

Preparation and application of a β -cyclodextrin-disperse/reactive dye complex

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Abstract A disperse and a disperse/reactive azo-dyes were prepared and characterised with spectroscopic methods. The complexes with β -cyclodextrin were prepared by a dry milling method. The characterisation of the complexes in solid state was performed by ^{13}C CP MAS NMR, FT-IR, Raman spectroscopies and TGA–DTA analysis. The presence of the complexes in solution was evidenced with ESI-MS experiments. The products were used to dye synthetic (nylon, PET), natural (cotton) and cotton-PET blend fibres. Colour intensity and uniformity were evaluated by means of tristimulus colorimetry. β -Cyclodextrin, used as additive in dyeing baths, enhanced the colour intensity and uniformity of dyed samples. The complexes gave rise to a generalised good result. The disperse/reactive dye showed better fastness to washing properties on nylon 6 and cotton fibres. β -Cyclodextrin easily substituted the surface active agents, normally used in

industrially dyeing processes, without loss in dyeing quality as dyeing uniformity, intensity and washing fastness.

Keywords Azodyes · β -Cyclodextrin complexes · ^{13}C CP MAS NMR · Dyeing · ESI-MS · FT-IR · Raman spectra · TGA–DTA · Tristimulus Colorimetry

Introduction

The dyeing of synthetic fibres is usually performed in presence of additives. These are used to obtain a levelling effect on the colouration of goods. In dyeing of synthetic fabrics, additives play also an important role to enhance the solubility of disperse dyes by the formation of disperse systems. Surfactants are commonly employed in order to achieve this goal. The presence of micelles in surfactant solutions, above the CMC (Critical Micellar Concentration), increases the total disperse dyes concentration for solvation phenomena. The solvated dye molecules slowly diffuse on the fibres surfaces, giving rise to a more uniform colour distribution. In previous articles, cyclodextrins have been examined as possible alternatives in dyeing processes [1–6]. Cyclodextrins can complex dyes molecules. The formation of complexes decrease the free dye concentration and, as a consequence, the rate of dyeing.

In the present work two novel dye structures, a disperse and a disperse-reactive dye, are proposed and prepared for the dyeing of nylon, polyester, cotton and cotton–polyester blend fibres. Interactions between dyes and β -cyclodextrin are studied to evidence the formation of complexes. The aim of the work is the dyeing with β -cyclodextrin as additive directly

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available in the dyeing bath or as component of previously prepared complexes with dyes and the evaluation of the effects on dyeing intensity, uniformity and on washing fastness.

Disperse dyes are commonly used in the dyeing of synthetic hydrophobic fibres. Usually cotton cannot be directly dyed with this procedure for its hydrophilic nature. Possible applications of the disperse-reactive dye on cotton were also evaluated.

Experimental

All chemicals and solvents used were purchased from Sigma-Aldrich (Milan, Italy) and used as received, unless otherwise stated. 2-(*N*-ethyl-*N*-phenylamino)ethyl chloride was prepared starting from 2-(*N*-ethyl-*N*-phenylamino)ethanol (Aldrich) as reported by Boon [7]. Reacting the product with a solution of methylamine, as reported by Bach et al. [8], the coupling agent **1** was obtained. β -Cyclodextrin (Cawamax W7 Pharma) was kindly supplied by Wacker-Chemie.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were performed on a Jeol EX400 Spectrometer in DMSO- d_6 solution (2%) using the DMSO signal as a reference. NMR signals are described by use of *s* for singlet, *d* for doublet, *t* for triplet, *m* for multiplet and the chemical shifts with respect to TMS are expressed in δ . ^{13}C CP MAS NMR spectra in solid state were recorded on Jeol GSX270 Spectrometer equipped with a Doty probe working at 67.8 MHz for ^{13}C , spinning at 7–8 kHz, acquisition time 0.05 s, recycle delay 3 s, spectrum amplitude 40 kHz, contact time 3.5 ms. The chemical shifts are reported with respect to TMS assuming the methyl peak of hexamethylbenzene at 17.4 ppm.

Mass spectra were collected by a Finnigan Mat TSQ700 Spectrometer. ESI-MS spectra were recorded using a LCQ Deca XP plus spectrometer (Thermo, Rodano, Italy), with electrospray interface and ion trap as mass analyzer. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas (flow rate 10 $\mu\text{L}/\text{min}$). The source voltage was set at 4.5 kV in the positive ion mode. The heated capillary was maintained at 270 $^\circ\text{C}$. The acquisition method used was previously optimised in the tuning sections for β -CD quasi-molecular ion (capillary, magnetic lenses and collimating octapole voltages) in order to maximise sensitivity. The tuning parameters adopted for the ESI source were the following: source current 5.00 μA , capillary voltage 3.00 V, tube lens 0.1 V; for ion optics, multipole 1 offset -4.00 V, inter multipole lens voltage -16.00 V,

multipole 2 offset -8.00 V. Mass spectra were collected in full scan positive mode in different ranges between 200 and 3000 amu. MS/MS spectrum of (+) 1461 m/z was collected with 30% collision energy (CE) in the range 1000–1500 amu.

