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A fluoride selective dipyrromethane-TCNQ colorimetric sensor based on charge-transfer

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ABSTRACT

A colorimetric sensor based on dipyrromethane(donor)-7,7′,8,8′-tetracyanoquinodimethane (acceptor) charge-transfer compound depicts excellent selectivity for naked-eye as well as spectrophotometric determination of F^- even in co-existence with other halide ions (Cl^-, Br^- and I^-). The sensing mechanism is ascribed to the interrupted charge-transfer between donor–acceptor in the presence of F^-. The sensing on solid support mimics the solution sensing process supported by the reflectance values. Thus this compound has potential for practical applications.

1. Introduction

In continuation of our interest in the synthesis of charge-transfer (CT) compounds and their development as the chemosensors/chemodosimeters [1], here in the present investigation, we have explored the sensing behaviour of dipyrromethane-7,7′,8,8′-tetracyanoquinodimethane (TCNQ) based CT compound towards halides. TCNQ is a good π-acceptor [2] and is expected to form CT compounds with the strong π-donors such as halides having π-donor ability in the order $F < Cl < Br < I$ [3]. Our preliminary investigations reveal that TCNQ forms CT compounds with all the halides manifested by the appearance of additional low energy absorption bands attributed to reduced (anionic) TCNQ [4] accompanied by insignificant colour change (Fig. 1). We envisaged if the acceptor strength of TCNQ is modulated by appending it to some donor species it may show different behaviour towards the halides subject to their π-donor ability. Keeping this in view, we have synthesised the dipyrromethane derivatives and have prepared their CT compounds with TCNQ (Scheme 1). One of these was found to be selective for F^- over other halides (Scheme 2). The determination of F^- is important as being a smallest nucleophilic water-soluble anion, plays crucial roles in a range of biological phenomenon and is implicated in many disease states. For instance, it is administered in the treatment of osteoporosis [5] and is often added in dental pastes and water because of its beneficial effects. However, its excess may lead to dental caries [6], fluorosis [7], urolithiasis [8] etc. Thus its functions, both beneficial and otherwise, necessitate the development of the 'easy-to-make' chemosensors selective for F^-. Recently, recognition of F^- ion has been successfully implemented using colorimetric and/or fluorescent chemosensors as these offer advantages in terms of high sensitivity and ease in monitoring of the recognition process [9]. Most of the known fluoride selective receptors operate in organic solvents through hydrogen bonding interactions [10] and the process of detection is often challenged by high dielectric constant of the aqueous environment in bioanalytical applications [11]. Thus the aqueous phase detection of fluoride through interactions other than hydrogen-bonding is extremely scarce and has become a topical objective. Some sensors have been reported wherein the fluoride binding site is either a Lewis acid, based on boron [12], tin [13] or aluminium [14] or a cationic borane [15] and proficiently transfer fluoride ion from water into organic or solid phases. Use of pyrrole based fluoride recognition motifs such as functionalised calixpyrroles, dipyrrolylquinoxaline operate either through hydrogen bonding and/or metal coordination [16].

We wish to report here that by using 'easy-to-make' CT compound in solution, a highly selective 'Naked-eye' sensing of F^- can be achieved both in solution as well as when supported on solid.

