

## Attachment of phosphonate-functionalised azo-dyes to oxide surfaces to give enhanced light and wet fastness†

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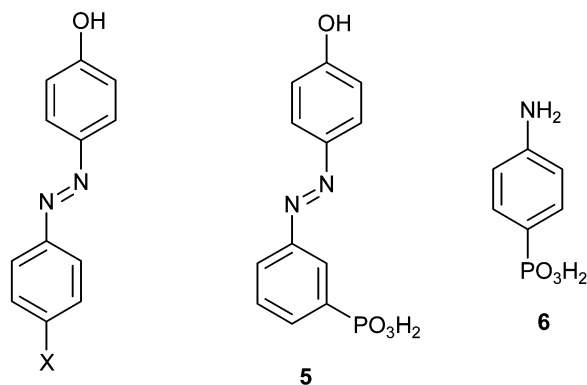
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Received (in Cambridge, UK) 31st March 2003, Accepted 23rd May 2003

First published as an Advance Article on the web 13th June 2003

Phosphonate-functionalised dyes have been shown to bind strongly to aluminium oxides and to form stable 1 : 1 complexes with cyclodextrins at the surface.

The rapid development of digital imaging has been accompanied by a need to generate high quality hard-copy output. Papers which give photorealistic images by inkjet printing are generally coated with oxides such as alumina and silica to improve the print quality and durability, and titanium dioxide to increase brightness.<sup>1,2</sup> In principle it should be possible to improve the performance of water-soluble dyes on metal oxide-treated papers, particularly with regard to wet fastness, by attaching good surface ligating functionalities. Previous work with iron(III) oxides has shown<sup>3,4</sup> that surface binding can be greatly enhanced by using donor sets which are capable of 'multisite attachment' via a combination of conventional metal-donor coordinate bonds and ligand-surface and ligand-ligand hydrogen bonding. With this in mind we have compared the uptakes on aluminium oxides of simple azo-dyes † 1–5 containing a potentially polynucleating phosphonic acid substituent§ with those of carboxylic and sulfonic acid analogues and related the results to their performance when inkjet printed onto alumina and silica-treated papers.



- 1, X = SO<sub>3</sub>H  
2, X = CO<sub>2</sub>H  
3, X = PO<sub>3</sub>H<sub>2</sub>  
4, X = CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>

Adsorption isotherms (Fig. 1)¶ were used to determine the uptake of the azo dyes from water onto high surface area Al(OH)<sub>3</sub>. The phosphonic acid substituted dyes 3 and 4 show stronger binding and higher surface coverage than do the sulfonic and carboxylic acid substituted compounds 1 and 2, respectively. Incorporation of the phosphonic acid group in the *meta*-position in 5 gives rise to similarly strong uptake, but a lower surface coverage than does *para* substitution. Presumably the *para*-isomer binds with its molecular backbone almost perpendicular to the surface, giving rise to a more efficient

packing than can be achieved by the *meta*-isomer. Strong surface binding of phosphonates to titania particles has also been reported recently.<sup>7</sup>

The phosphonate functionalised dye 3 performs significantly better in standard wet fastness tests|| than its sulfonic and carboxylic analogues (1 and 2, respectively) after inkjet printing onto aluminium oxide or silica-treated papers, supporting the hypothesis that attaching oxide-anchoring groups provides an effective way of enhancing the performance of inkjet dyes.

Recently it has been shown that enclosing the azo group of a "reactive" dye in the cavity of  $\alpha$ -cyclodextrin ( $\alpha$ -CD) significantly improves its resistance to reductive, oxidative and photo-bleaching when used on textiles.<sup>8</sup> In order to establish whether this approach can be used to protect inkjet dyes at oxide surfaces it is necessary to show that the surface ligating dyes form strong inclusion complexes with cyclodextrins, and that the resulting assemblies are strongly bound to the oxide surface through the pendant phosphonate group.

The formation of 1 : 1 complexes of 3 with  $\alpha$ -cyclodextrin was confirmed by making <sup>1</sup>H NMR measurements on solutions in D<sub>2</sub>O, with various values of cyclodextrin concentration and a fixed total dye concentration.\*\* The resulting fit of <sup>1</sup>H NMR data (Fig. 2) gave the values  $K = (2 \pm 1) \times 10^3$ ,  $\delta_{\text{free}} = 7.77 \pm 0.02$  ppm, and  $\delta_{\text{complex}} = 7.48 \pm 0.01$  ppm.

