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The synthesis and development of a dual-analyte colorimetric sensor: Simultaneous estimation of Hg^{2+} and Fe^{3+}

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ABSTRACT

The selectivity and sensitivity of a pH stable hetarylazo dye equipped with binding sites consisting of N, S and N, O combinations, towards Hg^{2+} and Fe^{3+} over a large number of other cations including lanthanides, is described. Hg^{2+} and Fe^{3+} ions coordinate to the dye through N, S binding site forming 2:1 and 1:1 complexes, respectively. Distinct naked-eye color changes for both Hg^{2+} (yellow to purple) and Fe^{3+} (yellow to red) were quantified for simultaneous estimation of these ions. To further establish the binding and sensing phenomenon, another analogous hetarylazo dye lacking N, O combination was evaluated and found to give similar results. For practical applicability in routine life, very handy and ready-to-use paper strips coated with the dye have been prepared for the detection of Hg^{2+}, just like the pH paper strips.

1. Introduction

The field of molecular sensing has witnessed considerable advancement as a myriad of different types of molecular sensors have been designed and demonstrate a high degree of predictability and selectivity towards a variety of ions and neutral species, from aqueous as well as non-aqueous environments [1–5]. Such sensing events are imperative for applications including environmental, biological, clinical and industrial waste management regimes [6]. Recently, this area of investigation has observed a paradigm shift [7] in the interest from selective receptors to differential receptors supporting multi-parameter functionality on a single platform (multi-analyte sensing) that has allowed rapid, sensitive, specific, non-expensive, analysis of several identical analytes suitable for realtime on-sight sensing which has been accomplished by such mathematical systems as PCA, PLS, ANNs etc [8]. A very interesting molecular architect "lab on a molecule" has been described for the analysis of Pb^{2+}, Hg^{2+} and Cu^{2+} using a quadruple-channel sensing [9]. However, inspite of the advantages in the simultaneous estimation of the analytes using minimal sensing system, the multi-analyte single molecular probes employing colorimetric [10] as well as fluorescent [11] detection are only limited. Further, detection of analytes using such systems is generally straightforward as the analysis of differential response of the analytes at different wavelengths does not require intricate mathematical systems, however, detection of a multianalyte mixture, where the optical responses are not fully resolved poses a challenge and such examples have eluded the chemical literature. In continuation of our interest in the development of colorimetric chemosensors [12], we envisaged, if differential binding sites comprising of NS (for soft metal ions [13]) and NOO (for hard metal ions [14] and lanthanides [15]) are incorporated in a chromophore of the type **3**, multianalyte sensing might result. Recently, Suzuki et al. [14] have reported a unique molecular system with similar binding sites which allowed determination of Cu^{2+}, Fe^{3+}, Pb^{2+}, Al^{3+} and Cr^{3+} based on the nature of the heteroatoms and their interaction with the cations.

Hetarylazo dyes are prized for their ease in preparation as well as intense absorptions in the visible region and are thus ideal candidates for colorimetric chemosensors. Indeed **3** shows differential behaviour towards Hg^{2+} and Fe^{3+} out of a number of compeititive cations tested and facilitates a naked-eye as well as colorimetric detection of these two metal ions, simultaneously. The fact that robust methods [16] based on the use of membrane ultrafilteration technology allow selective removal of Fe^{3+} ions from dilute aqueous solutions, **3** may well be visualized as a highly selective sensor for the detection of Hg^{2+} ions which pose very serious environmental as well as biological concerns [17]. A wide array of colorimetric [18] and fluorescent [19] molecular sensors with specific response to

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Hg^{2+} as well as Fe^{3+} have been reported [20]. Additionally, the detection process is facilitated, convincingly, without resorting to complex mathematical models inspite of the fact that the optical responses were not completely resolved. To further widen the scope of sensor **3**, we have also evaluated the binding with a number of lanthanide cations, as **3** possesses two ester functionalities. To establish the fact that the binding of **3** with Hg^{2+} involves N and S donor sites, the dye **4**, lacking ester functionalities was also evaluated. Finally, we have explored the possibility of preparing handy paper strips ("dip-stick") coated with **3** for determining Hg^{2+}, similar to the ones commonly used for pH determination.

