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A selective and sensitive 'naked eye' anion detector based on an imine-π-TCNQ assembly

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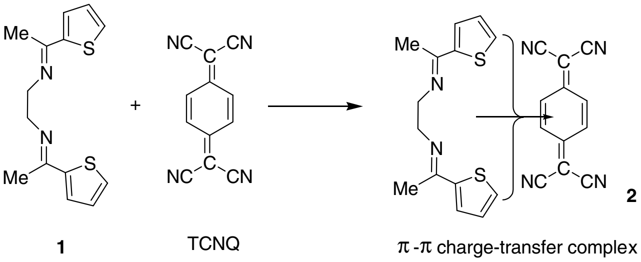
Abstract—A colorimetric heterocyclic imine based chemosensor is designed for detection of PO_4^{3-} and CO_3^{2-} under physiological pH conditions. The charge-transfer (CT) sensor is highly coloured with PO_4^{3-} and CO_3^{2-} recognition giving rise to a purple-to-yellow colour change that is visible to the naked eye and is reversible upon removal of anion.

Anion binding chemistry, whilst far less developed than cation chelation, has developed significantly following the concepts of supramolecular chemistry and molecular recognition. Suitably designed anion receptors[1] play critical roles in the development of fluorescent sensors[2] and other electrochemical signalling devices.[3] Anions are ubiquitous in Nature and their detection using small and readily accessible assemblies appeals to the chemical community especially when the sensing event is visually perceptible without resorting to spectroscopic techniques and yields instant qualitative information, which is quantifiable using absorption spectroscopy.[4] Such sensing processes involve inherently weak interactions based upon the receptor design and quite often are challenged by the interference of solvent molecules, which may interact more effectively with both the receptor and the guest. Over the years, many receptors covalently attached or intermolecularly linked to chromophoric units and guests have been prepared and studied for various applications ranging from physiology and medical diagnostics.[5] We have reported a number of different types of charge-transfer compounds[6] based on tetracyanoquinodimethane (TCNQ). In this Letter, we report the synthesis and use of a non-covalent charge-transfer assembly based on a neutral electron rich donor and the electron deficient acceptor TCNQ.

The sensor is based on imine **1**, where the heterocyclic thiophene moiety is an integral part of the donor system and furnish a very stable and intense π–π charge-transfer complex **2** with TCNQ. The synthesis of **1** began with Schiff-base condensation of 2-acetylthiophene and ethylenediamine using a single pot protocol, employing P_2O_5 supported on neutral alumina as a recoverable and recyclable catalyst under solvent-free conditions. Donor **1** was obtained in 80% purified yield and was characterized using spectroscopic and microanalytical data (^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 6H), 3.87 (s, 4H), 6.99–7.31 (m, 6H); IR (KBr): ν_{max} 1615 (C=N); Anal. Calcd for $C_{14}H_{16}N_2S_2$: C, 60.86; H, 5.80; N, 10.14; S, 23.19. Found: C, 60.56; H, 5.72; N, 10.42; S, 23.41).

For evaluation of the sensing properties, the purple charge-transfer complex **2** was obtained by mixing



Scheme 1.

Keywords: Anion detection; Charge-transfer; Sensor; TCNQ; Naked eye.

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acetonitrile solutions of **1** (1.0×10^{-4} mol dm^{-3}) and TCNQ (5×10^{-5} mol dm^{-3}) at room temperature (Scheme 1). The colour of the solution changed gradually from pale yellow to purple over 8 h, after which no significant spectroscopic or visual colour change (see Supplementary data) was observed. For an unequivocal determination of the stoichiometry of the complex involved in the sensing process, complex **2** was synthesized as described below.