Adsorption isotherm measurements showed that the phosphonate groups in 3, 4 and 5 allow the 1 : 1 dye : cyclodextrin complexes to be firmly tethered to the surface of Al(OH)<sub>3</sub>. The initial slopes of the plots (Fig. 3) of the uptake of 3 in the presence of  $\alpha$ - or  $\beta$ -cyclodextrin are very similar to that of the dye alone, indicating similar binding strengths. The increased bulk of the cyclodextrin complexes leads to a significant decrease in surface coverage from  $(20.0 \pm 0.8) \times 10^{-6}$ , to  $(6.3 \pm 0.3) \times 10^{-6}$  and  $(4.8 \pm 0.3) \times 10^{-6}$  mol g<sup>-1</sup> for 3 and its  $\alpha$ - and  $\beta$ -cyclodextrin complexes, respectively. These data correspond to coverages of  $58 \pm 2$ ,  $185 \pm 9$  and  $242 \pm 15$  Å<sup>2</sup> molecule<sup>-1</sup>, respectively, based on the surface area (7 m<sup>2</sup> g<sup>-1</sup>) for the Al(OH)<sub>3</sub> used and suggest almost complete close packing of both the  $\alpha$ - and  $\beta$ -cyclodextrin complexes, assuming these complexes have the same diameters (13.7 and 15.3 Å respectively) as those reported for the free cyclodextrins.<sup>9</sup>

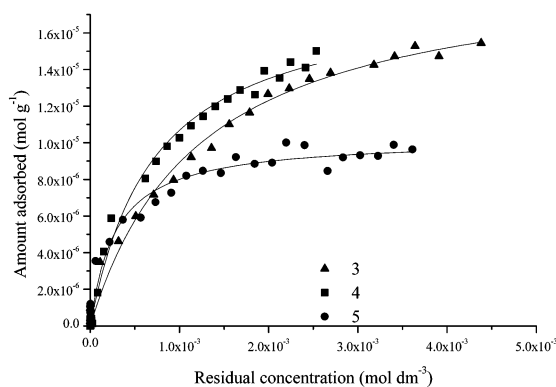
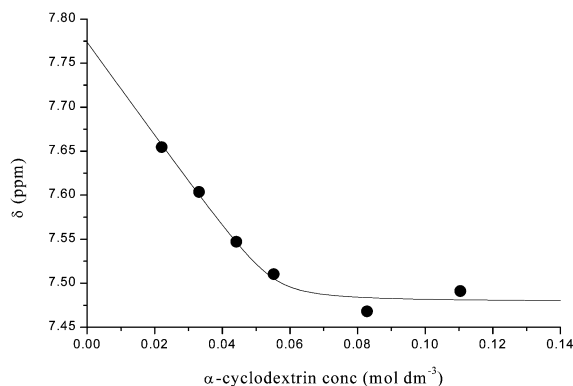
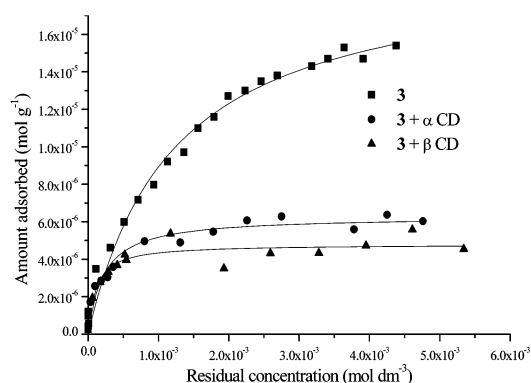


Fig. 1 Adsorption isotherms¶ showing uptake of 3–5 onto Al(OH)<sub>3</sub>.

† Electronic supplementary information (ESI) available: ROESY NMR spectrum of 1 and  $\alpha$ -cyclodextrin. See <http://www.rsc.org/suppdata/cc/b3/3303608c/>



**Fig. 2** Variation of the chemical shift of the  $^1\text{H}$  (7.4 ppm) signal of **3** ( $0.0552 \text{ mol dm}^{-3}$ ) in  $\text{D}_2\text{O}$  with concentration of  $\alpha$ -cyclodextrin.



**Fig. 3** Adsorption isotherms showing the uptake of **3** and its complexes with  $\alpha$ - and  $\beta$ -cyclodextrins on  $\text{Al}(\text{OH})_3$ .

The model sulfonate and carboxylate dyes **1** and **2** also form inclusion complexes and show similar decreases in surface coverage in the presence of cyclodextrins, consistent with the formation of stable ternary,  $\text{Al}(\text{OH})_3/\text{dye}/\text{CD}$  complexes. The assembly of such complexes could enhance light fastness by shielding the azo groups from attack by photo-bleaching agents. In solution, the ROESY  $^1\text{H}$  NMR spectrum of a 1 : 1 mixture of **1** and  $\alpha$ -cyclodextrin in  $\text{D}_2\text{O}$  indicates that the four H-atoms *ortho* to the azo group form close contacts with protons of the  $\alpha$ -cyclodextrin pointing towards the cavity (H3 and H5 protons) and suggests that a major part of the dye is enclosed in the cyclodextrin and should be screened from attack by photo-bleaching agents. Preliminary lightfastness tests support this proposition. After printing an ink containing the sulfonate model dye **1** ( $8.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) onto an alumina-treated paper (HG 201), the optical density loss after exposure for 14000 lux h is reduced from 85 to 50% when the ink contains a 0.9 molar ratio of  $\alpha$ -cyclodextrin. In these inkjet/light fastness tests on paper the solubility of the cyclodextrins is not high enough to allow them to be used in equimolar quantities at the concentrations needed in the test for the model dyes **1–5** which have relatively weak chromophores.†† Despite this, the results to date suggest that using a surface ligating dye in an ink containing organic host molecules provides a useful approach to improving both the wet and light fastness after printing on oxide-treated papers.

