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Simple naked-eye ratiometric and colorimetric receptor for anions based on azo dye featuring with benzimidazole unit

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ABSTRACT

A simple, tailor made receptor **2** based on azo dye featuring with benzimidazole unit with hybrid –OH and –NH binding sites was synthesized and characterized. The addition of CN^-, AcO^-, F^-, and $H_2PO_4^-$ in acetonitrile solution of **2** resulted in a large bathochromic shift from 315 nm to 470 nm allowing naked eye color change from colorless to orange. Anion sensing characteristics were determined using visual inspection, UV–vis and ^1H NMR spectroscopy pointing toward the improved chromogenic ability after introduction of —N=N— group in the azo dye **2**. The mechanism of anion binding with receptor **2** showed 1:2 (L/Anion) and the association constants were found in the order of $AcO^- > CN^- > F^- > H_2PO_4^-$.

Introduction

The development of receptors which undergo a color change on addition of an analyte has attained great significance in the area of supramolecular chemistry.[1] The colorimetric-based sensing has shown unique merit, as it provides naked-eye detection of the analyte without resorting to any expensive equipment.[2] In general, the design of such receptors is based on the receptor-chromophore general binomial, which involves the binding of a specific analyte with receptor sites and a chromophore responsible for translating the binding of receptor–analyte into an optical signal.[3] In colorimetric receptors, due to its interaction with the analyte, bathochromic or hypsochromic shift of absorption spectra or visual color change is affected by the respective increase or decrease in electron densities on the chromophore moiety.[4]

Owing to the ubiquity of anions and their importance as agricultural fertilizers and industrial raw materials, the development of anion sensing receptors received considerable attention.[5] In recent years, the development of chromogenic anion sensors is mainly based on the anion induced polarization/deprotonation (in extreme cases) of OH in case of appropriately substituted phenols and NH in case of appropriately substituted anilides and aryl ureas.[6–8] Anions particularly fluoride, cyanide, and phosphate are not only released by industries but are also the degradation products (hydrolysis) of chemical warfare agents such as sarin, soman, and tabun, making them harmful to the environment as well as to human health.[9] Among various anions, cyanide is an extremely toxic detrimental anion causing poisoning in biology; environment, and even relatively small amounts of this species are lethal to humans.[10] Moreover, raw materials for synthetic fibers, resins, herbicides, and the gold-extraction process releases cyanide into the environment as a toxic contaminant. So, the colorimetric sensors for determination of anions are big challenges for investigators and they attract much interest.

It is well known that azo colorants are the largest chemical class of industrial colorants. They represent a robust group of synthetic dyes, which cover the full range of shades of colors. Their ease of preparation and economy of the reaction resulted in a large number of dyes.[11] Azo dyes possessing an aromatic heterocyclic moiety increased the chromophoric strength and thus, have been reviewed comprehensively.[12] Benzimidazole and its derivatives have been studied in anion and cation recognition systems that display color changes or fluorescence quenching or enhancement upon binding.[13]

This paper describes the design and synthesis of a new and simple anion receptor 2-(1-*H*-benzoimidazol-2-yl)-4-(pyridine-3-ylazo)-phenol (**2**) containing both azo dye and benzimidazole and photophysical study of its anion recognition behaviors. In addition, the sensing processes can be realized by the 'naked eye' determination as it has a remarkable color response.

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Results and discussions

Synthesis of receptor 2

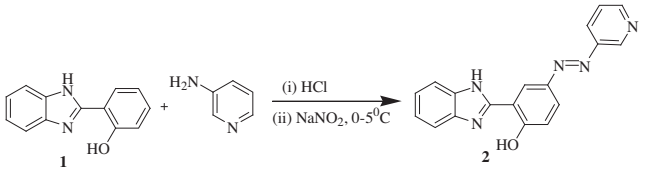
The preparation of receptor **2** based on the azo dye of benzimidazole was carried out by diazo-coupling reaction as shown in Scheme 1. The chemical structure of the newly synthesized chemosensor was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectral data.

