withdrawing 2,4-dinitrophenyl unit.

2.2. UV–vis titration studies of compound 1

The UV–vis absorption is one of the most interesting output signals not only because the instrumentation is widely available, but also because it would be possible to sense target species with the naked eye. In order to obtain the systematic knowledge on the photochemical properties of these sensing systems in solution and to estimate the possible absorption mechanism, we first studied the absorption spectra of **1** in various DMSO–H_2O mixtures [9:1, 8:2, 7:3, 6:4, and 1:1 of DMSO–H_2O (v/v), respectively]. As shown in Figure 2, compound **1** displayed an obvious absorption at 441 nm, giving a yellow solution in 9:1 DMSO–H_2O. However, with further increase of water, the absorption band fades along with a blue shift, giving a pale yellow solution. In 1:1 DMSO–H_2O (v/v), the absorption band completely disappeared, giving an almost colorless solution.

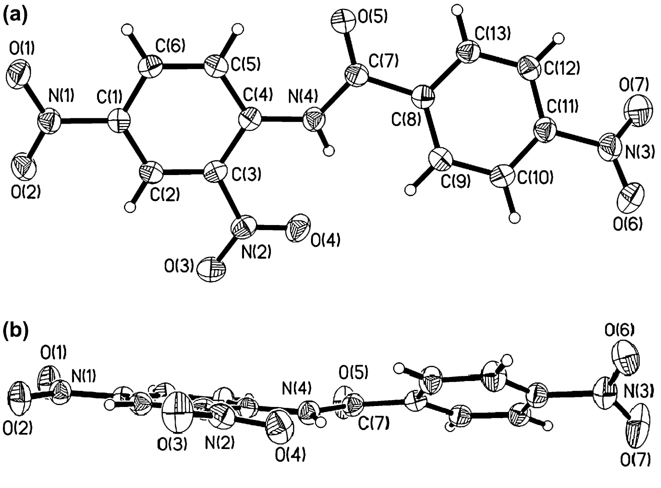


Figure 1. The single crystal X-ray structure of sensor **1**.

We speculate that the color change of **1** observed in the mixture of DMSO–H_2O should be originated from a deprotonated species due to an acidic ionization, that is, the corresponding anion of **1**, which enhanced the charge-transfer interactions between the electron-rich donor unit and the electron-deficient 2,4-dinitrophenyl moiety, resulting in a visible color change. The assumption could be supported by the following facts: upon addition of acid, such as TsOH or HCl, to the mixture of 9:1 DMSO–H_2O solution of **1**, the absorption at 441 nm disappears; however, upon addition of base, such as Et_3N or NaOH, to the mixture of 1:1 DMSO–H_2O solution of **1**, the strong absorption at 405 nm is observed (see Figs. S1 and S2). It appears that water plays a key role in inhibiting the acidic ionization of **1**, as shown in 1:1 DMSO–H_2O. While the detailed mechanism on water effect is plausible at present, the feature has been utilized by us to sense cyanide with high selectivity.

Next, in order to gain systematic knowledge on the effect of water on the binding affinity and selectivity for cyanide, we chose DMSO–H_2O mixtures as solvents (9:1, 7:3, and 1:1 of DMSO–H_2O (v/v), respectively) and various anions of present interest, namely, CN^-, F^-, Cl^-, Br^-, I^-, ClO_4^-, AcO^-, $H_2PO_4^-$, NO_3^-, and N_3^- as their sodium salts were added to the solution of **1**, respectively. The corresponding absorption spectra upon addition of different anions in DMSO–H_2O mixtures are shown in Figure 3. In 9:1 DMSO–H_2O, compound **1** displayed a strong absorption band at 441 nm, and CN^-, F^-, and AcO^- showed slight effect to the band, whereas less basic anions such as Cl^-, Br^-, I^-, ClO_4^-, $H_2PO_4^-$, NO_3^-, and N_3^- showed less or no effect (Fig. 3a). In 7:3 DMSO–water, only CN^-, F^-, and AcO^- showed obvious interaction with the sensor **1** (Fig. 3b), but, the selectivity for CN^- was rather poor due to the interference of F^- and AcO^-. However, to our delight, a remarkably higher selectivity for CN^- over the other anions were obtained in 1:1 DMSO–H_2O, and other anions tested did not cause any significant changes in the absorption intensity, even at a concentration of 100 equiv of guests (Fig. 3c).