2. Experimental

2.1. General

Mass spectra (LCMS) were recorded on Bruker Daltonics esquire 3000 spectrometer. ^1H NMR and ^{13}C NMR spectra have been recorded on JEOL-FT NMR-AL at 300 and 75 MHz, respectively, with TMS as internal standard using $CDCl_3$ as deuterated solvent and few on BRUKER Avance II 400 MHz and 100 MHz, respectively using CD_3CN as deuterated solvent. IR spectra were recorded on FT IR-SHIMADZU 8400 Fourier-transform spectrophotometer in the range 400–4000 cm^{-1} using KBr as medium. The purity of the solid products was checked by elemental analysis performed on Thermoelectron FLASH EA1112, CHNS analyzer. UV-visible spectral studies were conducted on Shimadzu 1601 PC spectrophotometer. The absorption spectra have been recorded between 1100 and 200 nm. The pH titrations have been performed with the Equip-Tronics Digital pH meter model-EQ 610.

2.2. Chemicals

Metal salts used in the spectrophotometric studies were of analytical grade and bought from Sigma–Aldrich. The solvents used were also of analytical grade purchased from Thomas Baker.

2.3. General procedure for synthesis of 3 and 4

2.3.1. Synthesis of 1

Thiosemicarbazide (6.07 g, 1.0 mol) was added (below 25 °C) portion wise, to a stirred mixture of formic acid (4.06 g, 3.4 ml, 1.32 mol, 98–100%) and sulphuric acid (12.27 g, 6.7 ml, sp. gr. 1.84) and the resulting mixture was heated for 3 hours at 90 °C and then drowned in ice/water mixture (150 ml). The pH was adjusted in the range 7.5–8.0 with ammonium hydroxide, whereupon precipitation occurred. The temperature was maintained in the range 10–15 °C during the addition. The precipitates were filtered, dried and crystallized from hot methanol.

2.3.2. Synthesis of 2a

Aniline (4.66 g, 4.6 ml, 0.10 mol) and ethyl acrylate (25.03 g, 27.3 ml, 0.50 mol) in acetic acid (9.01 g, 8.6 ml, 0.30 mol) with catalytic amount of cupric chloride were heated at 130–140 °C in a sealed stainless steel container for about 12–14 h to obtain a black tarry mixture which was neutralized with aqueous sodium bicarbonate solution and extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulphate and the solvent removed under reduced pressure to give the residue which was chromatographed over silica gel G (60-120 mesh) using 80% ethyl acetate/hexane as eluent. **2b** is commercially available as *N*,*N*-Diethyl aniline.

2.3.3. Synthesis of 3 and 4 [21] (Scheme 1)

A diazotization mixture was prepared by adding sodium nitrite (0.83 g, 0.012 mol) to sulphuric acid (14.7 g, 8 ml, 0.12 mol, 98%) at 30 °C and heating the stirred mixture to 60–65 °C to ensure complete dissolution. The reaction mixture was cooled to 5 °C and acetic acid (8 ml) and propionic acid (2 ml) were added and stirred. The temperature was then reduced to −5 °C, **1** (2.02 g, 0.01 mol) was added slowly and the whole reaction mixture stirred at the same low temperature for at least 2 h. The completion of diazotization was checked by TLC.