Sensing properties of receptor 1

To study the role of azo functionality in receptor **2**, the sensing abilities of **1** were primary investigated by adding various anions such as CN^-, F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, and HSO_4^- (tetrabutyl ammonium was used as a counter anion) to its CH_3CN solution (10 μM). The addition of 5 equiv of these anions did not cause any change in the absorption spectrum; however, further addition of these anions up to 50 equiv resulted in the emergence of a very weak charge transfer band at 374 nm with CN^- and F^- ions (Fig. 1), but the spectral changes were too small to calculate the corresponding association constants. Earlier results show that the addition of 5 equiv of F^- ions to a solution of receptor **1** in DMSO caused only a small bathochromic shift of 11 nm. Whereas, other anions did not induce any significant changes in the absorption spectra.[14] However, by changing the polarity of the solvent from DMSO to CH_3CN, the small bathochromic shift observed with the addition of 5 equiv of F^- ion gets diminished and requires higher equivalents of anions to cause only a small red-shift.

Colorimetric signaling of (2)

As the presence of the —N=N— group improves the chromogenic ability of the chemosensors, therefore, after introducing the azo functionality in the receptor **2**, both the colorimetric and absorption changes were greatly enhanced in CH_3CN itself. In naked-eye experiment (Fig. 2), receptor **2** (10 μM) responded with a dramatic color change from colorless to dark yellow with the addition of 50 equiv of CN^-, F^-, AcO^-, and $H_2PO_4^-$, which indicates the formation of host–guest complex between these anions and **2**. However, no obvious color change was observed in the case of Cl^-, Br^-, I^-, and HSO_4^- ions, even when these anions were added in excess, presumably due to weaker and insignificant interactions with the receptor.



Scheme 1. Synthetic procedure for receptor **2**.

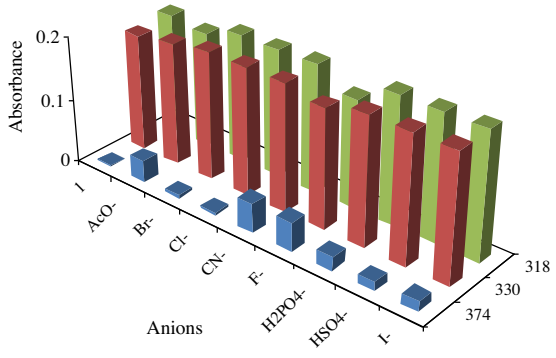


Figure 1. UV–vis absorbance of **1** (10 μM) in the presence of 100 equiv of anions in CH_3CN.

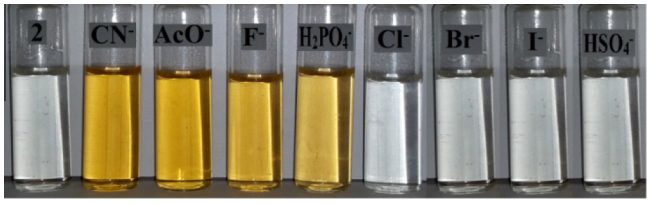


Figure 2. Naked-eye images of **1** in CH_3CN upon the addition of various anions (100 equiv).

UV–vis spectral studies

The qualitative anion sensing behavior of **2** was determined by recording the absorption spectra. In the UV–vis spectra of **2** (10 μM) in acetonitrile media, the receptor peak is characterized by the appearance of a band centered at 315 nm with a shoulder near 365 nm. Upon interaction with CN^-, F^-, AcO^-, and $H_2PO_4^-$ ions, a new intramolecular charge transfer band has been observed at 470 nm. UV–vis titrations were next carried out with increasing concentrations of CN^-, F^-, AcO^-, and $H_2PO_4^-$ anions. Upon addition of CN^- ions to a solution of receptor **2** (10 μM) in CH_3CN, a new band starts emerging at 470 nm with the addition of only 0.2 equiv of CN^- ions. However, after adding 3 equiv of CN^- ions, a sharp and gradual increase in intensity of the new band has been observed along with gradual decrease in absorbance of the 315 nm band (Fig. 3).

