

# The assembly of rotaxane-like dye/cyclodextrin/surface complexes on aluminium trihydroxide or goethite†‡

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Simple azo-dyes carrying phosphonic acid and arsonic acid substituents such as 4-(4'-hydroxyphenyl azo)phenylphosphonic acid (**5**) and 4-(4'-hydroxyphenylazo)phenylarsonic acid (**6**) bind more strongly to high surface area oxides such as aluminium trihydroxide and goethite than their carboxylic and sulfonic acid analogues and the phosphonate-functionalized dyes have been shown to have greater humidity fastness when printed onto commercial alumina-coated papers. Adsorption isotherm measurements provide evidence for the formation of ternary dye/cyclodextrin/surface complexes. Dyes which form such ternary complexes show higher light fastness when printed onto alumina coated papers in an ink formulation containing  $\alpha$ -cyclodextrin.

## Introduction

The rapid development of digital cameras has been accompanied by technologies which give photorealistic images by inkjet printing onto high quality papers.<sup>1</sup> These are usually treated with oxides such as alumina or silica to improve the quality and durability of the print and titanium dioxide to increase brightness.<sup>2,3</sup> The inks currently used for photographic quality prints are generally similar to those used on lower grade papers and it is important to establish whether their performance can be improved by functionalizing the dyes to meet the requirements of the higher grade papers. To this end we have previously described a strategy for enhancing the wet fastness of dyes for inkjet printing based on incorporating ligating groups which form very stable complexes with the oxides used in photo quality papers.<sup>4</sup> In this paper we discuss adsorption

isotherm measurements on the uptake of simple dyes containing pendant sulfonic, carboxylic, phosphonic and arsonic acid groups (Fig. 1) at high surface area aluminium trihydroxide (ATH) using this as a model for oxide treated papers. Results are compared with the uptake on goethite which while not used for paper treatment is an important pigmentary material.

Incorporation of chromophores into the cavities of cyclodextrins (CDs) can greatly enhance their stability towards photobleaching.<sup>5-7</sup> When "reactive dye" chemistry<sup>8</sup> based on the replacement of chlorine atoms in 1,3,5-trichlorotriazine was used to attach a chromophore-cyclodextrin complex to cellulose, a rotaxane was generated, "stopped" at one end by the cellulose surface and the other by a bulky naphthalene disulfonic acid group (Fig. 2).<sup>5</sup> In this paper we focus on the design requirements to form rotaxane-like ternary complexes in which an inclusion complex of the dye in the cyclodextrin is tethered to an ATH or goethite surface by a ligating group on the water-soluble dye.

## Experimental

### Instrumentation

1D Nuclear magnetic resonance spectra were recorded on Bruker AC 250 MHz and DPX Bruker 360 MHz instruments. All 2D NMR experiments (COSY, and ROESY) were acquired from 1024 increments of 2 K data points and 16 scans each. The data were zero-filled twice in the  $t_1$  dimension and multiplied by a squared sine bell function (SSB) in both dimensions. NMR spectroscopic data processing was carried out on a Bruker Silicon Graphics O2 station with standard UXNMR software as well as on a PC with 1D WIN NMR (960901) software (Bruker Franzen Analytic GmbH).

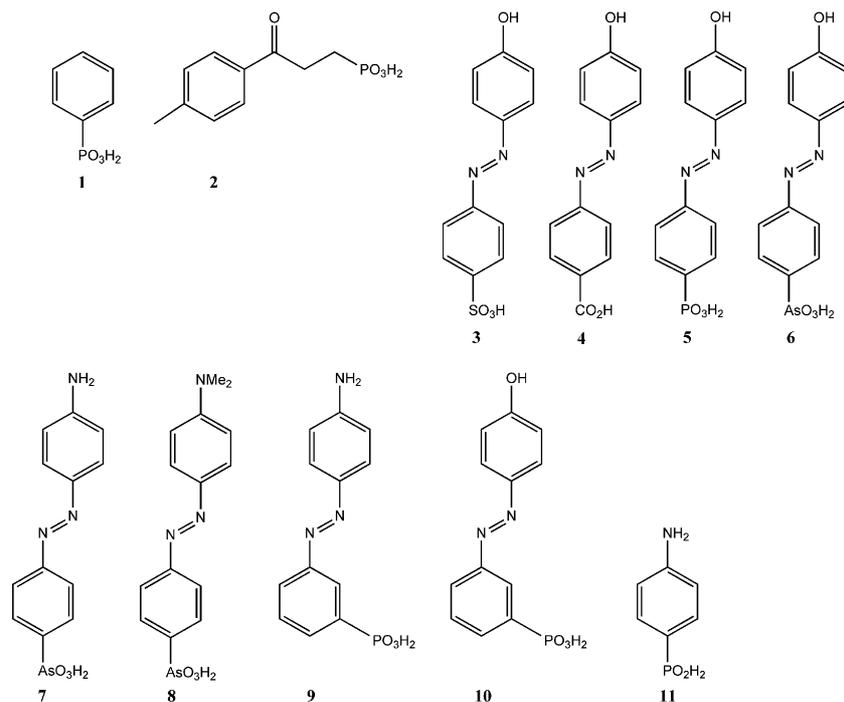
Fast atom bombardment (FAB) mass spectrometry was performed on a Kratos MS 50 machine. Electrospray (ESI) mass spectra were obtained on a Thermoquest LCQ spectrometer. FTIR spectra were recorded on a JABCO FTIR-460 spectrometer using KBr discs. Electronic spectra were measured on an ATI UNICAM UV/Vis spectrometer with 1 cm path length quartz

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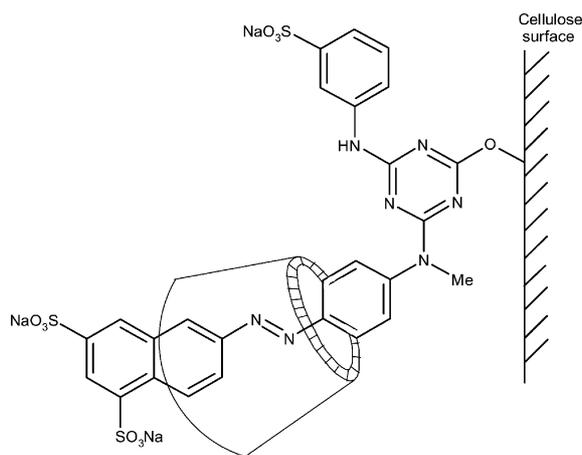
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‡ Electronic supplementary information (ESI) available: 1–2: Title page; 3–4: Data for isotherms of compounds **1** and **2** on ATH; 5–6: Data for Fig. 3 – isotherms of **5** and **6** on ATH; 7–8: Data for Fig. 4 – isotherms of **1** and **5** on goethite (plotted on a log scale); 9: Data for Fig. 5 – NMR data for formation of **5**:  $\alpha$ -CD complex; 10: Data for Fig. 6 – UV/Vis data for formation of **5**:  $\alpha$ -CD complex; 11–12: Data for Fig. 8 – isotherms of compound **5** with  $\alpha$ - and  $\beta$ -CD on ATH; 13–14: Data for Fig. 10 – isotherm of compound **6** with  $\alpha$ -CD on ATH; 15–16: Data for Fig. 11 – isotherm of compound **5** with  $\alpha$ -CD on goethite; 17–18: Data for Fig. 12 – isotherm of compound **1** with  $\alpha$ -CD on goethite; 19: Data for UV/Vis for formation of **4**:  $\alpha$ -CD complex; 20: Data for UV/Vis for formation of **6**:  $\alpha$ -CD complex; 21: Data for UV/Vis for formation of **7**:  $\alpha$ -CD complex; 22: Data for UV/Vis for formation of **8**:  $\alpha$ -CD complex; 23: Data for UV/Vis for formation of **9**:  $\alpha$ -CD complex; 24: Data for UV/Vis for formation of **10**:  $\alpha$ -CD complex; 25: ROESY NMR of **3**:  $\alpha$ -CD complex; 26: ROESY NMR of **4**:  $\alpha$ -CD complex; 27: ROESY NMR of **5**:  $\alpha$ -CD complex; 28: ROESY NMR of **6**:  $\alpha$ -CD complex; 29: ROESY NMR of **9**:  $\alpha$ -CD complex; 30: ROESY NMR of **10**:  $\alpha$ -CD complex; 31: Light fastness results of **3–6**, **9** and **10**; 32: Paper types used in inkjet tests; 33: Data for isotherm of **3** on ATH; 34: Data for isotherm of **4** on ATH; 35–36: Data for isotherms of **7** and **8** on ATH; 37–38: Data for isotherms of **9** and **10** on ATH. See DOI: 10.1039/b518260c