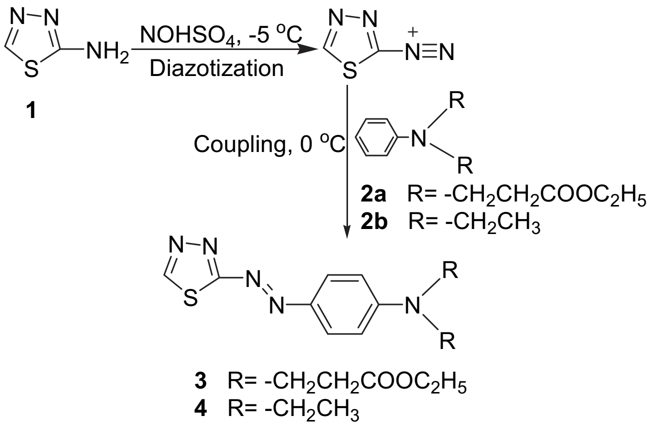
A solution of **2a**/**2b** (2.93 g, 0.015 mol) in acetic anhydride and acetic acid was added to ice/water mixture (200 g) in a beaker equipped with mechanical stirrer and pH meter. A pinch of sulphamic acid was added followed by the addition of diazonium salt liquor at 0–5 °C over 1 h and the mixture stirred for 3 h at ambient temperature. The pH was maintained in the range 1.5–2.0 during the addition using aqueous sodium hydroxide solution. The completion of reaction was checked by spotting the reaction mixture on a filter paper close to a spot of an alkaline aqueous solution of H-acid and detecting any color appearance at the interface of the two boundaries. No color indicated the completion of reaction. Finally the pH was raised to 4.0–4.5. The dye was extracted with dichloromethane, dried over anhydrous sodium sulphate, the solvent removed and the residue purified by column chromatography with silica gel G (60–120 mesh) using 50% ethyl acetate/hexane as eluent.

Dye 3: Yield 70%, m.p. 90–92 °C, ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.28 (t, $J = 7.2$ Hz, 6H, $2 \times COOCH_2CH_3$), 2.68 (t, $J = 7.2$ Hz, 4H, $2 \times NCH_2CH_2$), 3.83 (t, $J = 7.2$ Hz, 4H, $2 \times NCH_2CH_2$), 4.17 (q, $J = 7.2$ Hz, 4H, $2 \times COOCH_2CH_3$), 6.78 (d, $J = 9.3$ Hz, 2H, aromatic *H*), 7.97 (d, $J = 9.3$ Hz, 2H, aromatic *H*), 9.02 (s, 1H, NC*H*S). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 14.14, 32.45, 46.87, 61.01, 111.88, 143.39, 151.35, 151.87, 171.29. IR (KBr): ν_{max}/cm^{-1} 3050 (aromatic CH), 1745 (ester). MS: *m*/*z* 428 ($M^+ + 23$). Elemental Analysis: Calcd. for $C_{18}H_{23}N_5SO_4$: C, 53.33; H, 5.68; N, 17.28; S, 7.90 Found: C, 53.32; H, 5.67; N, 17.26; S, 7.89 (S1, Supplementary data).

Dye 4: Yield 70%, m.p. 138–140 °C, ^1H NMR(400 MHz, CD_3CN), δ (ppm): 1.24 (t, $J = 7.2$ Hz, 6H, $2 \times NCH_2CH_3$), 3.55(q, $J = 7.2$ Hz, 4H, $2 \times NCH_2CH_3$), 6.86 (d, $J = 9.6$ Hz, 2H, aromatic *H*), 7.87 (d, $J = 9.6$ Hz, 2H, aromatic *H*), 9.09 (s, 1H, NC*H*S). ^{13}C NMR (100 MHz, CD_3CN), δ (ppm): 11.54, 44.56, 111.49, 141.79, 151.46, 152.77, 181.08. IR (KBr): ν_{max}/cm^{-1} 2950 (aromatic CH). MS: *m*/*z* 284 ($M^+ + 23$). Elemental Analysis: Calcd. for $C_{12}H_{15}N_5S$: C, 55.17; H, 5.75; N, 26.82; S, 12.26 Found: C, 55.15; H, 5.75; N, 26.80; S, 12.25 (S1, Supplementary data).

3. Results and discussion

Out of the various metal ions tested, the hetarylazo dye **3** (yellow, λ_{max} 480 nm, ε_{max} 30,776 m^2mol^{-1}) detects Hg^{2+} (purple, λ_{max} 531 nm and 564 nm), and Fe^{3+} (red, λ_{max} 531 nm and 564 nm)



Scheme 1. Preparation of hetarylazo compound **3** and **4**.