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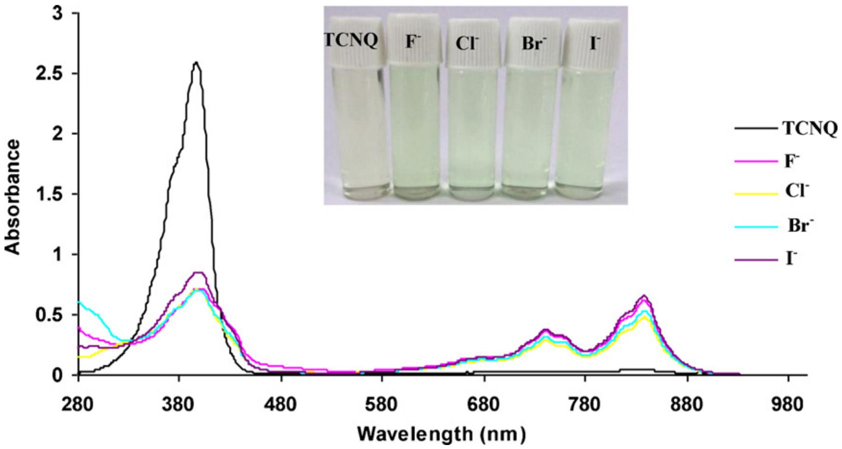
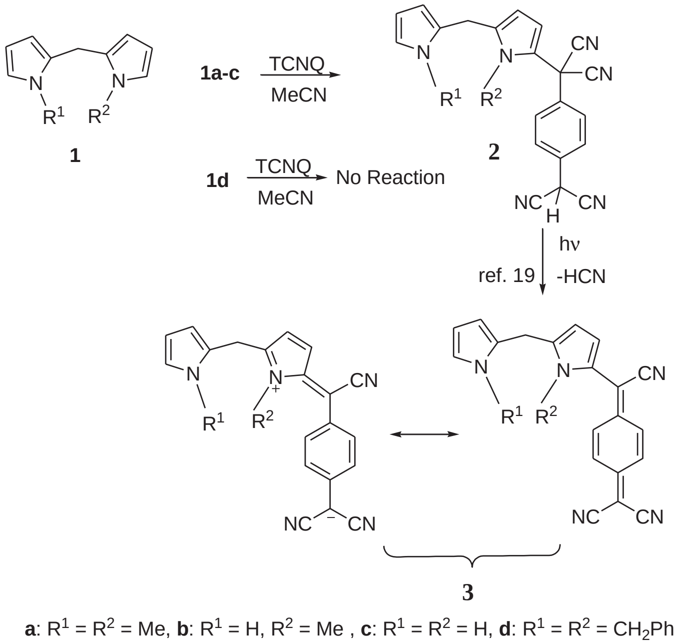


Fig. 1. Modulation of the absorption spectrum of TCNQ (5×10^{-5} M) upon addition of F^-, Cl^-, Br^- and I^- (5×10^{-2} M) in $MeCN/H_2O$.



Scheme 1. Proposed mechanism for formation of **2** and **3** from **1**.

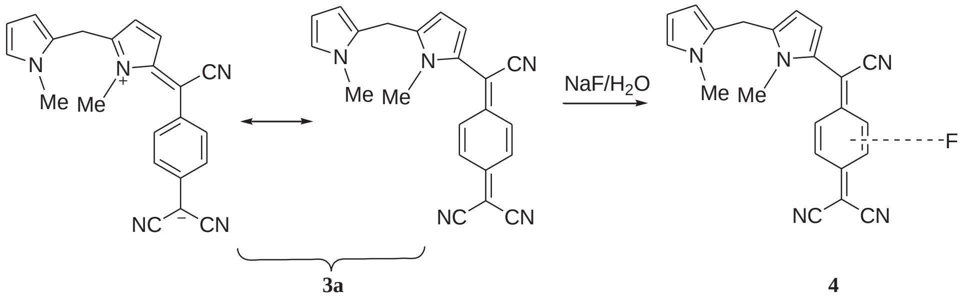
2. Experimental

2.1. Chemicals

All reagents were purchased from Aldrich and N-methylpyrrole was used after fresh distillation. Dichloromethane (DCM) was dried over benzophenone ketyl under inert atmosphere and distilled directly in the reaction flask. Acetonitrile (MeCN) was dried over P_2O_5 and over 4 Å molecular sieves. Silica gel G (60–120 mesh) was used for column chromatography.

2.2. Instrumentation

UV–vis spectra were recorded on a SHIMADZU 1601 PC spectrophotometer, with a quartz cuvette (path length, 1 cm) and studies were performed in AR grade MeCN and double distilled



Scheme 2. Proposed mechanism for the sensing process by **3a**.

water. The cell holder of the spectrophotometer was thermostatted at 25 °C for consistency in the recordings. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-FT NMR AL 300 MHz and BRUKER Avance II 400 MHz spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane ($SiMe_4$) as internal standard. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, m = multiplet), integration, coupling constant *J* (Hz) and assignment. The mass spectra were recorded with Esquire 3000–00037 mass spectrometer. Elemental analyses were performed with a Thermo Flash EA 1112 analyser and were within ±0.4% of the theoretical values. IR spectrum was recorded on FT IR-SHIMADZU 8400 Fourier-Transform Spectrophotometer in range 400–4000 cm^{-1}. The reflectance of the test-paper was determined using DATACOLOR SF-600 PLUS-CT (Datacolor International) spectrophotometer using D_{65} illumination and 10° observer as the standard measurement conditions.