Solid state high-resolution (1 cm^{-1}) FT-IR spectra (oven-dried KBr matrixes, 100 averaged scans) were recorded on a Bruker Equinox55 spectrophotometer. Solid state high-resolution (1 cm^{-1}) Raman spectra were recorded on a Bruker RFS100 spectrophotometer, equipped with a Nd:YAG laser irradiating source, emitting at 1.064 μm and a liquid nitrogen-cooled detection system (typical experimental laser powers were comprised within the 50–190 mW range, with 100–500 averaged scans).

Preparation of Dye 2

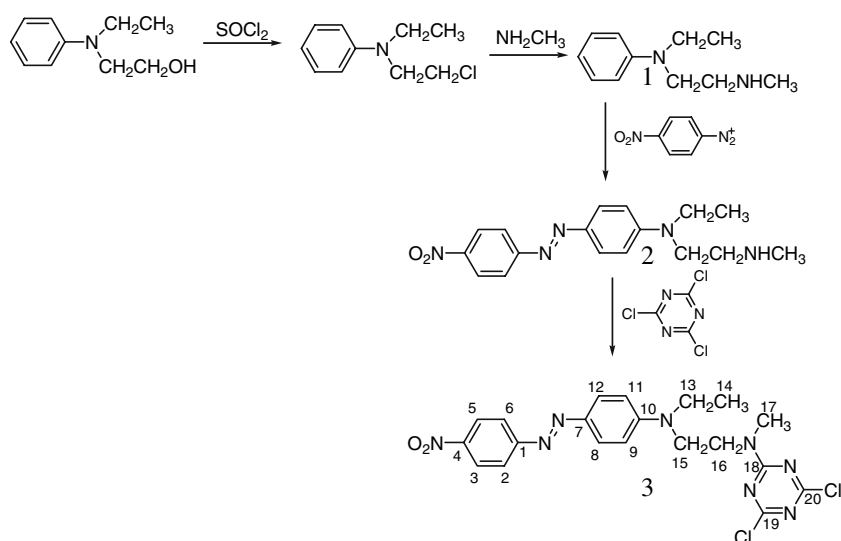
4-Nitroaniline, 20.70 g (0.15 mol), were treated with 37.25 ml (0.45 mol) of hydrochloric acid (37%) and 75 ml of water. The solution was warmed just to complete dissolution of solids. Then the temperature was lowered to 0 $^\circ\text{C}$ with precipitation of 4-nitroaniline hydrochloride. About 10.35 g (0.15 mol) of NaNO_2 , dissolved in water, were slowly added to the mixture. After 30 min urea was added until unreacted nitrous acid was eliminated. The solution of diazonium salt was added dropwise into a 26.74 g (0.15 mol) of **1** dissolved in 100 ml of acetic acid at a temperature controlled between 0 and 5 $^\circ\text{C}$. After 1 h the reaction mixture was neutralized with a solution of KOH. The solid was collected, stirred with a solution of 5% Na_2CO_3 , filtered and washed with water. The product was crystallized from ethanol. Yield: 30%, Mp: 108 $^\circ\text{C}$, λ_{max} (ethanol) = 447 nm, $\varepsilon = 33,000$. TLC on silica gel (Fluka), eluent:acetone/methanol 75/25, R_f = 0.23.

Mass spectra: CI (ionization gas isobutane) 328 m/z ($\text{M}+1$)⁺. EI 327 m/z (M)⁺; 283 m/z (100%).

^1H NMR (CDCl_3 , the first number is related to the proton assignment as reported in Scheme 1, the second is the chemical shift in ppm, the third is the multiplicity of the signal and the integration): 14, 1.22, *t* 3H; 18 (NH), 1.41, *s* 1H; 17, 2.48, *s* 3H; 16, 2.85, *t* 2H; 13 + 15, 3.50, *m* 4H; 9 + 11, 6.76, *d* 2H; 2 + 6, 7.87, *d* 2H; 8 + 12, 7.85, *d* 2H; 3 + 5, 8.27, *d* 2H.