Typically, to a stirred pale yellow solution of TCNQ (1 g, 0.0049 mol) in anhydrous acetonitrile (25 ml) under a blanket of dry nitrogen gas, imine **1** (1.35 g, 0.0049 mol) was added in portions. The colour of the solution turned dark green. After stirring for additional 20 min the colour changed to purple indicating formation of CT complex **2** and the reaction was stirred overnight to ensure completion. The solvent was removed under reduced pressure and the residue solidified. This was filtered and washed thoroughly with cold acetonitrile. The microanalytical data (Anal. Calcd for $C_{26}H_{20}N_6S_2{\cdot}3CH_3CN$: C, 63.68; H, 4.80; N, 20.8; S, 10.61. Found: C, 63.53; H, 4.95; N, 20.55; S, 10.77) of this complex corresponded to a 1:1 stoichiometry of the reactants. In the mass spectrum, CT complex **2** depicted a molecular ion peak at *m*/*z* 479 ($M^+{-}1$) corresponding to the molecular formula $C_{26}H_{19}N_6S_2$. A fragment at *m*/*z* 276 corresponded to M^+−TCNQ.

Figure 1 shows the changes in the absorption spectrum of TCNQ (5×10^{-5} mol dm^{-3}) in acetonitrile upon addition of colourless imine **1** (1×10^{-4} mol dm^{-3}). The free TCNQ absorption band at 395 nm is evidently blue shifted to 319 nm whilst a new absorption band appeared in the long wavelength region of the spectrum (λ_{max} at around 542 nm). This result indicates the formation of the π–π charge-transfer complex of TCNQ with imine **1** in acetonitrile.

The purple imine-TCNQ complex **2** was found to be stable (spectrophotometrically) in the MeCN/H_2O (1:1 v/v) mixture and can be utilised for the detection of anions in aqueous phase. Thus, the colorimetric properties of CT complex **2** were studied in aqueous acetonitrile. Aqueous solutions of anions of various sodium salts (F^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_3^{2-}, HSO_3^-, CO_3^{2-}, HCO_3^- and CH_3COO^-) were added to a solution of sensor **2**, and equilibrated at ambient temperature for 8 h. The changes in the absorption bands of complex **2** were measured after the addition of 1.0×10^{-2} mol dm^{-3} aqueous solutions of the anions. Upon addition of aqueous CO_3^{2-}, the charge-transfer absorption band (λ_{max} at 518 nm) of complex **2** decreased remarkably (Fig. 2) (nearly vanished) in intensity. This was manifested by a change in colour from purple to pale yellow (see Supplementary data). Similarly the addition of PO_4^{3-} to complex **2** resulted in an instant change in colour from purple to yellow. It is worth noting that sensing of CO_3^{2-} and PO_4^{3-} has been reported[4] using a dihydroxymethyl-di-(2-pyrrolyl)methane-TCNQ assembly, which required around 20 h for a complete colour change in the case of CO_3^{2-} sensing, whereas in keeping with the requirements of instant sensing, the colour change in the case of **2** was complete within a few seconds of addition of the anion. With the exception of bisulfate and sulfate, where only minor sensing was observed, none of the other anions gave a measurable change in the colour and absorption band of complex **2**. The sensing capabilities of complex **2** in aqueous solution follow the trend $PO_4^{3-} > CO_3^{2-} \gg F^-$, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, HPO_4^{2-}, $H_2PO_4^-$, SO_3^{2-}, HSO_3^-, HCO_3^-, CH_3COO^- (see Supplementary data).[7]

Further, experiments were conducted to see if the colour changes in case of CO_3^{2-} and PO_4^{3-} could be reversed when the selected anion was eliminated from the solution, which would indicate re-formation of π–π (non-covalent) charge-transfer interaction between TCNQ and **2**. An improved visualization of colour change was effected upon using high complex concentrations. For example, when an aqueous solution of CO_3^{2-} was