The above results indicate that the selectivity for CN^- is greatly influenced by water. In 1:1 DMSO–H_2O, anions such as F^- and AcO^- could interact with the aqueous medium through H-bonding, and this salvation leads to a decrease in their basicity, thus, resulting in the poor deprotonation reaction. In contrast, cyanide has much weaker H-bonding ability in comparison with F^- and AcO^- but has stronger carbonyl carbon affinity, which results in the addition reaction of CN^- to carbonyl carbon. Subsequent proton transfer of amide hydrogen to the developing alkoxide anion of **1** produces an active state (its anionic state) of **1**, which enhanced the charge-transfer interactions between the electron-rich and electron-

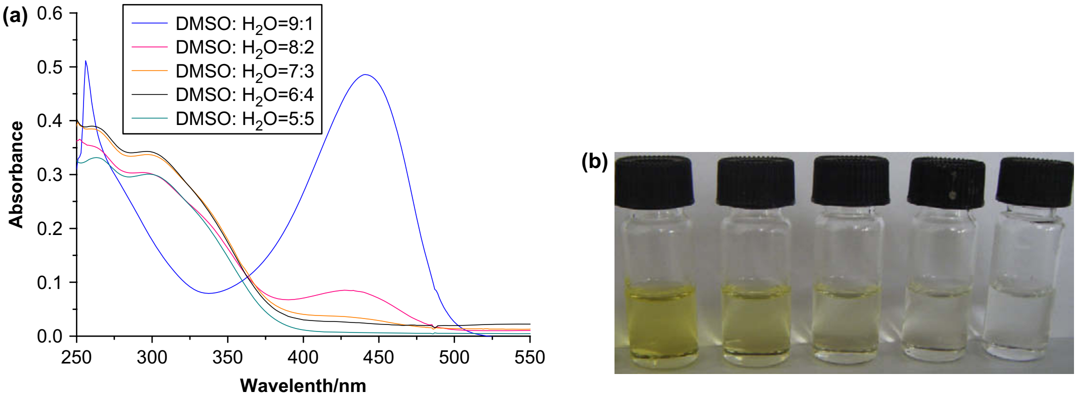


Figure 2. (a) Absorption spectra of sensor **1** (20 µM) in different DMSO–H_2O systems. (b) Color changes in the mixture of DMSO–H_2O, from left to right: 9:1, 8:2, 7:3, 6:4, 1:1 of DMSO–H_2O (v/v), respectively.

deficient moieties, resulting in a visible color change (Scheme 2). In addition, ^1H NMR titration experiments were carried out by addition of cyanide to the mixture of deuterated DMSO–water. With the increasing addition of cyanide, all the aromatic protons exhibited an upfield shift to different extent (Fig. 4). This upfield shift is due to the fact that after the addition reaction of CN^- to carbonyl carbon and subsequent proton transfer of amide hydrogen to the developing alkoxide anion of **1**, the electron density in the aromatic ring increases, which results in an upfield shift of the protons. The formation of cyanide adduct was further confirmed by mass spectroscopy. The electrospray ionization mass spectrum of the cyanide adduct showed a molecular mass of 652 (Fig. S3), which corresponds to the formula of [cyanide adduct+Bu_4N^++$2CN^-$]. The above results clearly demonstrate that a highly selective detection system for cyanide can be developed on the basis of the specific chemical reaction.

To quantitatively study the cyanide-sensing ability of **1** in 1:1 DMSO–H_2O mixture, UV–vis monitoring was performed by using 20 µM solution of **1** at room temperature. Upon addition of cyanide anions, the absorption peak at 305 nm decreased, and a new peak appeared at 405 nm, red-shifted by a $\Delta\lambda_{max}$ of 100 nm; the absorption intensity at 405 nm increased 60-fold and was saturated at 20 equiv of cyanide (Fig. 5a). The isosbestic point at 376 nm indicated a clean conversion throughout the titration process. Job analysis for the complexation of **1** and cyanide corroborated the 1:1 binding stoichiometry (Fig. 5b). Nonlinear least-squares regression analysis[14] of these changes gave a binding constant of 1.1×10^5 M^{-1}.