**Fig. 1** Structures of the azo-dyes and simple phosphonic acid derivatives used in this paper.



**Fig. 2** The proposed rotaxane structure for the attachment of a reactive dye to mercerized cotton.<sup>5</sup>

cuvettes. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis for Al, As, Fe, P and S was performed on either a Thermo Jarrell Ash IRIS ICP-OES or a Perkin Elmer Optima 5300 DV. C, H, N contents were obtained on a CE-440 elemental analyzer. Melting points were recorded on a Gallenkamp apparatus and the measurement of pH was carried out using an ORION 410A pH meter.

Curve fitting was performed using the programs Origin 5.0 (c) Microcal Software Inc and SigmaPlot 2000 (demo version) (c) 1986-2000 SPSS Inc.

### Solvent and reagents

All reagents were used as obtained from Aldrich, Lancaster or Fluka. Solvents were used as received. High surface area "superfine Al(OH)<sub>3</sub>" was supplied by Alcan Chemicals and

Goethite by Bayer (Bayferrox<sup>®</sup> 415).  $\alpha$ -Cyclodextrin was dried at 100 °C under vacuum prior to use. Water was purified before use on a Milli-Q<sup>®</sup> water purification system.

### Synthesis of the ligands shown in Fig. 1

Phenylphosphonic acid, **1**, 4-(4'-aminophenylazo)phenylarsonic acid, **7** and 4-(4'-dimethylaminophenylazo)benzenearsonic acid hydrochloride, **8** were obtained from Aldrich.

**3-Oxo-3-*p*-tolylpropylphosphonic acid (2).** **2** was prepared in three steps<sup>9,10</sup> from 4-methylacetophenone. Yield (70%); mp 157–159 °C. Found: C, 52.60; H, 5.72. C<sub>10</sub>H<sub>13</sub>O<sub>4</sub>P requires C, 52.64; H, 5.74%.  $\delta_{\text{H}}$  (d<sub>6</sub>-DMSO, 250 MHz) 7.85 (d, 2H, Ar-*H*), 7.32 (d, 2H, Ar-*H*), 3.15 (m, 2H, CH<sub>2</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 1.90 (m, 2H, CH<sub>2</sub>P).  $\delta_{\text{C}}$  (d<sub>6</sub>-DMSO, 63 MHz) 197.66 (C=O), 143.46 (Ar C), 133.95 (Ar C), 129.44 (Ar 2CH), 128.08 (Ar 2CH), 38.76 (CH<sub>2</sub>), 21.97 (CH<sub>2</sub>P), 21.28 (CH<sub>3</sub>).  $\delta_{\text{P}}$  (d<sub>6</sub>-DMSO, 101 MHz) 27.30. MS (FAB, NOBA)  $m/z$  229 (MH<sup>+</sup>, 99.2%).  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3500 br (OH), 1681 (C=O), 1251 (P=O).

**4-(4'-Hydroxyphenylazo)benzenesulfonic acid (3).** Dye **3** was obtained from sulfanilic acid.<sup>11</sup> Yield (58%); mp 282–285 °C (decomp.) (lit.,<sup>11</sup> 283 °C).  $\delta_{\text{H}}$  (D<sub>2</sub>O, 250 MHz) 7.73 (d, 2H, Ar-*H*), 7.58 (m, 4H, Ar-*H*), 6.54 (d, 2H, Ar-*H*).  $\delta_{\text{C}}$  (D<sub>2</sub>O, 63 MHz) 174.94 (C–OH), 154.58 (C–S), 142.58 (C–N=N), 142.07 (C–N=N), 127.08 (Ar 4CH), 122.15 (Ar 2CH), 120.29 (Ar 2CH). MS (ES, MeOH–CH<sub>3</sub>CN)  $m/z$  277 (M<sup>-</sup>, 100%).  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3244 br (OH), 1187 (O=S=O).

**4-(4'-Hydroxyphenylazo)benzoic acid (4).** Dye **4** was similarly prepared from 4-aminophenylcarboxylic acid.<sup>11</sup> Yield (66%);

§ As is the norm for water-soluble dyes, CHN values are not included in the paper since the dyes are isolated in their salt form.

mp 275–277 °C (decomp.) (lit.,<sup>12</sup> 277–279 °C).  $\delta_{\text{H}}$  (D<sub>2</sub>O, 250 MHz) 7.98 (d, 2H, Ar–H) 7.76–7.84 (m, 4H, Ar–H), 6.98 (d, 2H, Ar–H).  $\delta_{\text{C}}$  (D<sub>2</sub>O, 63 MHz) 183.01 (CO<sub>2</sub>H), 157.59 (C–OH), 157.32 (C–N=N) 145.20 (C–N=N), 133.15 (Ar C–CO<sub>2</sub>H), 130.40 (Ar 2CH), 122.61 (Ar 2CH), 124.09 (Ar 2CH), 116.11 (Ar 2CH). MS (ES, MeOH–CH<sub>3</sub>CN)  $m/z$  241 (M<sup>–</sup>, 100%).