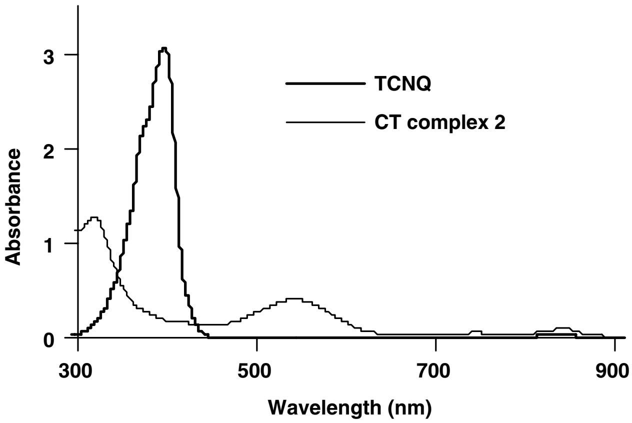

Figure 1. Absorption spectra of TCNQ (5×10^{-5} mol dm^{-3}) in MeCN at 28 °C and CT complex **2**, after addition of **1** (1×10^{-4} mol dm^{-3}), and equilibration for 8 h.

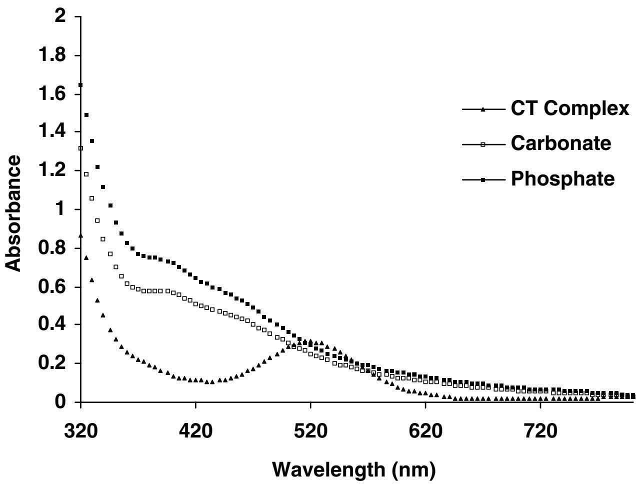

Figure 2. Absorption spectra of the complex **2** ([TCNQ] = 5×10^{-5} mol dm^{-3}, [**1**] = 1×10^{-4} mol dm^{-3}) in MeCN (5 ml) after the addition of 0.01 M solutions of CO_3^{2-} (1.2 ml), PO_4^{3-} (1.0 ml) (see Supplementary data) recorded immediately after mixing.

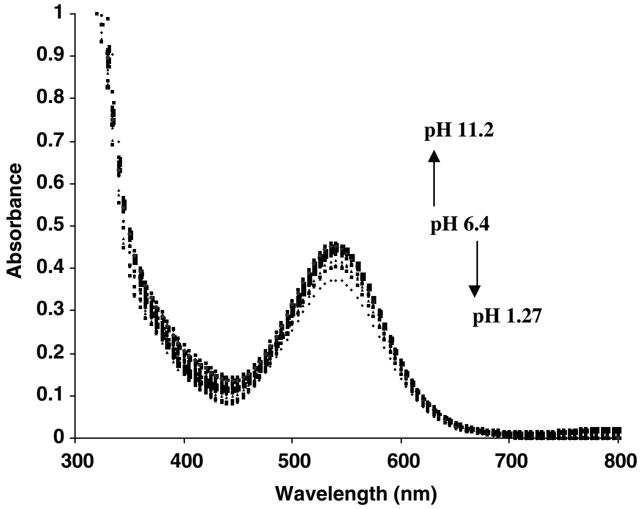

Figure 3. Changes in the UV–vis spectra of **2** upon pH titration of an acetonitrile solutions (pH 6.4) of **2** with HCl and $NaHCO_3$.