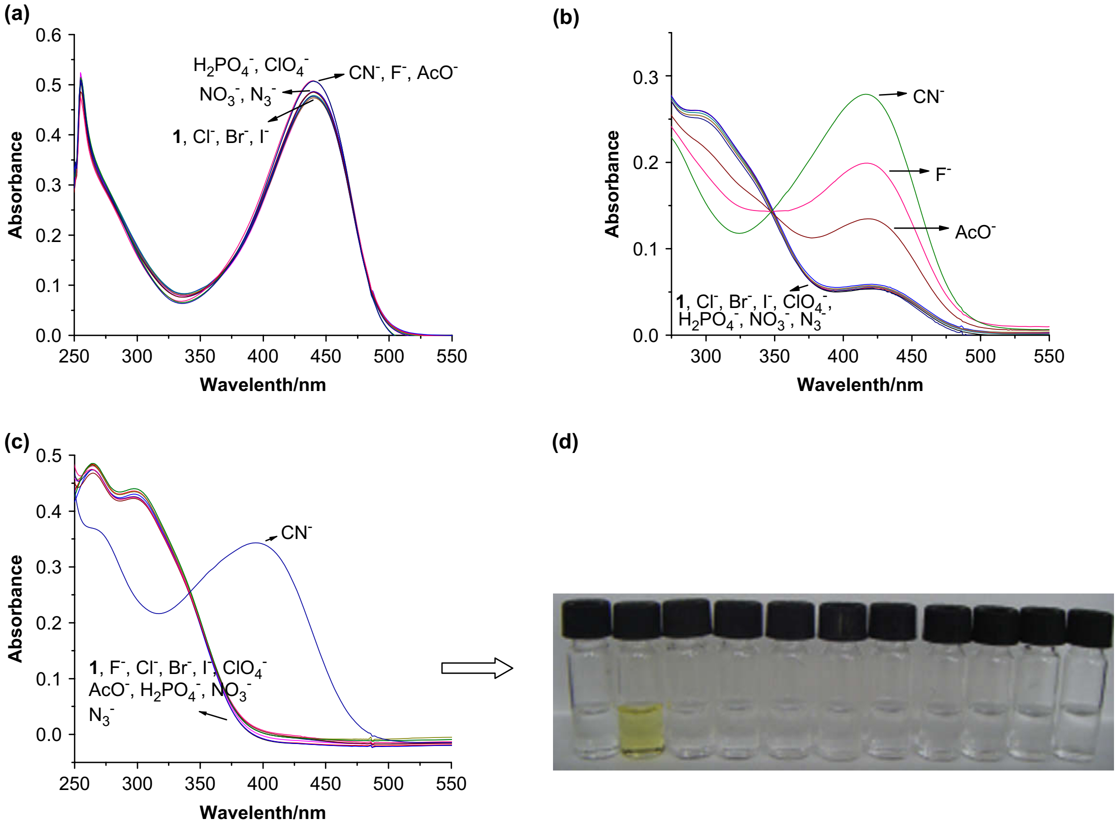
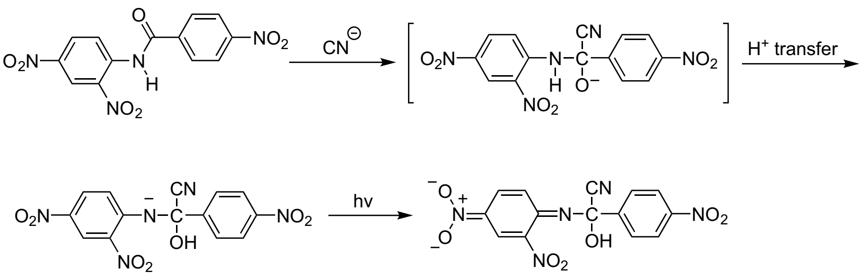


Figure 3. Absorption spectra of **1** (20 µM) on addition of various anions in different DMSO–H_2O (v/v). (a) 9:1 DMSO–H_2O, 10 equiv of anions; (b) 7:3 DMSO–H_2O, 10 equiv of anions; (c) 1:1 DMSO–H_2O, 10 equiv of CN^- and 100 equiv of other anions; (d) the corresponding color changes in (c), vials from the left: only **1**, CN^-, F^-, Cl^-, Br^-, I^-, ClO_4^-, AcO^-, $H_2PO_4^-$, NO_3^-, and N_3^-.



Scheme 2. The proposed sensing mechanism of **1** for cyanide.

The selectivity of the system for cyanide was then examined by competition experiments. Figure 6 shows UV–vis intensity changes upon addition of cyanide when 100 equiv of F^-, Cl^-, Br^-, I^-, ClO_4^-, AcO^-, NO_3^-, and N_3^- except for $H_2PO_4^-$ are also present. The absorption intensity was almost identical to that obtained in the absence of anions. However, $H_2PO_4^-$ caused a decrease in absorption intensity when 10 equiv of it were added, possibly resulted from the protonation of the cyanide adduct by $H_2PO_4^-$, thus, decreasing the absorption intensity, which is consistent with our proposed mechanism depicted in Scheme 2.