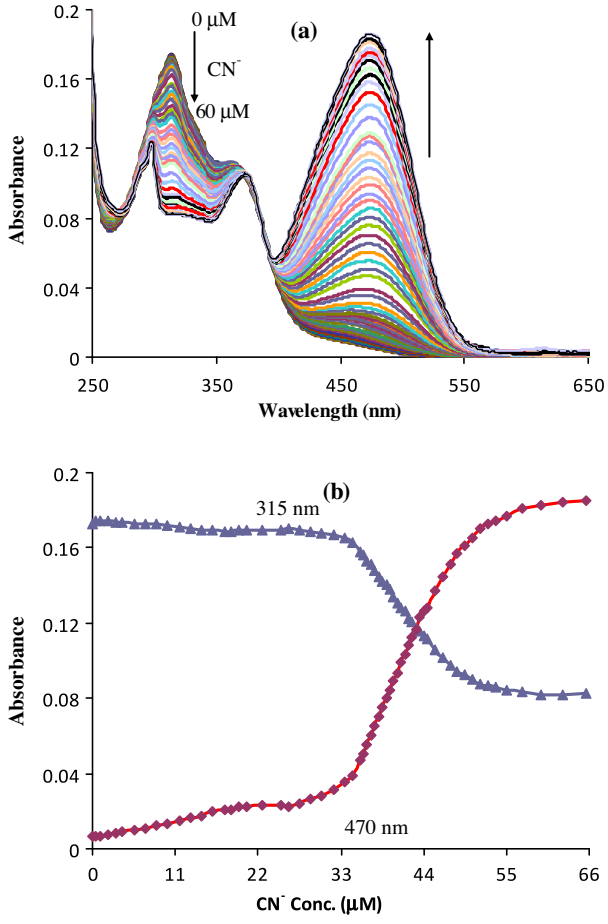


Figure 3. Evolution of the UV–vis spectrum of receptor **2** (10 μM in CH_3CN) during the titration of the CN^- ion; (b) plot of absorbances at 315 and 470 nm vs the concentration of CN^- added.

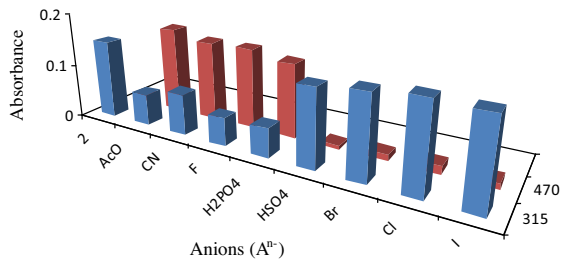


Figure 4. UV–vis absorbance of **2** (10 μM) in the presence of 100 equiv of anions in CH_3CN.

Table 1
Association constants (K_{ass}, M^{-2}) of receptor **2** with different anions and the respective number of equivalents required for achieving saturation in CH_3CN

Anions	Number of equiv required for saturation	K_{ass}
CN^-	5	9.54×10^9
AcO^-	3	5.01×10^{10}
F^-	15	8.8×10^8
$H_2PO_4^-$	50	1.03×10^7

The absorbance increases nearly thirtyfold at 470 nm which is responsible for the generation of a yellow color after the addition of CN^- into the solution of the receptor **2** (Fig. 3b). After addition of 5.0 equiv of tetrabutylammonium cyanide, it reaches a saturation level. However, the presence of a protic solvent such as H_2O will compete with anions for binding sites. This will disturb the H-bond interactions between the receptor and the anionic guest and will lead to a reversal of the visual color and spectral change.

Similar effects were observed in the UV–vis spectra of **2** upon the addition of AcO^-, F^-, and $H_2PO_4^-$ ions (Figs. S1–S3). Addition of these three ions resulted in the appearance of a new red shifted band at 470 nm; however, their higher equivalents are required for achieving saturation. In the case of weak basic ions such as Cl^-, Br^-, I^-, and HSO_4^-, only nominal changes are observed in the UV–vis spectra (Fig. 4).

The sigmoidal shape of the titration curve observed in **2** with CN^- is remarkable and characteristic of cooperative binding. The best fit corresponds to a stoichiometry of 1:2 (1igand/anion) and the stability constant is 9.54×10^9 M^{-2}.[15] Thus, in accordance with the 1:2 stoichiometry, the possible binding mode between **2** toward CN^- has been proposed in Scheme 2. The respective stability constants and number of equivalents required for achieving saturation with various anions are tabulated in Table 1. The stability constant values reveal that the AcO^- ion binds most strongly and interaction with various anions is in the order of $AcO^- > CN^- > F^- > H_2PO_4^-$. This could be due to more stabilization of negative charge on the acetate oxygen as compared to the negative charge on the benzimidazole nitrogen. Thus intermolecular proton transfer occurs from phenyl OH to the acetate ion rather than proton transfer to the benzimidazole nitrogen.[16] The association constant values of receptor **2** with other anions, that is, CN^-, $H_2PO_4^-$, and HSO_4^- follows the order of basicity of anions.