**4-(4'-Hydroxyphenylazo)phenylphosphonic acid (5).** Dye 5 was prepared by a procedure developed at Avecia.<sup>13</sup> *p*-Bromoacetanilide (50.0 g, 0.21 mol) and NiCl<sub>2</sub> (3.5 g, 0.03 mol) were heated under N<sub>2</sub> at 190 °C and triethyl phosphite (45.0 ml, 0.26 mol) was added dropwise, collecting the 1-bromoethane formed in a Dean–Stark apparatus fitted with a solid CO<sub>2</sub> condenser. After addition was complete, the reaction was allowed to cool to 150 °C and stirred for 1 h. The solution was allowed to cool to room temperature and stirred with light petroleum (bp 40–60 °C) overnight. The white solid which separated was recrystallised from ethyl acetate to give 4-acetylaminophenylphosphonic acid diethyl ester, as white crystals. Yield (29.4 g, 52%); mp 138–140 °C. Found: C, 52.33; H, 6.60; N, 5.19. C<sub>12</sub>H<sub>18</sub>NO<sub>4</sub>P requires C, 53.14; H, 6.69; N, 5.16%.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 250 MHz) 9.44 (s, 1H, NH), 7.76 (m, 4H, Ar–H), 4.09 (m, 4H, 2CH<sub>2</sub>), 2.22 (s, 3H, CH<sub>3</sub>C=O), 1.33 (t, 6H, 2CH<sub>3</sub>).  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 63 MHz) 169.48 (C=O), 142.68 (Ar C–N), 132.55 (Ar 2CH), 122.65 (Ar CH), 120.52 (Ar CH), 119.14 (Ar C–P) 62.09 (2 OCH<sub>2</sub>), 24.30 (CH<sub>3</sub>C=O), 16.14 (2 CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{P}}$  (CDCl<sub>3</sub>, 101 MHz) 20.20. MS (FAB, NOBA)  $m/z$  272 (MH<sup>+</sup>, 100%).  $\nu_{\text{max}}/\text{cm}^{-1}$  3311 br (OH), 1701 (C=O), 1259 (P=O). 4-Acetylaminophenylphosphonic acid diethyl ester (20.0 g, 0.07 mol) was stirred at reflux (*ca.* 100 °C) in concentrated HCl (500 ml) overnight. Ethanol (70 ml) was added to aid dissolution. The solution was concentrated to 100 ml and placed in the fridge for 48 h. The resulting white precipitate, 4-aminophenylphosphonic acid, **11** was collected and dried *in vacuo*. Yield (8.0 g, 62%); mp 251–252 °C (lit.,<sup>14</sup> 254–256 °C).  $\delta_{\text{H}}$  (D<sub>2</sub>O 250 MHz) 7.52 (m, 2H, Ar–H), 6.84 (m, 2H, Ar–H).  $\delta_{\text{C}}$  (D<sub>2</sub>O, 63 MHz) 147.89 (C–NH<sub>2</sub>), 131.92 (Ar 2CH), 129.66 (C–P), 115.84 (Ar 2CH).  $\delta_{\text{P}}$  (D<sub>2</sub>O, 101 MHz) 14.70. MS (FAB, NOBA)  $m/z$  174 (MH<sup>+</sup>, 71%).  $\nu_{\text{max}}/\text{cm}^{-1}$  2865 br (OH), 1226 (P=O). 4-Aminophenylphosphonic acid was converted to 4-(4'-hydroxyphenylazo)phenylphosphonic acid, **5** using the method of Suh *et al.*<sup>11</sup> Yield (95%); mp 277–280 °C (decomp.).  $\delta_{\text{H}}$  (D<sub>2</sub>O, 250 MHz) 7.72–7.83 (m, 4H, Ar–H), 7.65 (m, 2H, Ar–H) 6.75 (d, 2H, Ar–H).  $\delta_{\text{C}}$  (D<sub>2</sub>O, 63 MHz) 173.91 (C–OH), 152.90 (C–P), 142.00 (C–N=N), 141.09 (C–N=N), 131.68 (Ar 2CH), 126.42 (Ar 2CH), 121.08 (Ar 2CH), 120.12 (Ar 2CH).  $\delta_{\text{P}}$  (D<sub>2</sub>O, 101 MHz) 11.79. MS (ES, MeOH–CH<sub>3</sub>CN)  $m/z$  277 (M<sup>–</sup>, 100%).  $\nu_{\text{max}}/\text{cm}^{-1}$  3470 br (OH), 1247 (P=O).

**4-(4'-Hydroxyphenylazo)phenylarsonic acid (6).** Dye 6 was prepared from 4-aminophenylarsonic acid using the same method<sup>11</sup> as **3**. Yield (62%); mp 288–289 °C (decomp.).  $\delta_{\text{H}}$  (D<sub>2</sub>O, 250 MHz) 7.72 (d, 2H, Ar–H), 7.60–7.64 (m, 4H, Ar–H), 6.57 (d, 2H, Ar–H).  $\delta_{\text{C}}$  (D<sub>2</sub>O, 63 MHz) 174.52 (C–OH), 154.50 (C–As), 142.23 (C–N=N), 141.08 (C–N=N), 131.48 (Ar 2CH), 126.93 (Ar 2CH), 121.98 (Ar 2CH), 120.37 (Ar 2CH). MS (ES, DMF–MeOH–CH<sub>3</sub>CN)  $m/z$  321 (M<sup>–</sup>, 22%).  $\nu_{\text{max}}/\text{cm}^{-1}$  3103 br (OH).

**3-(4'-Aminophenylazo)benzenephosphonic acid (9) and 3-(4'-hydroxyphenylazo)benzenephosphonic acid (10).** Dyes **9** and **10**

were prepared by procedures developed at Avecia.<sup>13</sup> Phenylphosphonic acid (25.0 g, 0.14 mol) was dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> (102 ml) at 0 °C and a mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (10 and 13 ml) was added dropwise at 0 °C. After stirring for 2 h, the reaction was quenched by the addition of ice (*ca.* 300 g). The precipitate was recrystallised from hot acetic acid to give 3-nitrophenylphosphonic acid as colourless crystals. Yield (13.3 g, 42%); mp 148–150 °C. Found: C, 34.86; H, 3.17; N, 6.46. C<sub>6</sub>H<sub>6</sub>NO<sub>3</sub>P requires C, 35.48; H, 2.98; N, 6.90%.  $\delta_{\text{H}}$  (D<sub>2</sub>O, 250 MHz) 8.35 (d, 2H, Ar–H), 8.21 (d, 2H, Ar–H), 7.94 (q, 2H, Ar–H), 7.58 (t, 2H, Ar–H).  $\delta_{\text{C}}$  (D<sub>2</sub>O, 63 MHz) 147.92 (C–NO<sub>2</sub>), 136.88 (Ar CH), 133.14 (C–P), 130.42 (Ar CH), 126.53 (Ar CH), 125.54 (Ar CH).  $\delta_{\text{P}}$  (D<sub>2</sub>O, 101 MHz) 12.47. MS (FAB, THIOG)  $m/z$  204 (MH<sup>+</sup>, 100%).  $\nu_{\text{max}}/\text{cm}^{-1}$  2873 br (OH), 1279 (P=O). 3-Nitrophenylphosphonic acid (10.0 g, 0.05 mol) in methanol (25 ml) was reduced under H<sub>2</sub> for 6 h in the presence of 10% Pd/C (0.3 g) to form 3-aminophenylphosphonic acid. Yield (8.5 g, 56%); mp 290 °C (decomp.) (lit.,<sup>15</sup> 315 °C).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 250 MHz) 7.02 (d, 1H, Ar–H), 6.60 (d, 1H, Ar–H) 6.40 (d, 2H, Ar–H).  $\delta_{\text{C}}$  (CD<sub>3</sub>OD, 63 MHz) 150.11 (C–NH<sub>2</sub>), 137.89 (C–P), 129.14 (Ar CH), 121.80 (Ar CH), 117.41 (Ar CH), 112.32 (Ar CH).  $\delta_{\text{P}}$  (CDCl<sub>3</sub>, 101 MHz) 25.04. MS (FAB, NOBA)  $m/z$  174 (MH<sup>+</sup>, 100%). 3-Aminophenylphosphonic acid was converted to 3-(4'-aminophenylazo)benzenephosphonic acid (**9**) and 3-(4'-hydroxyphenylazo)benzenephosphonic acid (**10**) by coupling with aniline or phenol respectively, following the method of Suh *et al.*<sup>11</sup>

**9:**  $\delta_{\text{H}}$  (CD<sub>3</sub>OD, 250 MHz) 8.2 (d, 1H, Ar–H), 7.72–7.84 (m, 2H, Ar–H), 7.71 (d, 2H, Ar–H), 7.44 (t, 1H, Ar–H), 7.02 (d, 2H, Ar–H).  $\delta_{\text{P}}$  (CD<sub>3</sub>OD, 101 MHz) 16.25. MS (ES, NOBA)  $m/z$  276 (M<sup>–</sup>, 100%).