^{13}C NMR (CDCl_3 , the first number is related to the carbon assignment as reported in Scheme 1, the second is the chemical shift in ppm): 14, 12.12; 17, 36.62; 16, 45.57; 13, 49.44; 15, 50.33; 9 + 11, 111.26; 2 + 6, 122.50; 3 + 5, 124.56; 8 + 12, 126.21; 7, 143.44; 4, 147.13; 10, 151.49; 1, 156.72.

Scheme 1 Synthesis procedures for Dye **2** and Dye **3**



Preparation of Dye **3**

At Dye **2**, 2.62 g (8×10^{-3} mol), dissolved in 100 ml of dichloromethane, was added 0.97 g (8×10^{-3} mol) of collidine. After cooling at 0 °C 1.47 g (8×10^{-3} mol) of trichlorotriazine were slowly added. The system was stirred at 0 °C for 2 h. The solid was filtered and washed three times with iced water. Dye **3** was then crystallized from dichloromethane. Yield: 25%, Mp: 210 °C, λ_{max} (ethanol) = 474 nm, $\epsilon = 26,000$. TLC on silica gel (Fluka), eluent: ethyl acetate/petroleum benzene 70/30, R_f = 0.80.

Mass spectra: CI (ionization gas isobutane) 475 m/z (M+1)⁺ isotopic peaks at 477 and 479 are in agreement with the presence of two chlorine atoms. EI 474 m/z (M)⁺; 476 m/z (M+2)⁺, 478 m/z (M+4)⁺, 283 m/z (100%).

¹H NMR (DMSO-*d*₆, the first number is related to the proton assignment as reported in Scheme 1, the second is the chemical shift in ppm, the third is the multiplicity of the signal and the integration): 14, 1.16, *t* 3H; 17, 3.21, *s* 3H; 16, 3.55, *t* 2H partially overlapped to the water signal; 15, 3.68, *t* 2H; 13, 3.76, *q* 2H; 9 + 11, 7.05, *d* 2H; 8 + 12, 7.84, *d* 2H; 2 + 6, 7.94, *d* 2H; 3 + 5, 8.36, *d* 2H.

¹³C NMR (DMSO-*d*₆, the first number is related to the carbon assignment as reported in Scheme 1, the second is the chemical shift in ppm): 14, 13.91; 17, 36.49; 13, 45.41; 15, 45.43; 16, 46.91; 9 + 11, 112.24; 2 + 6, 123.09; 3 + 5, 125.53; 8 + 12, 126.61; 7, 143.50; 4, 147.50; 10, 152.18; 1, 156.80; 18, 164.90; 19 and 20, 169.52 and 169.31.

Preparation of complexes

Solid β -cyclodextrin–dye complexes were prepared with a modified dry mixing method [9] by milling a mixture of the reactants in molar ratio 2:1 for 3 days. Products were then analysed by Thermo Gravimetric Analysis (TGA) and Differential Temperature Analysis (DTA) performed on a simultaneous DTA-TGA SDT 2960 model (TA Instruments). Samples (20 mg) were heated from room temperature to 350 °C (10 °C/min). TGA and DTA curves were continuously recorded. Milled samples were also characterized by ¹³C CP MAS NMR, FT-IR and Raman spectra. Crude products were used in dyeing experiments without further purifications.

Dyeings

Laboratory dyeing tests were carried out on a Linitest apparatus (Hanau-Germany), using liquor ratio 20:1, dyeing intensity 1% over weight fibres, pH 7. For each dye four different dyeing conditions were tested. Dyeing 1: without additives; Dyeing 2: in the presence of surfactant (Ethofor RO/40, ICAI, Turin, Italy, ethoxylated castor oil average degree of ethoxylation 1/40) 1 g/L; Dyeing 3: in the presence of dye and β -cyclodextrin in molar ratio 1:2; Dyeing 4: in the presence of dye/ β -cyclodextrin complex in molar ratio 1:2. Dyeing baths were sonicated to improve dye dispersion (ultrasonic apparatus Vibra-cell 120 W). Dyeings were performed on synthetic (nylon 6, PET), natural (cotton), and cotton-PET blend fibres. Samples

were introduced into dyeing bath at 40 °C. Dyeing cycles for each fibres are reported in Table 1.

A basification with sodium carbonate solution, between the step I and II, after cooling at 40 °C, was performed on cotton nylon and blend specimens. For blend samples a further third step at 130 °C for 60 min was performed. Dyed fibres were then removed, washed at 40 °C with water solution (liquor ratio 1:200) containing soap (2.5 g/L) and sodium carbonate (2.5 g/L), for 40 min, rinsed and dried at room temperature.