^{1}H NMR titrations

To further elucidate the nature of the intermolecular interactions between anions and receptor **2**, as an example, ^{1}H NMR spectral changes upon the addition of CN^- as their tetrabutyl ammonium salts to the DMSO-d_6 solution of **2** (5×10^{-2} mol L^{-1}) were investigated. The formation of the hydrogen bond (deprotonation in extreme cases) between the binding sites of the host and the anion may give rise to two effects: (i) through-bond effects, which increase the electron density of the benzene ring and promote upfield shifts in ^{1}H NMR spectrum, and (ii) through-space effects, which polarize the C–H bond in proximity to the hydrogen bond, create the partial positive charge on the proton and cause downfield shifts.[17] In Figure 5, the broad band at δ 13.91 has been assigned to –OH and –NH groups. Addition of 0.5 equiv of CN^- results in disappearance of this broad band. Moreover, all the aromatic protons especially phenyl protons of rings possessing the –OH group present at δ 7.21–7.28 as multiplets clearly split into a doublet at δ 6.70–6.73 and a singlet at δ 7.05 and give an upfield shift, indicative of the increase in the electron density of the phenyl ring owing to the through-bond effects. Thus, the results of ^{1}H NMR titration and UV–vis titrations, both, point to the occurrence of tautomeric equilibrium during the anion recognition process as shown in Scheme 2.

Possible sensing mechanism

The appearance of a new red-shifted band with the addition of anions (CN^-, AcO^-, F^- and $H_2PO_4^-$) to a solution of receptor **2** may be attributed to the possible hydrogen bonding interaction and/or the deprotonation of the –OH and imidazole-NH groups, rather than ESIPT (excited state intramolecular proton transfer) with the benzimidazole nitrogen atom, which favored the intramolecular charge transfer (ICT) transition within the whole molecule. However, ^{1}H NMR titration of receptor **2** with CN^- reveals that deprotonation of both –OH and –NH occurs upon CN^- addition (Fig. 5). Prior to coordination with anions, the azophenol isomer of receptor **2** dominates in solution which attributes to the 315 nm band. Upon interaction with anions, deprotonation of the –OH group occurs, which will reinforce the formation of hydrazone via azophenol to quinone-hydrazone tautomerization (Scheme 2).[18] This will result

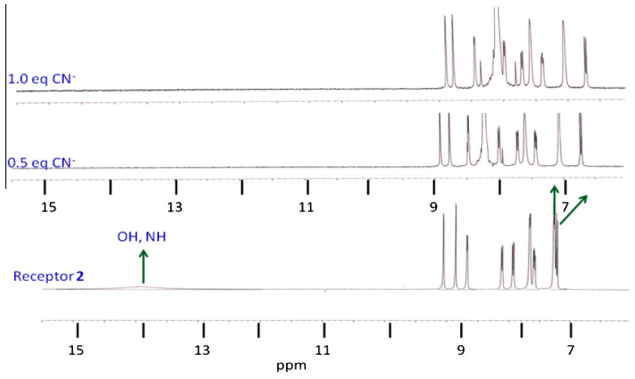
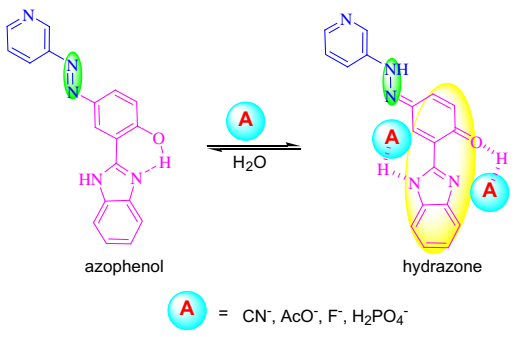


Figure 5. Partial ^{1}H NMR titration of **2** (5×10^{-2} M) in DMSO-d_6 with $[BuN_4]CN$.



Scheme 2. Proposed binding mode of receptor **2** with anions in solution.

in a band at longer wavelength, that is, 470 nm allowing for visual naked-eye detection.

Conclusions

In summary, we have synthesized a simple azo-dye **2** featuring with benzimidazole group. The presence of —N=N— group in receptor **2** improves the chromogenic and sensing ability toward CN^-, F^-, AcO^-, and $H_2PO_4^-$ in CH_3CN. Presence of these anions resulted in a naked-eye color change from light yellow to dark yellow. Other weak basic ions such as Cl^-, Br^-, I^-, and HSO_4^- did not cause any changes in the UV–vis spectra. In particular, a tautomeric equilibrium might have occurred during the anion recognition whose different electronic properties are responsible for the observed color and spectral changes.