**10:**  $\delta_{\text{H}}$  (CD<sub>3</sub>OD, 250 MHz) 7.73–7.93 (m, 4H, Ar–H), 7.55 (m, 2H, Ar–H) 6.84 (d, 2H, Ar–H).  $\delta_{\text{P}}$  (CD<sub>3</sub>OD, 101 MHz) 16.2. MS (ES, NOBA)  $m/z$  277 (M<sup>–</sup>, 100%).

#### Adsorption isotherm measurements‡

Aqueous stock solutions (5 × 10<sup>–3</sup> M) of each of the ligands shown in Fig. 1 were prepared and the pH was adjusted to *ca.* 8.5 by addition of sodium hydroxide. In experiments with cyclodextrin,  $\alpha$ - or  $\beta$ -CD was added in equimolar quantities. Accurately pre-weighed quantities of ATH or goethite, (*ca.* 0.4 g) in polycarbonate centrifuge tubes were stirred with solutions of the ligand in water (10.0 ml) of known concentrations for 2 h at 25 °C. The mixtures were centrifuged, filtered and analysed by ICP-OES. The determined concentrations of phosphorus, sulfur or arsenic defined the amounts of dye remaining in solution and hence the amount adsorbed on the ATH or goethite. No significant levels of aluminium or iron were detected in the aqueous phase after equilibration with ATH or goethite. The data, plotted using Origin 6.1, were subject to a non-linear curve fit. By default, the maximum surface coverage (*A*) and equilibrium adsorption constant (*K*) were obtained from the standard Langmuir adsorption isotherm

$$y = \frac{AK(c/c^*)}{1 + K(c/c^*)} \quad (1)$$

where *y* is the surface coverage, *c* is the residual dye concentration in solution, and *c*\* = 1 mol dm<sup>–3</sup>. In some cases, it was necessary

to modify this function to take into account the formation of a second adsorbate layer. It was found that a suitable function was of the 'double-Langmuir' form

$$y = A \left[ \frac{K_1(c/c^\ominus)}{1 + K_1(c/c^\ominus)} + \frac{K_2(c/c^\ominus)}{1 + K_2(c/c^\ominus)} \right] \quad (2)$$

where  $K_1$  and  $K_2$  are the adsorption constants for the first and second layers. These equations are all appropriate to ideal-solution conditions, which is justified for the range of residual dye concentrations obtained in this work (less than  $10^{-2}$  mol dm $^{-3}$ ).

### UV/Vis measurements

Stock solutions ( $7 \times 10^{-5}$  M) of each dye were prepared in a phosphate buffer<sup>16</sup> (ca. pH 8) and the absorption spectrum of the dye was measured both independently and in the presence of increasing concentrations of  $\alpha$ -CD ( $1 \times 10^{-7}$  to  $1 \times 10^{-2}$  M) at a constant wavelength (ca. 300–400 nm) at 25 °C. The results from the latter experiments were analysed to yield complexation constants ( $K$ ) as follows. It is assumed that the concentrations of dye ([dye]), cyclodextrin ([CD]), and complex ([CD-dye]) are sufficiently low for the respective activity coefficients to be assumed equal to unity. If the total dye concentration is denoted by [dye] $_0$ , the mole fraction of 'free' (uncomplexed) dye molecules by  $x_{\text{free}}$ , and the total cyclodextrin concentration by [CD] $_0$ , then we have that [CD-dye] = [dye] $_0(1 - x_{\text{free}})$  and [CD] = [CD] $_0 - [dye]_0(1 - x_{\text{free}})$ . Inserting these relations into the mass-action law

$$K = \frac{[\text{CD} - \text{dye}]c^\ominus}{[\text{CD}][\text{dye}]} \quad (3)$$

and solving for  $x_{\text{free}}$  yields

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

where  $\Delta = ([\text{CD}]_0 - [\text{dye}]_0)/c^\ominus$ . The measured absorption coefficient of the dye at fixed wavelength  $\lambda$  is a weighted sum of the free and complex absorption coefficients:

$$\varepsilon([\text{CD}]_0, \lambda) = x_{\text{free}}\varepsilon_{\text{free}}(\lambda) + (1 - x_{\text{free}})\varepsilon_{\text{complex}}(\lambda) \quad (5)$$

Substituting eqn (4) into eqn (5) yields the dependence of the measured absorption coefficient on cyclodextrin concentration.

### NMR measurements

In the  $^1\text{H}$  NMR experiments, the total dye concentration was fixed at 0.05 M and adjusted to ca. pH 8 by addition of sodium carbonate. The total cyclodextrin concentration was varied between 0.4[dye] to 2.0[dye] and the variation of the peak position of a well resolved signal in the region of  $\delta_{\text{H}} = 7\text{--}8$  ppm was measured at 25 °C. The approach outlined in the section 'UV/Vis measurements' was employed to extract the dye-cyclodextrin complexation constant ( $K$ ); the only difference is that eqn (5) now reads

$$\delta([\text{CD}]_0) = x_{\text{free}}\delta_{\text{free}} + (1 - x_{\text{free}})\delta_{\text{complex}} \quad (6)$$

COESY and ROESY spectra (see ESI $^\ddagger$ ) were recorded in D $_2$ O, 0.03 mol of dye + 0.03 mol of  $\alpha$ -CD, adjusted to pH 8 by addition of NaHCO $_3$ .

### Print testing

**Ink preparation and printing.** The dye (0.35 g) was dissolved in a mixture of glycerol (0.75 g), thiodiglycol (0.75 g), urea (0.75 g), Surfynol 465 (0.1 g) and distilled water (7.3 g) and was stirred for 30 min. The pH was raised to 8.5–9.5 by the addition of LiOH and the solution was microfiltered through a 0.45  $\mu\text{m}$  syringe filter. The filtrate was placed in a nib to generate prints using a contact method of ink lay-down. When inkjet printing was used the ink was microfiltered through a 0.45  $\mu\text{m}$  syringe filter, and injected (3–7 ml) into a clean BC21 monochrome ink cartridge. A small volume of ink was pulled through using a vacuum line, and the cartridge was inserted into HP560 printer to generate prints. Reflected optical density (ROD),  $L$ ,  $a$ ,  $b$ ,  $C$  and  $h$  of the prints were measured using a Gretag–Macbeth spectrodensitometer 24 h after printing.

**Humidity fastness.** Sections of prints were sealed in a humidity jar for 16 h at 60 °C. The prints were then analysed by optical microscopy and the colour bleed into non-printed areas was evaluated qualitatively using a scale 1–10 (1 indicating undetectable migration) by comparison with control prints supplied by Avecia.

**Light fastness.** The ROD of printed cards was measured (see above) before and after exposure to known illuminances, measured at 420 nm, in an Atlas Ci5000 weatherometer for up to 100 h at 63 °C and 50% humidity.