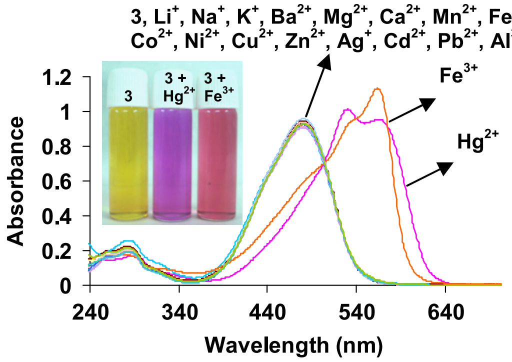


Fig. 1. UV–vis spectra of **3** (3×10^{-5} M, in CH_3CN) in the presence of different metal ions (2×10^{-5} M, in H_2O). The CH_3CN:H_2O ratio in the resulting solution is 9:1.

from their aqueous solutions (Fig. 1), while other relevant metals do not modulate the absorption spectrum of **3**, or its complex with Hg^{2+} and Fe^{3+} in any significant way.

The absorption band at 480 nm in acetonitrile solution, corresponding to yellow color of **3** is attributed to the internal charge-transfer (ICT) of the chromophore due to the push-pull effect of the electron-donating *N*,*N*-di(β-ethoxycarbonylethyl) aniline group and electron-withdrawing thiadiazole moiety. To see if the chemosensing properties of **3** are dependent upon the pH of the system, the effect of pH variation was noted during titration of a solution of **3** with $NaHCO_3$ as well as HCl in the concentration range 0.01 M to 0.1 M (Fig. S2, Supplementary data). The charge-transfer absorption band at 480 nm observed an insignificant shift in its wavelength position coupled with no change in the color of **3**, over the whole pH range (1.0–11.0) tested. Thus **3** demonstrates considerable stability to pH variation which is often considered an advantage for rapid monitoring of aqueous analytes in environmental or biological settings without resorting to buffered media.

The change in the absorption spectrum of **3** in the presence of aqueous solutions of upto 10 equivalents of 18 metal cations (group I, II and transition metal ions Li^+, Na^+, K^+, Ba^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+} Zn^{2+} and Al^{3+} added as perchlorates and Ag^+ and Cd^{2+} as nitrates) was read at pH 7.78. Only in case of Hg^{2+} and Fe^{3+}, the absorption spectrum showed changes compared to the ion-free solution (Fig. 1). In both of these cases, the single absorption band of **3** at 480 nm was red shifted to show twin absorptions at 531 and 564 nm with variable intensity [Hg^{2+}: 531 nm (ε_{max} 45,415 m^2mol^{-1}) and 564 nm (ε_{max} 41,355 m^2mol^{-1}), Fe^{3+}: 531 nm (ε_{max} 37,455 m^2mol^{-1}) and 564 nm (ε_{max} 38,845 m^2mol^{-1}), Fig. 2]. The observed color changes allowed a visual distinction of Hg^{2+} and Fe^{3+} from other metal ions, as well as from each other with naked eye also (Fig. S3(a), Supplementary data). Further, these changes were fully reversible as the addition of EDTA reversed the spectroscopic as well as color changes (Fig. S4, Supplementary data). In the titrations of Hg^{2+} or Fe^{3+} with **3**, increasing the concentration of the appropriate metal salt, a decrease in the intensity of the absorption band of **3** at 480 nm was attended by appearance of the twin absorption bands at 531 and 564 nm, in both the cases. The formation of isosbestic points were noticed at 502 nm and 512 nm in the titrations of Hg^{2+} and Fe^{3+}, respectively (Fig. 2). The observed pattern of the changes in the absorptions during titrations continued until 2×10^{-5} M concentration of the metal ions. At this point, the titrations were adjudged complete resulting in the formation of respective complexes. In these titrations (metal ion concentration: 2×10^{-6} M to 2×10^{-5} M), the observed change in the absorbances were used for the quantitative estimation of concentration of both the metal ions.

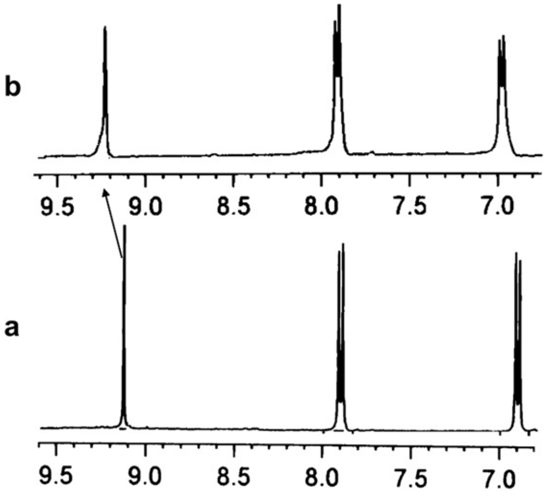


Fig. 3. Partial ^1H NMR (CD_3CN) spectrum of **3** (a) before and (b) after addition of Hg^{2+} ion.