The limits for detecting cyanide by using **1** as a colorimetric sensor were also determined. A plot of (A–A_0) versus [CN^-] in DMSO–water (1:1, v/v) gave a linear relationship (see Fig. S4). The detection limit in DMSO–H_2O (1:1, v/v) was determined to be 0.87 μM, which corresponds to 1.74 μM of [CN^-] in pure water. Therefore, the system base on **1** can be used to detect the WHO suggested maximum allowed cyanide concentration in drinking water (1.9 μM).

2.3. Anion binding studies of 2–5

In order to obtain the knowledge on the effect of substituted groups on the binding affinity and selectivity for cyanide, we repeated these measurements using compounds **2**–**5** in 1:1 DMSO–H_2O system (Figs. S5–S8). Similar to the case of **1**, high selectivity for cyanide was also observed for all these compounds. However, the lower binding constants for **2**–**5** toward cyanide compared with **1** indicate the poor sensitivities of these compounds to cyanide [binding constants (M^{-1}): 3.4×10^4, 4.9×10^3, 2.9×10^2 and 5.5×10^2 for **2**–**5**, respectively]. It seems that the electron-withdrawing substituted groups in benzamide unit can activate the amide carbonyl, favoring nucleophilic addition reaction of cyanide, while in aniline unit will favor the proton transfer of amide hydrogen to the developing alkoxide anion upon cyanide attack, both of which are important to develop such type of chemosensors toward cyanide. In addition, the strongly electron-withdrawing nitro group in benzamide unit is important for the charge-transfer interaction in our studies. For example, when the sensing ability of **6** was evaluated, no any discernible spectral change could be induced upon addition of various anions.

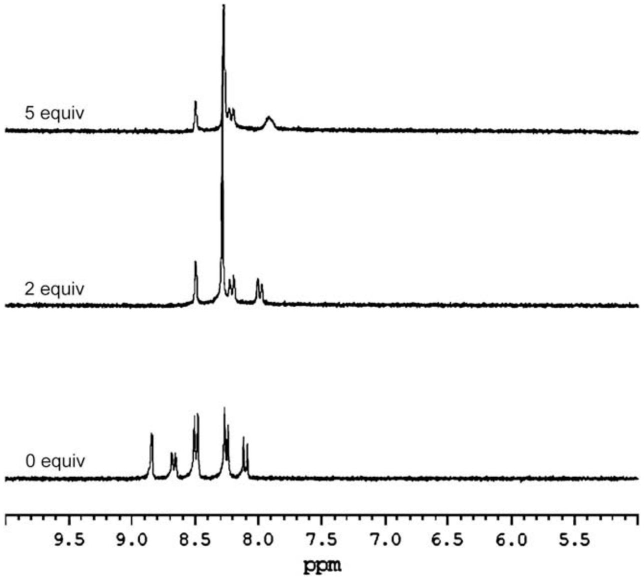


Figure 4. Plots of ^1H NMR spectra of **1** on addition of cyanide in the mixture of deuterated DMSO–water.

3. Conclusions

In conclusion, we have developed a series of simple nitroaniline-based benzamide compounds (**1**–**5**) for the 'naked-eye' detection of cyanide in aqueous environment with high selectivity. These compounds react with CN^- in a 1:1 stoichiometric manner, a process which induces a large enhancement in absorption intensity and a marked color changes from colorless to yellow in DMSO–H_2O (1:1, v/v) at room temperature. Importantly, the selectivity of this system for CN^- over other anions is extremely high. In addition, the detection limit of **1** for CN^- falls below the WHO detection level. Therefore, the chemosensor **1** appears to be a practical system for monitoring CN^- concentrations in aqueous samples.

4. Experimental

4.1. General

Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Huanghai GF_{254} silica gel coated plates. Flash chromatography (FC) was carried out using silica gel 60 (230–400 mesh). Absorption spectra were taken on a Varian Cary 300 absorption Agilent 8453 UV–vis spectroscopy system using a 1-cm quartz cell. The ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. The following abbreviations were used to explain the multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; m=multiplet; br=broad. Mass spectra were recorded by EI method.