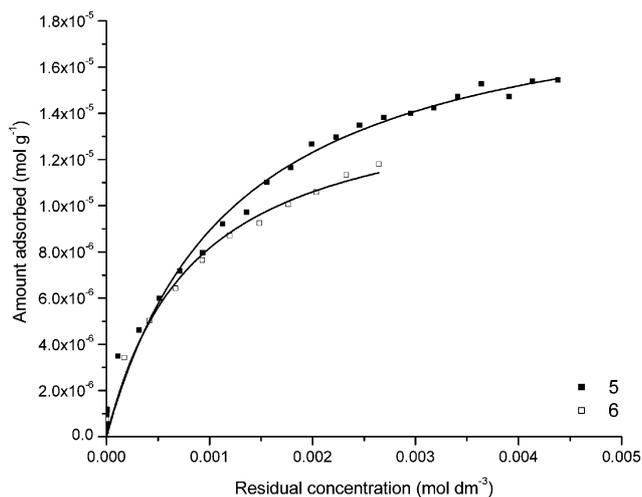
**Ozone fastness.** The ROD of printed cards was measured (see above) before and after 24 h exposure to 1 ppm ozone at 40 °C and relative humidity 50% in a Hampden 903 ozone cabinet.

### Results and discussion

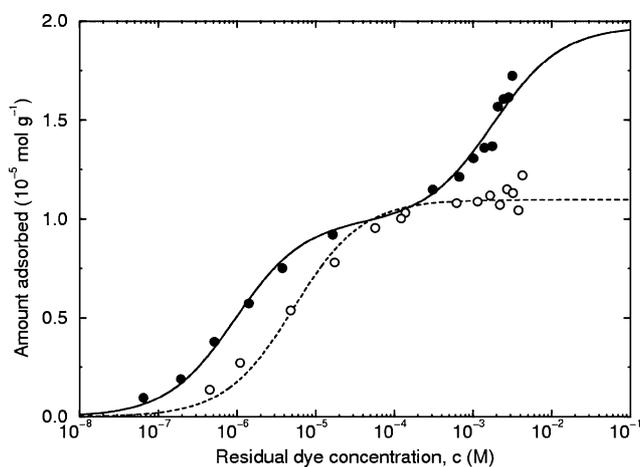
It was assumed that a necessary condition for the formation of a stable ternary surface/dye/CD complex analogous to the rotaxane in Fig. 2 is that the ligating group on the dye should afford strong binding to the oxide surface. A comparison of the isotherms for the four dyes 3–6, which vary only in the nature of acid group *para* to the azo unit, allowed us to define suitable ligating groups. The phosphonic and arsonic acid derivatives 5 and 6 show isotherms (Fig. 3) on high surface area aluminium trihydroxide with similar equilibrium adsorption constants and surface coverages [800 ( $\pm 100$ ) and  $20 \times 10^{-6}$  mol g $^{-1}$ ] and [1400 ( $\pm 200$ ) and  $10 \times 10^{-6}$  mol g $^{-1}$ ] respectively, based on curve-fitting for a Langmuir model.<sup>17,18</sup> The isotherms for 3 and 4 are poorly defined (see ESI $^\ddagger$ ) suggesting that sulfonic and carboxylic acids attach much more weakly to ATH. $\P$

The phosphonic acid and arsonic acid dyes 5 and 6 bind very strongly to goethite (see ESI $^\ddagger$ ). For such strong binding it is helpful to present the isotherms with a logarithmic scale for the residual concentration (see Fig. 4 and equations in the Experimental section). When this is done the system provides evidence for double layering. Once a coherent monolayer of 5 or 6 is formed it would be possible for phenol groups of a second layer of dye molecules to interact with the array of phenolic OH groups terminating the monolayer. Such a mode of binding for the second layer is supported by the observation that benzene phosphonic acid 1 also gives an isotherm characteristic of very strong binding but the

$\P$  Some variations in the shape of the isotherms could result from different hydration energies of the dyes but this has not been analysed.



**Fig. 3** The uptake of **5** and **6** on high surface area aluminium trihydroxide as a function of residual concentration in the aqueous phase.



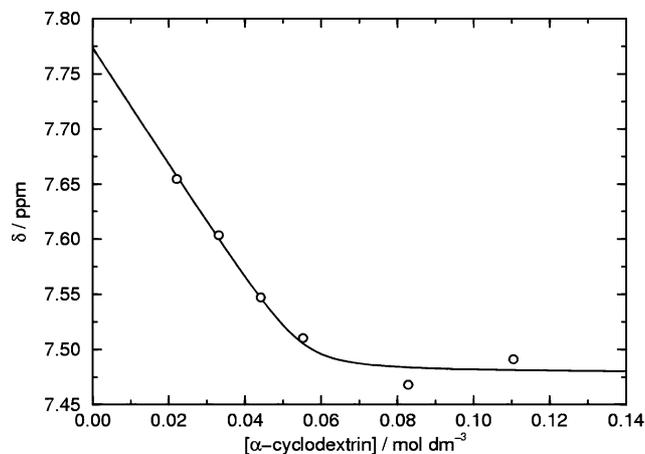
**Fig. 4** The uptake of **1** (○) and **5** (●) on goethite, plotted on a logarithmic scale. The equilibrium adsorption constants for the monolayer shown in **1** is  $[19 (\pm 3) \times 10^4]$  and the first and second layers in **5** is  $[11 (\pm 2) \times 10^5]$  and  $[560 (\pm 220)]$  respectively.

surface coverage ( $10.9 \times 10^{-6} \text{ mol g}^{-1}$ ) corresponds closely to the value for the monolayer of **5** ( $9.86 \times 10^{-6} \text{ mol g}^{-1}$ ).

The relatively weak attachment of sulfonic and carboxylic acids to ATH and goethite suggested that dyes containing phosphonic and arsonic acid tethering groups would be more suitable for the assembly of ternary rotaxane-like complexes at the surface.

Another necessary condition for the formation of such rotaxane-like structures is that the dye should form stable inclusion complexes within the cavity of the cyclodextrin. A wide range of techniques have been applied to the study of the formation of such cyclodextrin complexes.<sup>19</sup> NMR, in particular, offers the possibility of defining the orientation of the guest in the cavity<sup>5,20–22</sup> and of measuring formation constants for the dye-CD complex.<sup>4</sup> An analysis of the ROESY <sup>1</sup>H NMR spectra of 1 : 1 mixtures of  $\alpha$ -cyclodextrin and **5** or **10** in D<sub>2</sub>O indicates that the four H-atoms *ortho* to the azo group form close contacts in the cavity with the cyclodextrin's H3 and H5 protons. Such an assembly with azo dyes can lead to protection from photobleaching.<sup>5–7</sup> In this work,

measurement of the variation in chemical shifts of H-atoms *ortho* to the azo group of **5**, using a fixed dye concentration of 0.05 M in D<sub>2</sub>O, with various cyclodextrin concentrations (Fig. 5) gave values  $K = (2 \pm 1) \times 10^3$ ,  $\delta_{\text{free}} = 7.77 \pm 0.02 \text{ ppm}$ , and  $\delta_{\text{complex}} = 7.48 \pm 0.01 \text{ ppm}$ .