*2.3. Synthesis and characterization of compounds **1a–d** (Scheme 1)*

The dipyrromethanes **1a–d** were prepared as described by us [17] (S1, *See the Supporting Information*).

*2.4. Synthesis and characterization of compound **2a** (Scheme 1).*

To a stirred pale yellow solution of TCNQ (0.117 g, 0.57 mmol) in anhydrous MeCN (40 ml), under dry nitrogen atmosphere, dipyrromethane **1a** (0.100 g, 0.574 mmol) was added. After stirring for additional 4 h the colour changed to blue and the reaction was stirred for 10 h to ensure completion. The solvent was removed under reduced pressure and whereupon the residue solidified. The residue was dissolved in DCM and treated with charcoal to remove coloured impurities. After removing charcoal by filtration, the DCM was removed under reduced pressure and resulting residue was recrystallized from DCM and hexane to obtain white solid.

Yield 70%; Mp 140 °C; MS *m/z*, 376.8 (M^+-1), 349.7 (($M^+-1-HCN$); ν_{max} (KBr/cm^{-1}) 2245 and 2121 (CN); ^{1}H NMR ($CDCl_3$): δ 3.40 (s, 3H), 3.53 (s, 3H), 3.85 (s, 2H), 5.15 (s, 1H), 5.75 (m, 1H), 5.84 (d, 1H, *J* 4.0 Hz), 6.04 (t, 1H, *J* 3.0 Hz), 6.08 (t, 1H, *J* 3.8 Hz), 6.59 (m, 1H), 7.67–7.73 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 24.9, 27.7, 31.9, 33.8, 40.5, 106.9, 107.8, 111.0, 111.9, 113.0, 119.4, 122.2, 128.0, 128.6, 134.5 and 135.9; Elemental analysis: Found C, 72.60; H, 4.38; N, 21.99%. $C_{23}H_{18}N_6$ requires C, 73.00; H, 4.79; N, 22.21%.

(For copies of the NMR, EI Mass, S2 in Supporting Information).

3. Results and discussion

3.1. UV–vis studies

For the preparation of the CT compounds, a colourless MeCN solution of **1a–d** (2×10^{-3} M) and TCNQ (5×10^{-5} M) were kept at room temperature. The colour of the solutions changed from pale yellow to intense blue in case of **1a–c** [18]. However, no change in colour in case of **1d** was observed indicating the non formation of the corresponding CT compound. Thus **1a–c** were used for further experimentation.

The colour change starts instantly but completes after 10 h in light which hints at the formation of adduct, possibly **3** with extensive charge delocalisation (Scheme 1). The proposed mechanism is based upon our recent findings where a similar CT compound between N-methylpyrrole and TCNQ has been isolated [1f]. Also in the presence of literature precedence [19], **2** may transform to **3** when exposed to light.

To check the feasibility of this hypothesis, when equimolar amounts of **1a** and TCNQ were reacted under the conditions of solution studies (r.t., stirring), a white solid compound **2a** was isolated which was characterised using spectroscopic data (S2, *See the Supporting Information*). A colourless solution of **2a** gradually transforms to the blue solution and takes 10 h for the complete conversion. This blue solution depicts the same absorption spectrum and sensing characteristics as of **3a**. It is therefore proposed that in solution also the formation of blue coloured compound **3** proceeds via the formation of **2** [1f]. However, in this case the attempted isolation of the analytically pure CT compound **3a** was unsuccessful, rendering spectral characterisation difficult. But the confirmation of its formation was ascertained from correct mass spectral data (*m*/z 350.1 (M^+-1), S3, *See the Supporting Information*).