4.2. General procedure for the preparation of compounds 1–6

Under nitrogen atmosphere, a mixture of substituted aniline (10 mmol), substituted benzoyl chloride (12 mmol), and Et_3N (15 mmol) in dry CH_2Cl_2 (200 mL) was stirred at room temperature for 6 h, and then under reflux condition for another 12 h. After completion of reaction (monitored by TLC), the volatile was

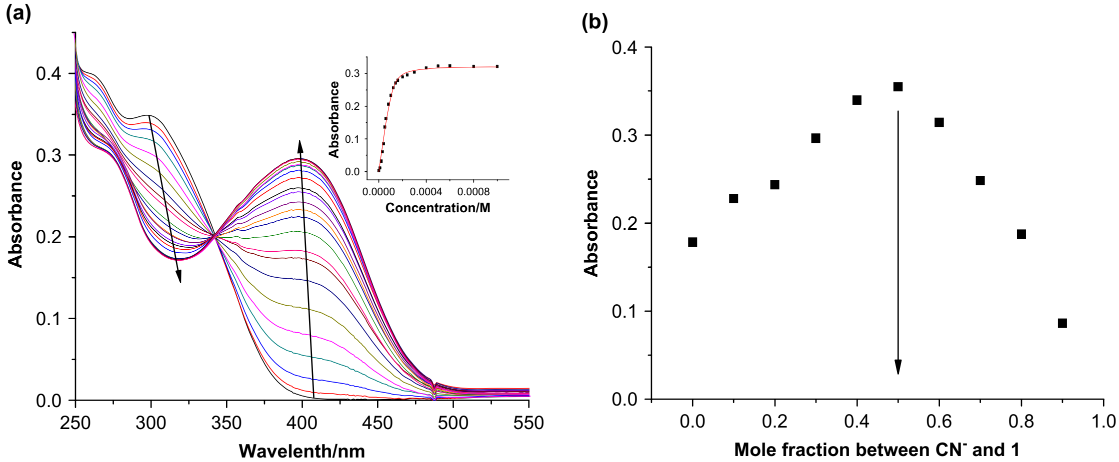


Figure 5. (a) Absorption spectra changes of sensor **1** (20 μM) upon addition of CN^- (0–40 equiv) in DMSO–H_2O (1:1, v/v) at room temperature. Inset: plot of absorption intensity at 405 nm versus the concentration of CN^-. (b) Job's plot between **1** and cyanide anion.

removed under vacuum. The residue was washed with 3 M hydrochloric acid (200 mL) to give crude product. Recrystallization of the crude product from acetone gave the corresponding compounds (**1**–**6**).

4.2.1. *Compound **1***

Yellow solid. Yield: 36%. Mp: 199–200 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 11.46 (s, 1H), 8.74 (s, 1H), 8.60 (d, J=9.0, 1H), 8.41 (d, J=8.4, 2H), 8.19 (d, J=8.4, 2H), 8.03 (d, J=9.0, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 158.3, 144.0, 137.5, 135.7, 132.5, 130.6, 123.6, 122.7, 120.4, 118.1, 115.3. IR (KBr): 3329, 1697, 1521, 1508, 1338. MS (m/z): 331 $(M-1)^+$. Anal. Calcd for $C_{13}H_8N_4O_7$: C, 47.00; H, 2.43; N, 16.86. Found: C, 47.23; H, 2.52; N, 16.76.

4.2.2. *Compound **2***

Brown solid. Yield: 45%. Mp: 203–204 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 11.27 (s, 1H), 8.77 (s, 1H), 8.62 (d, J=9.0, 1H), 8.11 (d, J=9.0, 1H), 8.02 (d, J=8.4, 2H), 7.72 (d, J=8.4, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): 159.7, 136.9, 135.0, 131.5, 127.1, 123.0, 122.8, 122.1, 119.7, 115.3. IR (KBr): 3317, 1695, 1500, 1332. MS (m/z): 321 (M^+). Anal. Calcd for $C_{13}H_8ClN_3O_5$: C, 48.54; H, 2.51; N, 13.06. Found: C, 48.48; H, 2.56; N, 13.15.