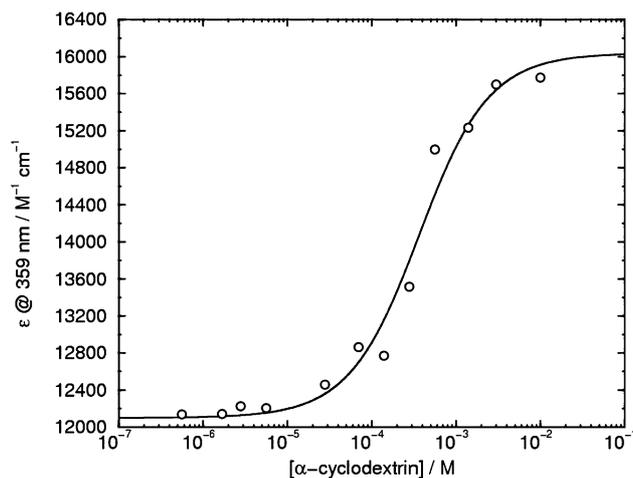
**Fig. 5** Variation of the chemical shift ( $\delta$ ) of the <sup>1</sup>H signal (7–8 ppm) of **5** (0.05 M) in D<sub>2</sub>O with  $\alpha$ -cyclodextrin concentration: pH 8 at 25 °C.

The incorporation of azo-dyes into the cavities of cyclodextrins is often accompanied by a significant change in wavelength of the chromophore<sup>22</sup> and consequently it is also possible to use variations in UV/Vis spectra to monitor complex formation. Spectra are also dependent on pH and concentration as azo dyes are known to aggregate in aqueous solutions with a resultant decrease in adsorption and a departure from the Beer-Lambert law.<sup>23</sup> At the dye concentrations used in this study ( $7 \times 10^{-5} \text{ M}$ ) absorbances were found to vary linearly with concentrations. Using  $7 \times 10^{-5} \text{ M}$  solutions at pH 8 in phosphate buffer, variations in absorption coefficient of major adsorption peaks were measured as a function of the concentration of added cyclodextrin. Appropriate peaks and concentration ranges of cyclodextrin were then used to obtain data to allow curve fitting to confirm the stoichiometry of the dye : cyclodextrin complex and determine its formation constant. Data for the  $\alpha$ -cyclodextrin complex of **5** are shown in Fig. 6. The resulting fit of absorption coefficients at increasing concentrations of  $\alpha$ -CD gave values of  $K = (3 \pm 1) \times 10^3$ ,  $\epsilon_{\text{free}}(359 \text{ nm}) = 12100 (\pm 100) \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{\text{complex}}(359 \text{ nm}) = 16000 (\pm 200) \text{ M}^{-1} \text{ cm}^{-1}$ . Results for the other dyes are included in Table 1.

Formation constants for the *para*-substituted phenolic dyes **3–6** fall in the range  $(1.8–13.2) \times 10^3$ , whilst that for the

**Table 1** Equilibrium constants and absorption coefficients of the free dye and the inclusion complexes for dyes **3–10** in phosphate buffer at 25 °C

Dye	$K$	$\epsilon_{\text{free}}/\text{M}^{-1} \text{ cm}^{-1}$	$\epsilon_{\text{complex}}/\text{M}^{-1} \text{ cm}^{-1}$
<b>3</b>	1800 ( $\pm 60$ )	13350 ( $\pm 200$ )	16500 ( $\pm 200$ )
<b>4</b>	8500 ( $\pm 3000$ )	14000 ( $\pm 60$ )	15000 ( $\pm 50$ )
<b>5</b>	3000 ( $\pm 700$ )	12100 ( $\pm 100$ )	16000 ( $\pm 200$ )
<b>6</b>	13200 ( $\pm 1000$ )	12900 ( $\pm 20$ )	14500 ( $\pm 18$ )
<b>7</b>	8600 ( $\pm 1000$ )	17300 ( $\pm 42$ )	19400 ( $\pm 40$ )
<b>8</b>	15700 ( $\pm 2500$ )	26100 ( $\pm 40$ )	24700 ( $\pm 40$ )
<b>9</b>	2400 ( $\pm 2000$ )	13000 ( $\pm 100$ )	13000 ( $\pm 100$ )
<b>10</b>	60 ( $\pm 100$ )	14000 ( $\pm 100$ )	37000 ( $\pm 5000$ )



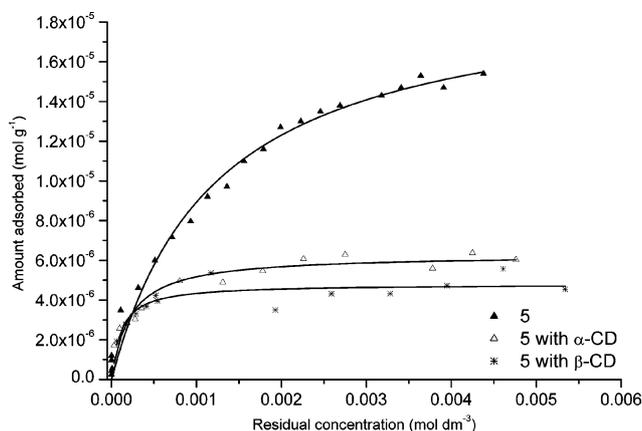
**Fig. 6** Variation of the absorption coefficient ( $\epsilon$ ) of cyclodextrin-dye complex of **5** ( $7 \times 10^{-5}$  M) at pH 8 with concentration of  $\alpha$ -cyclodextrin in phosphate buffer at 25 °C.

*meta*-substituted analogue **10** is an order of magnitude lower.  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies of the phosphonates **1** and **2** with CD indicate much weaker binding and provided evidence for the formation of complexes with other stoichiometries.

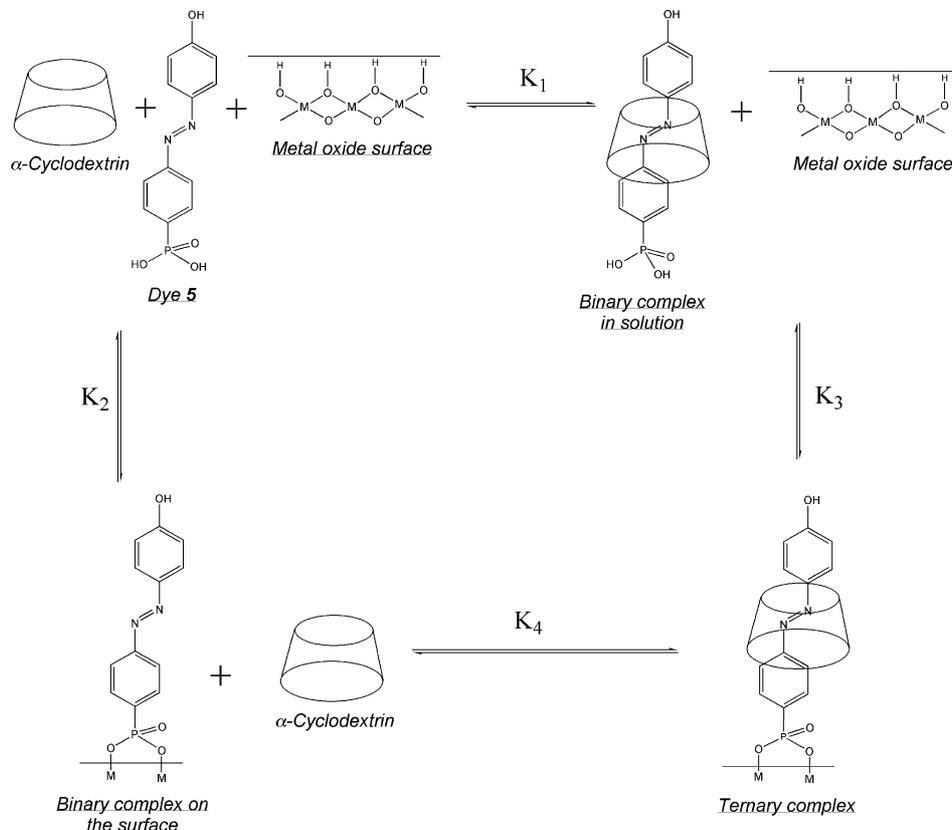
The adsorption isotherm data and the formation constants for binary complex formation allow us to define which combinations of surface, dye and cyclodextrin are most likely to form the ternary, rotaxane-like, complex (see Fig. 7). Comparable stability of the

dye-surface and the dye-cyclodextrin complexes will be needed for the formation of the rotaxane structure to be favoured.