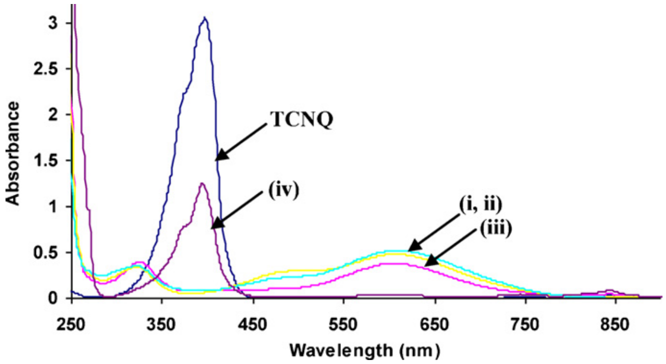


Fig. 2. Absorption spectrum of TCNQ (5×10^{-5} M) and the observed changes upon the addition of 2×10^{-3} M of **1a** (i), **1b** (ii), **1c** (iii) and **1d** (iv) in MeCN, after 10 h.

The process of formation of blue CT compound in solution was monitored spectrophotometrically in which, upon addition of **1a**–**c**, the absorption band of the free TCNQ at 395 nm got blue shifted to 325 nm with concomitant appearance of a new band at 606 nm attributed to **3a**–**c** (Fig. 2). The blue shift in the TCNQ band from 395 to 325 nm is attributed to the interchange of quinoid and benzenoid forms of TCNQ as shown in Scheme 1. When the process was repeated in MeCN:H_2O (1:1, v/v), the absorption bands were shifted to 320 nm and 612 nm, respectively, but the presence of water did not impede the formation of the CT compound.

The CT compound **3a** [**1a** (2×10^{-3} M) and TCNQ (5×10^{-5} M) in MeCN] in solution exhibited a drastic change in UV–vis absorption spectrum upon addition of F^- but with other halides (Cl^-, Br^- and I^-) corresponding change was not observed (Fig. 3). Upon varying the molarity of F^-, the intensity of the CT band at 612 nm decreased gradually to completely disappear at 5×10^{-2} M (S4, *See the Supporting Information*) with appearance of a new band at 510 nm indicating the completion of the titration. This is manifested by a colour change from intense blue to light pink (Fig. 3, inset). The colour change starts within 5 min of the addition of F^- and completes in about 45 min. (Fig. 3, inset). In Job's plot (Fig. 4), a maximum absorbance change was observed when the mole fraction of **3a** versus F^- was 0.5, which indicated the formation of 1:1 stoichiometry between **3a** and F^-. Further, the titration data of **3a** with F^- was fitted using HypSpec [20] – a non-linear least-squares fitting programme. It allowed the establishment of the stoichiometry (1:1) of the most stable species (**3a**: F^-) present in the solution with the binding constant (log β) = 2.227. Utilising the affinity of fluoride to silyl reagents [21], when the pink coloured solution obtained at the end of the titration was treated with *tert*-butyldimethylsilyl chloride, the original blue coloured **3a** (612 nm) was restored indicating the reversal of the sensing event.

Surprisingly, a similar CT compound **3b** obtained by mixing solution of **1b** and TCNQ upon treatment with F^- under similar experimental conditions depicted insignificant shift in the absorption band without a visual colour change, whereas that **3c** of **1c** and TCNQ did not respond at all to the halide sensing (Figs. 5 and 6). Even