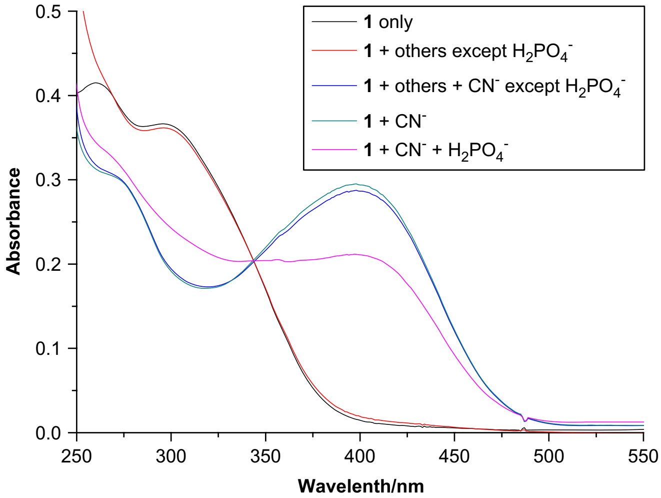


Figure 6. Absorption spectral of **1** (20 μM) in DMSO–H_2O (1:1, v/v) in the presence of various anions except $H_2PO_4^-$ (CN^-, $H_2PO_4^-$: 10 equiv; other anions: 100 equiv).

4.2.3. *Compound **3***

Orange solid. Yield: 40%. Mp: 193–194 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 11.22 (s, 1H), 8.76 (s, 1H), 8.59 (d, J=9.0, 1H), 8.15 (d, J=9.0, 1H), 7.97 (d, J=8.4, 2H), 7.69 (t, J=11.4, 1H), 7.60 (t, J=11.4, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): 159.1, 137.4, 135.6, 132.3, 131.5, 126.0, 125.6, 124.4, 123.4, 123.0, 120.3, 115.6. IR (KBr): 3336, 1695, 1500, 1336. MS (m/z): 287 (M^+). Anal. Calcd for $C_{13}H_9N_3O_5$: C, 54.36; H, 3.16; N, 14.63. Found: C, 54.47; H, 3.33; N, 14.75.

4.2.4. *Compound **4***

Brown solid. Yield: 62%. Mp: decomposed >190 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 11.09 (s, 1H), 8.37 (d, J=8.4, 2H), 8.28 (d, J=8.4, 2H), 8.18 (d, J=9.0, 2H), 8.04 (d, J=9.0, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): 159.1, 143.9, 139.4, 137.3, 134.3, 124.0, 119.3, 118.1, 114.5. IR (KBr): 3369, 1684, 1519, 1496, 1332. MS (m/z): 287 (M^+). Anal. Calcd for $C_{13}H_9N_3O_5$: C, 54.36; H, 3.16; N, 14.63. Found: C, 54.50; H, 3.29; N, 14.52.

4.2.5. *Compound **5***

Yellow solid. Yield: 66%. Mp: 272–273 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 11.14 (s, 1H), 8.42 (d, J=9.0, 2H), 8.32 (d, J=9.0, 2H), 8.24 (d, J=9.0, 2H), 8.09 (d, J=9.0, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): 159.1, 144.1, 139.4, 137.6, 134.5, 123.9, 119.2, 118.0, 114.5. IR (KBr): 3373, 1685, 1519, 1506, 1332. MS (m/z): 287 (M^+). Anal. Calcd for $C_{13}H_9N_3O_5$: C, 54.36; H, 3.16; N, 14.63. Found: C, 54.30; H, 3.27; N, 14.48.

4.2.6. *Compound **6***

White solid. Yield: 74%. Mp: 218–219 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 10.55 (s, 1H), 8.35 (d, J=8.4, 2H), 8.17 (d, J=8.4, 2H), 7.76 (d, J=8.1, 2H), 7.36 (t, J=7.5, 2H), 7.12 (t, J=7.5, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): 179.3, 150.4, 141.8, 139.9, 130.4, 129.9, 125.4, 124.8, 121.7. IR (KBr): 3322, 1653, 1532, 1348. MS (m/z): 242 (M^+). Anal. Calcd for $C_{13}H_9N_3O_5$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.33; H, 4.27; N, 11.45.

4.3. Crystallographic data for 1

Single crystal **1** was obtained from MeOH solution. Crystallographic data: molecular formula: $C_{13}H_8N_4O_7$, crystal size: 0.30×0.20×0.20, M=332.23, monoclinic, space group: $P2(1)/n$, a=7.039(3) Å, b=20.787(6) Å, c=9.423(3) Å, $\alpha=\beta=90°$; γ=92.08(5)°, V=1377.8(8), T=293(2) K, d_{calcd}=1.602 g/cm^3, $F(000)$=680, 5449 reflections measured, 2394 unique (R_{int}=0.0200), 1939 with

$I>2\sigma(I)$. The final $R_1=0.0396(I>2\sigma)$, 0.0492 (all data), $wR_2=0.1085(I>2\sigma)$, 0.1159 (all data).

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.023.

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