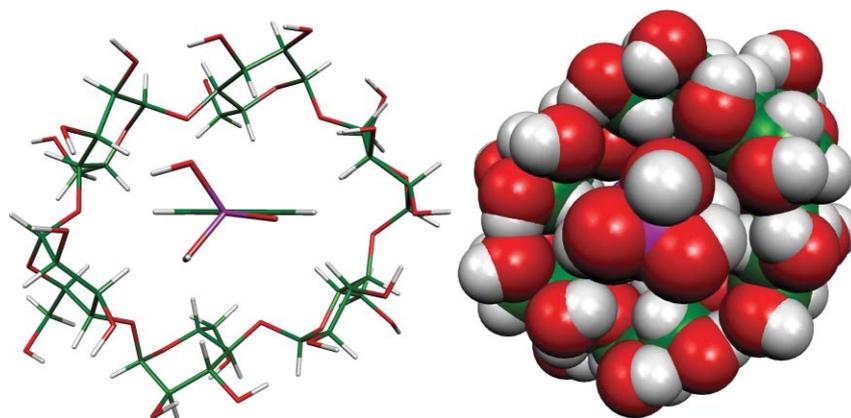
The isotherms presented in Fig. 8 follow the uptake of the phosphonate dye **5** onto ATH in the presence of equimolar quantities of  $\alpha$ - or  $\beta$ -cyclodextrin. The initial slopes at low residual dye concentration are comparably steep with the curve for the dye alone, indicating that similar binding strengths are involved. However, the surface coverages differ significantly. The increased bulk of the dye-cyclodextrin complexes leads to a decrease in surface coverage from  $20.0 \times 10^{-6}$  to  $6.3 \times 10^{-6}$  and  $4.8 \times 10^{-6}$  mol  $\text{g}^{-1}$  for **5** and its  $\alpha$ -CD and  $\beta$ -CD complexes, respectively.



**Fig. 8** The effect of addition of  $\alpha$ - or  $\beta$ -CD on the uptake of **5** onto high surface area aluminium trihydroxide.



**Fig. 7** Schematic representation of the various equilibria associated with the formation of the ternary, rotaxane-like complex on high surface area metal oxides.



**Fig. 9** The energy minimised structure of the  $\alpha$ -CD: **5** complex with the phosphonic acid group protruding through the secondary hydroxyl rim of the cyclodextrin.

These data correspond to coverages of  $58 (\pm 2)$ ,  $185 (\pm 9)$  and  $242 (\pm 15) \text{ \AA}^2$  per molecule for the dye and its  $\alpha$ -CD and  $\beta$ -CD complexes, based on the surface area ( $7 \text{ m}^2 \text{ g}^{-1}$ ) of the ATH used.

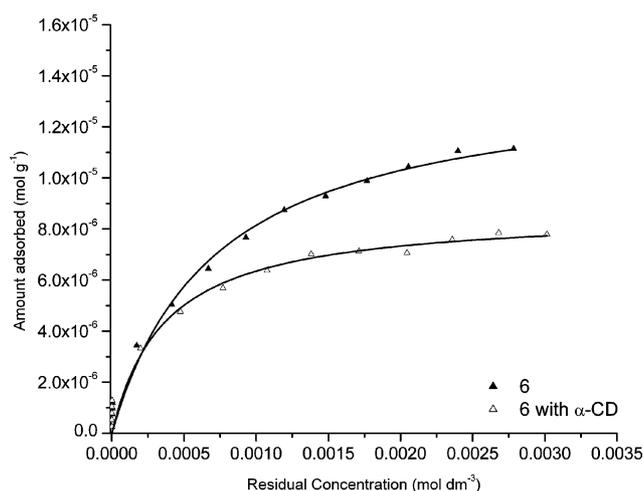
The surface coverages correspond fairly closely to values which would be predicted by close packing discs with diameters similar to those reported<sup>24</sup> for  $\alpha$ - and  $\beta$ -CD, 13.7 and 15.3  $\text{\AA}$ , respectively. For primitive cubic and hexagonal cubic close packing of  $\alpha$ -CD the areas predicted are 188 and  $163 \text{ \AA}^2$ , respectively.\* The significance of the similarity between observed and calculated surface coverages of the CD complexes needs to be interpreted with caution because the surface area of the ATH is determined under very different conditions and it is unlikely that the material will have substantial areas of flat surface. Also it is unlikely that the cross-sections of dye-cyclodextrin complexes will be strictly circular. Molecular modelling using the Dreiding force field method<sup>25</sup> indicates that  $\alpha$ -CD complexes of these simple azo-dyes have an elliptical cross section (Fig. 9) with elongation away from the edges and compression towards the faces of the encapsulated benzene ring.<sup>††</sup> The shortest and longest distances between diametrically opposed internal oxygen atoms in the cyclodextrin are 7.02 and 9.60  $\text{\AA}$ .

When the uptake of the comparable arsonate dye **6** onto ATH was measured in the presence of  $\alpha$ -CD (Fig. 10) the isotherm indicated, as with **5** (Fig. 8) that the surface-binding of the dye:cyclodextrin complex occurs. In this case the surface coverage of dye is not reduced so substantially by the addition of  $\alpha$ -CD which is consistent with the higher solution stability of the binary CD : **6** complex (Table 1).

In cases where the surface binding of the dye is very strong, *e.g.* for the phosphonic acid and arsonic acid dyes **5** and **6** on goethite, the uptake of the dye alone over the dye:cyclodextrin complex is preferred and there is no evidence for the *mono*-layer coverage of

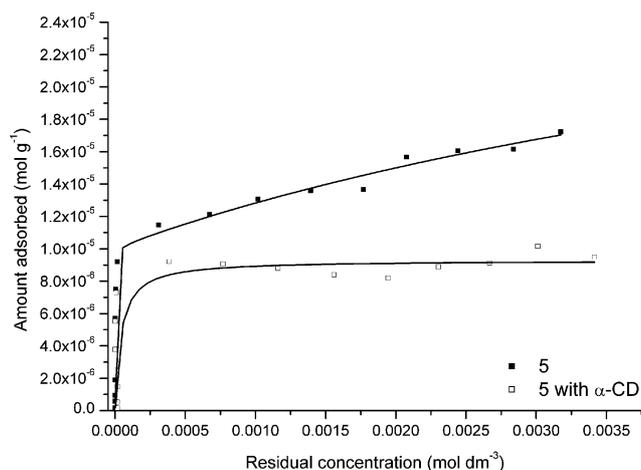
\* Each square representing the primitive cubic packing has an area =  $13.7^2 = 188 \text{ \AA}^2$  and contains four quarters of an  $\alpha$ -CD. Each triangle representing contacts for hexagonal packing has an area =  $1/2 \times 13.7 \times 13.7 \sin 60^\circ = 81.3 \text{ \AA}^2$  and contains  $3 \times 1/6$ th of an  $\alpha$ -CD.