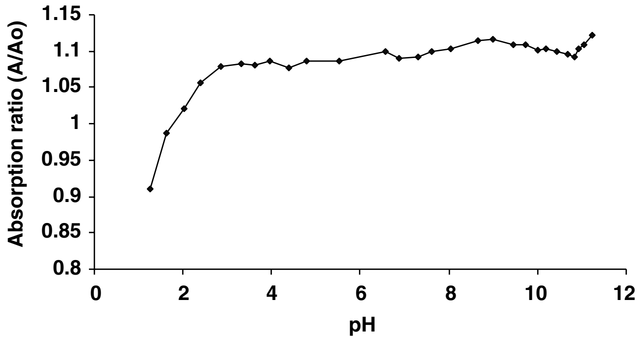

Figure 4. Changes in the UV–vis spectra of **2** (542 nm band) upon pH titration of acetonitrile solutions of **2** with HCl and $NaHCO_3$.

added to a purple solution of CT complex **2** in a 1:1 volume ratio an instant diminishing of the purple colour to pale yellow occurred. Subsequently, treating this solution with a concentrated aqueous $BaCl_2$ solution resulted in the reappearance of the purple colour with concomitant precipitation of $BaCO_3$.

As the CT complex **2** was soluble in acetonitrile (pH 6.4), effect of pH variation was observed by monitoring the changes in the UV–vis spectra upon titration with acid and base solutions covering pH range 1.27–11.2 (see Supplementary data). The response of **2** to this variation is depicted in Figures 3 and 4. Over the whole pH range, the intense charge-transfer band at λ_{max} 542 was blue shifted by only 6 nm. As can be seen from these changes, the variation in the absorption intensity was only minimal and thus the CT assembly demonstrates considerable stability to pH variation. This clearly demonstrates that **2** can be used in the physiological environment where the $pH > 5$, as well as at extreme pH conditions, which is an added advantage.

In summary, we have developed a new, efficacious colorimetric anion sensor based on a Schiff-base-TCNQ charge-transfer complex in CH_3CN, which allows a facile colorimetric detection of CO_3^{2-} and PO_4^{3-} in the presence of other inorganic and organic anions in aqueous solutions. This sensor is efficient in that instant determination of CO_3^{2-} and PO_4^{3-}, especially in the presence of interfering anions, is possible.

Acknowledgement

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.210.

References and notes

1. Sessler, J. L.; Camiolo, S.; Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 17.
2. De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
3. Beer, P. D. *Chem. Commun.* **1996**, 689.
4. Guo, Y.; Shao, S.-J.; Xu, J.; Shi, Y.-P.; Jiang, S.-X. *Inorg. Chem. Commun.* **2004**, *7*, 333.
5. (a) Anslyn, E. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 3119; (b) *Chemical Sensors and Biosensors for Medical and Biological Applications*; Spichiger-Keller, U. E., Ed.; Wiley-VCH: Weinheim: Germany, 1998; (c) *Chemosensors of Ion and Molecular Recognition*; Desvergue, J. P., Czarnik, A. W., Eds.; NATO ASI Series C; Kluwer Academic: Dordrecht, 1997; p 492; (d) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P. *Acc. Chem. Res.* **1999**, *32*, 846.
6. (a) Kaur, P.; Jyoti.; Robinson, W. T.; Singh, K. *J. Coord. Chem.* **2002**, *55*, 281; (b) Kaur, P.; Sarangal, A.; McInnes, E.; Robinson, W. T. *J. Coord. Chem.* **2004**, *57*, 797; (c) Kaur, P.; Sarangal, A.; Hundal, G.; Chandrasekhar Rao, T. V. *J. Coord. Chem.* **2005**, *56*, 495; (d) Kaur, P.; Sarangal, A.; McInnes, E.; Hundal, G. *J. Coord. Chem.* **2006**, *59*, 821.
7. The exclusive sensing of PO_4^{3-} and CO_3^{2-} over other anions can be deduced from the correlation of the pK_a values[8] of their corresponding acids with other species used in this investigation. Thus, the approximate pK_a values of phosphoric acid (12.4) and carbonic acid (10.33) (with respect to water) are much higher than the other species (<7).
8. March, J. In *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 4th ed.; John Wiley & Sons: New York, 2000; p 250.