The authors wish to thank Dr J. Bella, Mr J. R. A. Millar, Mr W. Kerr and Mr E. Perez for their help with NMR spectroscopy. This work has been supported by the EPSRC and by Avevia plc.

## Notes and references

‡ Azo-compounds **1** and **2** were prepared by coupling of the appropriate diazonium salts with phenol under basic conditions.<sup>10</sup> *p*-Aminophenylphosphonic acid **6** was produced from *p*-bromoacetanilide (0.08 moles) and triethyl phosphite (0.05 moles) in the presence of  $\text{NiCl}_2$  (0.04 moles) at  $145\text{--}180^\circ\text{C}$ . The resulting grey solid was recrystallised from ethyl acetate then hydrolysed with conc. HCl to give **6** (41% overall); mp  $253\text{--}254^\circ\text{C}$  (lit.,<sup>11</sup>  $254\text{--}256^\circ\text{C}$ ). Azo coupling was carried out as above<sup>10</sup> to give **3** mp  $277\text{--}280^\circ\text{C}$  (dec).  $\delta_{\text{H}}$  (360 MHz,  $\text{DMSO-}d_6$ ) 6.98 (d, 2H), 7.89 (d, 2H) and 7.76–7.84 (m, 4H);  $\delta_{\text{C}}$  (63 MHz,  $\text{DMSO-}d_6$ ) 116.2, 121.6, 125.2, 131.8, 140.5, 145.3, 153.5 and 161.7;  $\delta_{\text{P}}$  (101 MHz,  $\text{DMSO-}d_6$ ) 11.47; *m/z* (ES, negative ion), 277 ( $\text{M} - \text{H}$ )<sup>-</sup>. (Found: C, 51.8; H, 3.9; N, 10.0.  $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_4\text{P}$  requires: C, 51.8; H, 4.0; N, 10.1%). Azo-dyes **4** and **5** were prepared from the appropriate anilines by standard methods<sup>10</sup> and were characterised as above.

§ Three dimensional zeolite-like structures are observed for metal phosphonates containing multiple bridging  $\text{RPO}_3^{2-}$  units,<sup>5,6</sup> suggesting that phosphonate ligands will show multisite attachment<sup>3,4</sup> and hence strong binding to the surface of aluminium oxy/hydroxides.

¶ Accurately weighed samples of  $\text{Al}(\text{OH})_3$  (ca. 0.4 g) in polycarbonate centrifuge tubes were stirred with the desired concentration of dye in water ( $10 \text{ cm}^3$ ) for 2 h ( $25^\circ\text{C}$ , pH 8). The suspensions were centrifuged and filtered, and the phosphorus concentration was measured by ICP-OES to determine the concentration of dye remaining in solution and hence the amounts adsorbed. The data for each dye were fitted to the Langmuir adsorption equation for the plots in Figs. 1 and 3.

|| Wet fastness tests were performed 1 and 24 h after printing, and were compared against the results obtained for control inks.

\*\* The total dye concentration  $[\text{D}]_0$  and the total cyclodextrin concentration  $[\text{C}]_0$  were sufficiently low that the respective activity coefficients could be taken as equal to unity. With this approximation, the mole fraction of 'free' (uncomplexed) dye molecules,  $x_{\text{free}}$ , is given by,

$$x_{\text{free}} = \frac{-(1 + K\Delta) + \sqrt{(1 + K\Delta)^2 + 4K[\text{D}]_0/c^{\ominus}}}{2K[\text{D}]_0/c^{\ominus}} \quad (1)$$

where  $K$  is the equilibrium constant,  $\Delta = ([\text{C}]_0 - [\text{D}]_0)/c^{\ominus}$ , and  $c^{\ominus} = 1 \text{ mol dm}^{-3}$ . In the NMR experiments, the total dye concentration was held fixed at  $[\text{D}]_0 = 0.0552 \text{ mol dm}^{-3}$ , and  $[\text{C}]_0$  was varied between  $0.4[\text{D}]_0$  and  $2.0[\text{D}]_0$ . The variation of the peak position of a well resolved signal in the region of  $\delta_{\text{H}} = 7\text{--}8 \text{ ppm}$  with  $[\text{C}]_0$  was attributed to an average of the signals from the 'free' dye with  $\delta = \delta_{\text{free}}$ , and the complexed dye with  $\delta = \delta_{\text{complex}}$ , i.e.,

$$\bar{\delta}([\text{C}]_0) = x_{\text{free}}\delta_{\text{free}} + (1 - x_{\text{free}})\delta_{\text{complex}} \quad (2)$$

where  $x_{\text{free}}$  is given by eqn. (1).

†† A new test protocol involving direct application to oxide treated papers of solutions of dyes + cyclodextrins is being used to compare light fastness with the stability of ternary  $\text{Al}(\text{OH})_3/\text{dye}/\text{CD}$  complexes of **1–5** and related systems.

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