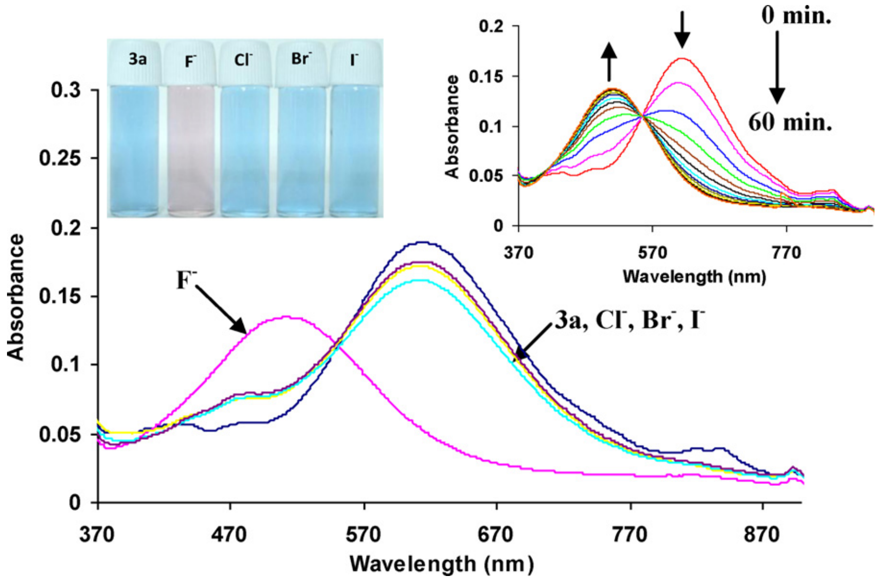


Fig. 3. Changes in the absorption spectrum of **3a** [TCNQ (5×10^{-5} M), **1a** (2×10^{-3} M)] in the presence of F⁻, Cl⁻, Br⁻ and I⁻ (5×10^{-2} M). Inset: Changes in the absorption spectrum in the presence of F⁻ in MeCN/H_2O (1:1, v/v) with time and observed colour changes.

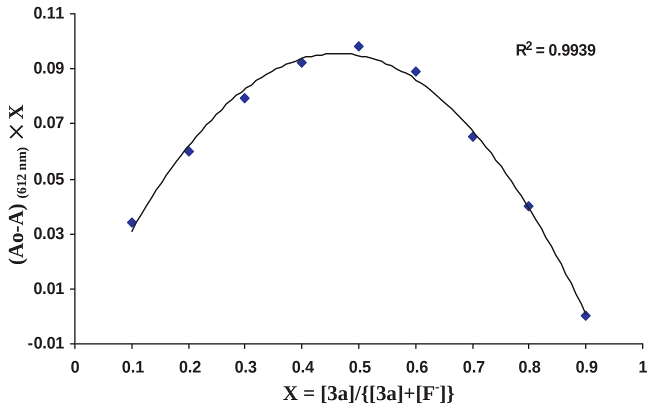


Fig. 4. Job's plot between **3a** and F⁻.

1c itself having free NHs did not show any change in the absorption spectrum when treated with aqueous solution of F⁻ in contrast to the ability of the systems containing pyrrolic NH groups to act as molecular receptors for anions [22].

Earlier investigations [23] on the use of pyrrolic sensors for the detection of sulphite [23c], report splitting of CT assemblies, and propose the formation of a TCNQ-sulphite species at the end of the titration. But on the basis of our investigations involving titration of TCNQ and F⁻ under similar conditions (Fig. 1), where the absorption spectrum is characterised by the presence of low energy bands attributed to anionic TCNQ as against 510 nm, observed in the titration of **3a**, we rule out the formation of TCNQ-F and propose the formation of **4**, transformed from the adduct **3a** (Scheme 2). Further blue shift in the CT band from 612 to 510 nm in the sensing process also supports the formation of **4** as the fluoride will interrupt the charge-transfer. NMR studies involving interaction of **3a** with F⁻ gave insignificant results.

4. Practical application

Further, to develop an efficient probe for instant sensing of fluoride on a solid support, we developed an easy-to-use test paper. A sonicated solution of **3a** [**1a** (0.010 g, 5.74×10^{-5} M) and TCNQ (0.0117 g, 5.74×10^{-5} M) in MeCN (2 ml)], after 2 h at ambient temperature turned intense blue. A Whatman paper strip (10 × 4 cm) was impregnated with this solution, repeatedly with intermittent drying. The blue strip thus formed was dipped in a saturated aqueous solution of fluoride, which subsequent to the sensing, led to the development of pink colour (Fig. 7). Reflectance values (Fig. 8) of the strips depicted good agreement with the solution phase absorption values thus mimicking the solution sensing process which show promise in real life applications. In comparison the solution absorptions [λ_{max} 612 nm (**3a**); 510 nm (**3a + F⁻**)], the reflectance minima