Experimental

Synthesis of 2-(1*H*-benzoimidazol-2-yl)-phenol (1)

The receptor **1** was synthesized according to the literature reported.[19] A mixture of *o*-hydroxy benzaldehyde (4 mmol), *o*-phenylenediamine (4.5 mmol) and PEG-400 (0.1 ml) were taken together and heated in a microwave oven at 110 °C, 600 W for 10 min. After completion of the reaction (tlc), the product was directly recrystalized from hot methanol to afford pure **1**. Light pale yellow solid, yield 82%, mp 142 °C, IR (cm^{-1}): 3318 (ν_{O-H}, H-bonded), 3232 (ν_{N-H}), 3055 ($\nu_{Aromatic\ C-H}$). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.94 (dd, J_1 = 11.8, J_2 = 6.0 Hz, 2H, C_4,Ar-H), 7.23 (dd, J_1 = 5.16, J_2 = 2.88 Hz, 2H, Ar-H), 7.32 (t, J = 5.85 Hz, Ar-H), 7.60 (s, 2H, Ar-H), 7.98 (d, J = 5.88 Hz, 1H, Ar-H), 13.11 (s, 2H, –OH phenolic ring, –NH– benzimidazole ring). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 112.5, 117.0, 118.8, 123.1, 125.9, 131.4, 151.6, 158.0 (aromatic carbons). Mass: *m*/*z* calcd for $C_{13}H_{10}N_2O$ (relative abundance (%), assignment) = 211 [100, $(M+1)^+$]. Elemental analysis calcd for for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.35; H, 4.58; N, 13.42.

Synthesis of 2-(1-*H*-benzoimidazol-2-yl)-4-(pyridine-3-ylazo)-phenol (2)

3-Aminopyridine (0.94 g, 0.01 mol) was suspended in 30 ml of water at 0–5 °C. Then 1.0 ml of 6.0 M HCl was added to the mixture. After 15 min, 10.0 ml aq solution of $NaNO_2$ (0.076 g) along with a solution of receptor **1** in THF was added. Then the pH was adjusted to 8–9 with 2 M NaOH solution. Mixture was stirred for 2 h and then neutralized with 1 N HCl solution. The precipitates were filtered and washed with deionized water. The crude product was purified by silica column chromatography to yield pure **2**. Orange solid, yield 50%, mp 182 °C, IR (cm^{-1}): 3355 (ν_{O-H}, ν_{N-H}, H-bonded (broad)), 3060 (ν_{C-H}, aromatic), 1634 ($\nu_{C=N}$), 1386, 1424 ($\nu_{-N=N-}$). ^1H NMR ($CDCl_3$+DMSO-d_6, 400 MHz) δ (ppm): 7.22 (d, J = 6.66, 1H, Ar-H), 7.26 (dd, J_1 = 4.47, J_2 = 2.25 Hz, 2H, Ar-H), 7.58 (dd, J_1 = 6.0, J_2 = 3.5 Hz, 1H, Ar-H), 7.66 (dd, J_1 = 4.2, J_2 = 2.4 Hz, 2HAr-H), 7.94 (d, J = 6.63, 1H, Ar-H),8.12 (d, J = 6.09 Hz, 1H, Ar-H), 8.68 (d, J = 2.82 Hz, 1H, Ar-H), 8.86 (s, 1H, Ar-H), 9.05 (s, 1H, Ar-H), 13.9 (br s, 2H, –OH phenolic ring, –NH– benzimidazole ring) (Fig. S4). ^{13}C NMR ($CDCl_3$+DMSO-d_6, 100 MHz) δ (ppm): 112.8, 118.0, 122.9, 123.1, 124.1, 124.9, 126.6, 144.9, 145.8, 147.4, 150.7, 150.9, 161.8 (Fig. S5). Mass: *m*/*z* calcd for $C_{18}H_{13}N_5O$: (relative abundance (%), assignment) = 316 [53.5, $(M+1)^+$]. Elemental analysis calcd for $C_{18}H_{13}N_5O$: C, 68.56; H, 4.16; N, 22.21. Found: C, 68.38; H, 4.28; N, 22.40.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.01.128.

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