Conceptually, in accordance with the hard soft acid base (HSAB) principle [22], complexation of Hg^{2+} and Fe^{3+} is most likely to involve the sulfur atom of thiadiazole moiety of **3** and nitrogen atom of the –N=N– link resulting in the enhanced intramolecular charge transfer causing the observed red shift in the absorption band. This is further attested by the observed shift in the C5-H signal of the thiadiazolyl moiety in the ^1H NMR experiment depicted in Fig. 3. However, different extents of the red shift in Hg^{2+} complex [($\Delta\lambda$, 51 nm), dominating peak 531 nm] and Fe^{3+} complex [($\Delta\lambda$, 84 nm), dominating peak 564 nm] may be attributed to the difference in electronegativity [23] of both the metal ions in their

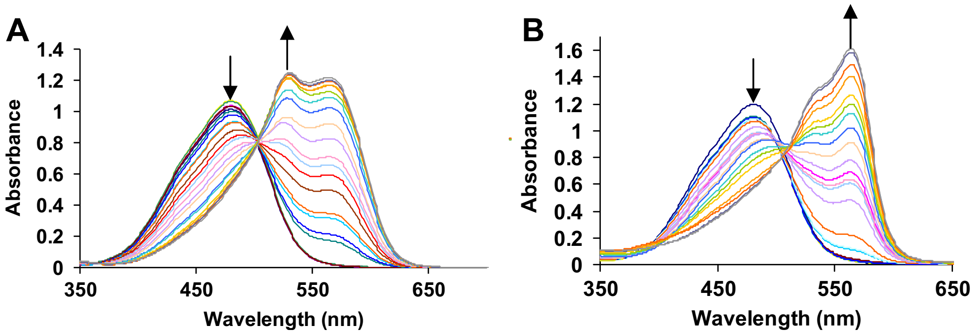


Fig. 2. Changes in the absorption spectrum of **3** (3×10^{-5} M, in CH_3CN) upon addition of increased concentrations of (A) Hg^{2+} solution and (B) Fe^{3+} solution (2×10^{-6} M to 5×10^{-5} M).

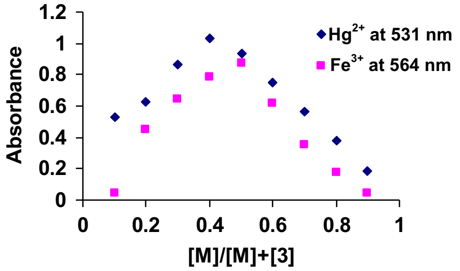


Fig. 4. Job's plots of Hg^{2+} and Fe^{3+} complex formation. [M]/[M]+[**3**] is the mole fraction of the respective metal ion.

respective oxidation states and consequent stabilization of the LUMO (Fig. S5, Supplementary data) could be expected.

The spectral features in Job's plots (Fig. 4) are consistent with the 1:2 (Hg^{2+}: **3**) and 1:1 (Fe^{3+}: **3**) binding ratios, respectively, for the two metal ions. The spectral fitting of the titration data of **3** using SUPERQUAD [24] programme furnished very similar log β values, 8.8572 and 8.7175 for Hg^{2+} and Fe^{3+}, respectively.

The difference in wavelengths of maximum absorptions of both the complexes (Hg^{2+} complex, λ_{max} 531 nm and Fe^{3+} complex, λ_{max} 564 nm) and observed identical formation constants were used for the simultaneous estimation of metal ions from their mixture solution with the limiting condition that the total metal ion concentration should not exceed 2×10^{-5} M in solution in the current assay. The detailed calculations are provided in Supporting Information (S6, Supplementary data).