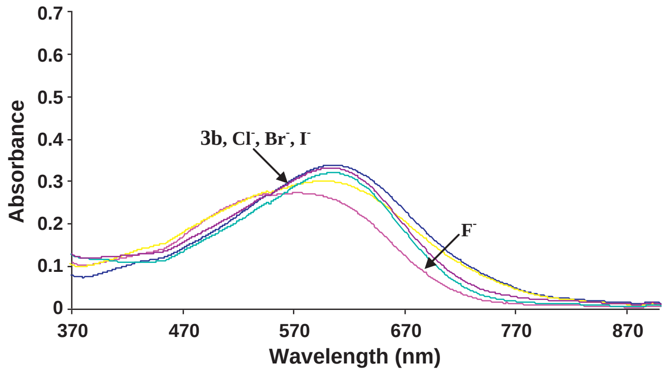


Fig. 5. Changes in the absorption spectrum of the **3b** [TCNQ (5×10^{-5} M) and **1b** (2×10^{-3} M)] in the presence of F⁻, Cl⁻, Br⁻ and I⁻ (5×10^{-2} M).

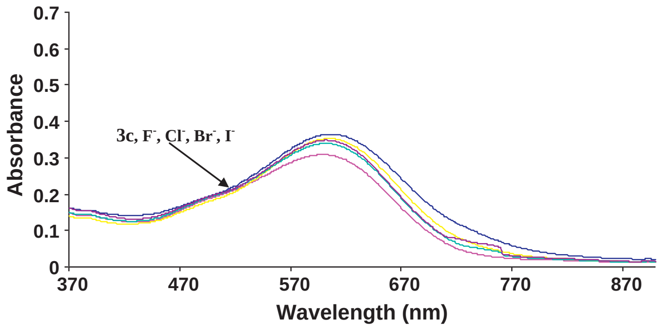


Fig. 6. Changes in the absorption spectrum of the **3c** [TCNQ (5×10^{-5} M) and **1c** (2×10^{-3} M)] in the presence of F⁻, Cl⁻, Br⁻ and I⁻ (5×10^{-2} M).

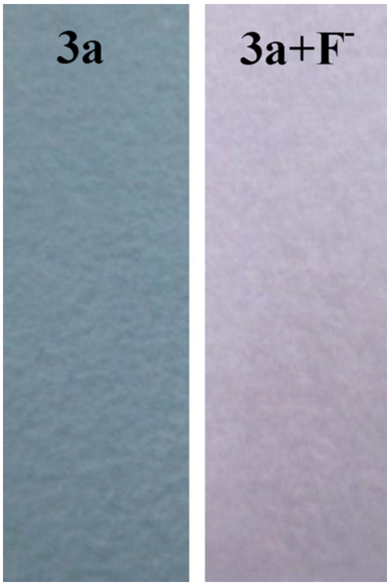


Fig. 7. Observed colour changes of the test-paper of **3a** upon detection of F^- in aqueous solution.

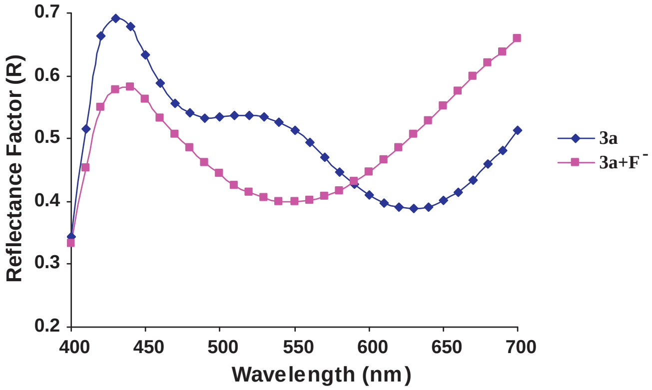


Fig. 8. The reflectance spectra of **3a** and **3a** + F^-.

($R_{min.}$) generally show some shift [λ 630 nm (**3a**); 550 nm (**3a** + F^-)] owing to the contribution of the solid substrate [24].

5. Conclusion

In conclusion, the colorimetric sensor based on a CT compound of dipyrromethane **1a** and TCNQ, allows the selective determination of F^- from aqueous solutions even in coexistence with other halide ions. This sensing event displayed visual as well as spectrophotometric colour changes. Further, sensing event has been demonstrated on solid support also. Thus this compound has potential for practical applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.02.034.

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