<sup>††</sup> A CD-guest structure was selected from the Cambridge Structural Database, CDEXIA01 (*\alpha*-cyclodextrin-*para*-iodoaniline trihydrate);<sup>26</sup> the guest and water of solvation were removed and replaced by **5**. The energy minimised structure with the phosphonate adjacent to the rim with secondary alcohol groups is slightly more stable ( $-162 \text{ kcal mol}^{-1}$ ) than that with the phosphonate adjacent to the primary alcohol groups ( $-152 \text{ kcal mol}^{-1}$ ).



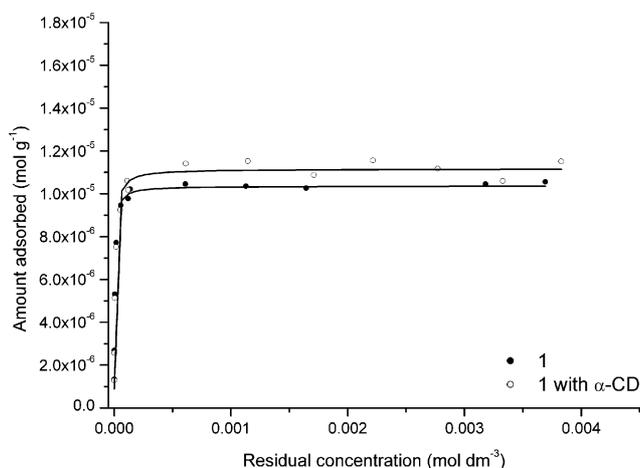
**Fig. 10** The effect of addition of  $\alpha$ -CD on the uptake of **6** onto high surface area aluminium trihydroxide.

the dye being reduced by the addition of cyclodextrin (see Fig. 11). In these systems the addition of  $\alpha$ -CD suppresses multilayering of the dye.



**Fig. 11** The effect of the addition of  $\alpha$ -CD on the uptake of **5** onto high surface area goethite. Comparable results for **6** are included in the ESI.<sup>‡</sup>

For the phosphonic acids **1** and **2** which do not form well defined 1 : 1 inclusion complexes with  $\alpha$ -CD in solution (see above), no reduction of the total uptake on goethite was expected on the addition of  $\alpha$ -CD in an isotherm determination and none was found (see Fig. 12).



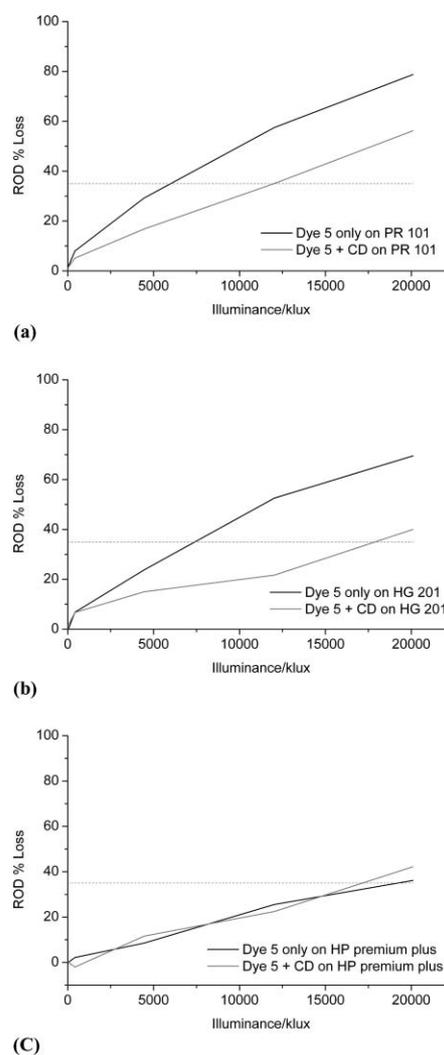
**Fig. 12** The insignificant effect of the addition of  $\alpha$ -CD on the uptake of **1** onto high surface area goethite. Very similar results were obtained with **2** (see ESI†).

The effects of incorporation of surface-ligating groups and of the formation of cyclodextrin complexes on the performance of the dyes when printed onto various papers were evaluated using a variety of test methods. Humidity fastness of **3–5** and **9** was compared by exposing printed text on three types of paper in sealed humidity jars at 60 °C. The phosphonates **5** and **9** showed (Table 2) a smaller degree of dye migration on alumina coated papers than sulfonate and carboxylate analogues. Such an improvement in wet fastness is consistent with the strong binding of **5** and **9** to high surface area ATH, as revealed by the adsorption isotherm studies described above. The phosphonate-functionalized dyes also showed a greater wet fastness on silica-treated papers and it is clear that attachment of surface ligating groups offers an effective method of improving the performance of dyes on oxide-treated papers.

It has been shown previously<sup>27,28</sup> that light fastness of inkjet dyes is very dependent on the nature of the media onto which they are printed, and, as might be expected, the incorporation of surface ligating groups into the simple dyes shown in Fig. 1 had no beneficial effect on their light fastness (see ESI†). Indeed, the phosphonate-functionalised dyes faded faster than **3** and **4** when they were printed on alumina-coated papers. However, the light fastness of these dyes on alumina-coated papers (HG 201 and PR101 in Fig. 13) is significantly enhanced when the ink formulation contains  $\alpha$ -cyclodextrin. The protection of the

**Table 2** Humidity fastness values for **3–5** and **9** on a 1–10 scale, with 1 representing an undetectable migration of dye

Papers/dyes	3	4	5	9
HG 201 (alumina coated)	1	7	1	1
PR 101 (alumina coated)	2–3	7	1	1
PGPP (silica coated)	2	2–3	1	1



**Fig. 13** The effect of the incorporation of  $\alpha$ -cyclodextrin into inks on the reflected optical density loss of **5** on exposure in an Atlas Ci 5000 weatherometer when printed on alumina-coated (HG 201 and PR 101) or silica coated (HP premium) papers.

azo-chromophore from photo-induced bleaching reactions by formation of ternary dye–cyclodextrin–surface complexes could account for this effect.<sup>5–7</sup> In contrast, the incorporation of  $\alpha$ -cyclodextrin into ink formulations of **5** and of some of the other dyes in Fig. 1 gave no improvement in ozone stability. Ozone fastness appeared to be dependent much more on the nature of the paper than on the ability of the simple dye to form complexes with the  $\alpha$ -cyclodextrin and/or alumina in the paper. These results contrast with work which has shown that formation of cyclodextrin rotaxanes on the surface of cellulose leads to improved ozone-fastness.<sup>5,21,22</sup>

## Conclusions

The measurement of isotherms at high surface area oxides provides a simple method to assess the efficacy of different surface ligating groups which might be used to attach effect molecules to solid supports and thus generate new functional materials. Systematic comparisons of isotherms provides evidence for the formation of

ternary dye–cyclodextrin–surface complexes which have rotaxane-like structures and offer the possibility of protecting the dye or other types of guest molecule from chemical or photolytic degradation in such functional materials, e.g. in light harvesting devices.

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