Further the possibility of binding of hard oxygen sites, generally considered as good binding sites for lanthanides, was also explored. Addition of upto 10 equivalents of Ho^{3+}, Tm^{3+}, Lu^{3+} (as nitrates in THF), Er^{3+}, Tb^{3+}, Gd^{3+} (as chlorides in DMSO), Ce^{3+} (as sulfate in DMSO), Eu^{3+} (as triflate in CH_3OH) and Dy^{3+} (as sulfonate in DMSO) to **3** (3×10^{-5} M, in CH_3CN) did not alter the absorption spectrum of **3** (Fig. 5) (Fig. S3(b), Supplementary data). Thus, dye **3** can be regarded as highly selective sensor for Hg^{2+}, even in the presence of lanthanide cations tested herein.

When dye **4** was used in place of **3**, a similar response to the metal ions as well as selectivity pattern was noted (Fig. S7, Supplementary data). This is suggestive of only insignificant participation of ester moieties of **3** in the binding phenomenon. However, the choice of **3** as a selective Hg^{2+} sensor was guided by the clarity of color changes which were superior to **4**.

In order to see if the results obtained in the solution studies could be visualized on paper strips to obtain ready to use "dip sticks", when paper strips coated with **3** (S8, Supplementary data) were introduced in aqueous solutions of Hg^{2+} ions of varying concentrations, an instant purple color was developed, however, compared to solution, the detection limit on paper was limited to 5×10^{-3} M. Fig. 6 shows the colors developed on paper strips *vis-à-vis* corresponding standard colors obtained in solution studies. Development of such dip-sticks is useful as instant qualitative information is obtained without any special equipment.

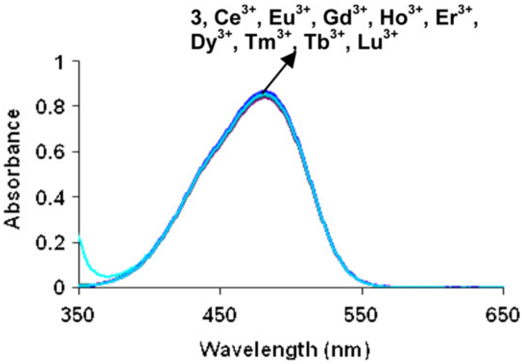


Fig. 5. UV–vis spectra of **3** (3×10^{-5} M, in CH_3CN) in the presence of different lanthanides.

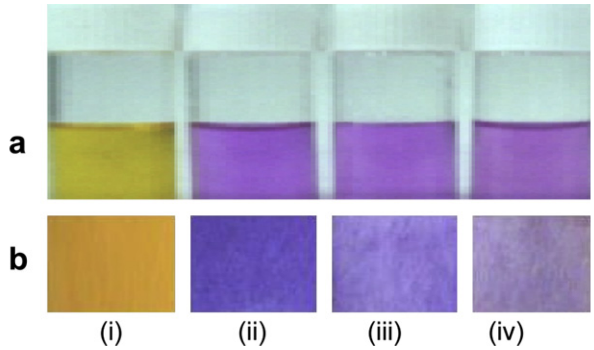


Fig. 6. Demonstration of colours of (i) dye **3** with (ii)10^{-1} M, (iii) 10^{-2} M and (iv) 5×10^{-3} M Hg^{2+} in (a) solution and (b) on coated dip sticks.

4. Conclusion

In summary, we have demonstrated that the hetarylazo derivative **3** can be used for the detection of Hg^{2+} and Fe^{3+}, simultaneously and selectively over the other thiaphilic metal ions such as Ag^{+} and Pb^{2+} as well as a number of other cations including lanthanides. The observed spectral responses allowed simultaneous quantitative estimation of both Hg^{2+} and Fe^{3+} ions, from their mixture solution and this aspect makes it a rare example. The fact that **3** can be prepared in multi gram quantities using simple laboratory preparative method, the practicability of the method is obvious. Further, development of dip-sticks is attractive although the process is limited by higher detection limit compared to solution study but provides an excellent opportunity to obtain readily accessible handy detection devices.

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Appendix. Supplementary information

Characterization of **3** and **4** and additional spectral data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2010.07.012.

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