To evaluate colour uniformity tristimulus colorimetry was used [10]. Colour measurements were carried out with a Minolta CR 200 instrument. The colour difference between dyed and undyed specimen (ΔE) was measured on five different positions for each specimen. ΔE represents a mean value of the colour difference. The standard deviation of ΔE , $\sigma_{\Delta E}$, is a measure of colour uniformity.

Washing fastness were performed at 60 °C accordingly to standard procedures [11].

Results and discussion

Synthesis and characterisation of dyes

The coupling agent **1**, disperse azodye **2** and disperse/ reactive azodye **3** were synthesised following the procedures briefly described in Scheme 1.

The products **1–3** were characterised by means of TLC, ^1H and ^{13}C NMR, and MASS spectra. Spectral data are in agreement with the proposed structures. Some details of ^{13}C NMR spectrum of dye **3** are reported in Fig. 1.

Carbons 19 and 20 of the triazine ring show two chemical shift values (169.52 and 169.31 ppm) accordingly with the non-equivalence of the positions. This is a consequence of stereodynamic effect giving rise to hindered rotation of the triazine ring. A similar behaviour have been previously reported for dichloroamino-s-triazine derivatives [12].

β -Cyclodextrin-dye complexes: synthesis and spectroscopic characterization

Solid β -cyclodextrin-dye complexes were prepared by a milling process of reactants. Products were then analysed by solid phase ^{13}C CP MAS NMR, high resolution FT-IR and Raman spectra. In Fig. 2 ^{13}C CP MAS NMR spectrum in the solid state of a mixture of dye **3** and β -cyclodextrin is reported.

The signals of β -cyclodextrin (between 60 and 100 ppm) and of dye can be assigned as a function of their chemical shift. In Fig. 3 the spectrum of the corresponding complex is reported. The presence of the complex is suggested by the broadening of cyclodextrin (compare Figs. 2a and 3a) and dye (compare Figs. 2b and 3b) signals due to the presence of an host-guest systems. It is commonly accepted that loss in resolution of the cyclodextrin carbon signals is a clear indication of the inclusion of guests within the cavity [13, 14].

In Fig. 4 FT-IR spectra of the dye **3**, its β -cyclodextrin inclusion complex and a mechanical mixture of the two compounds are reported. Small but significant shifts of peaks and discrete variations of their relative intensities are observed for the dye in the β -CD complex, suggesting an host-guest interaction [15]. As far as the Raman spectra are concerned, with respect to the infrared patterns, similar trends are observed for the dye in the β -CD complex (signals broadening, peaks shifts, relative intensity variations), evidencing again the inclusive interaction [16] displayed by the hosting cyclodextrin structure (Fig. 5).

It can be pointed out that β -cyclodextrin signal intensity, in the spectral range reported, is very low. In the mechanical mixture the spectral pattern of the dye is not perturbed.

β -Cyclodextrin-dye complexes: thermal characterization

The dye/ β -cyclodextrin interaction are also evidenced by means of thermal methods: Thermo Gravimetric

Table 1 Dyeing cycles

Fibres	I Step			II Step		
	Ramp (°C/min)	Temperature (°C)	Time (min)	Ramp (°C/min)	Temperature (°C)	Time (min)
Cotton	1	70	30	1	70	60
PET	2	130	60	–	–	–
Nylon	1	90	60	1	90	60
Blend	1	70	30	1	70	30

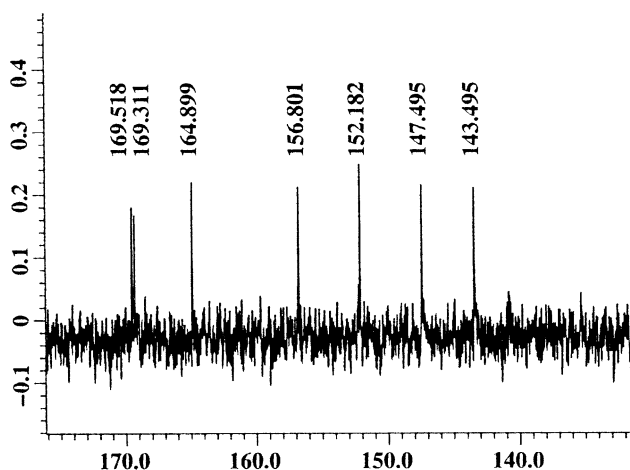


Fig. 1 ^{13}C NMR spectrum of Dye 3, a detail

Fig. 2 (a) ^{13}C CP MAS NMR spectrum in the solid state of a mixture of Dye 3 and β -cyclodextrin, (b) spectrum amplified

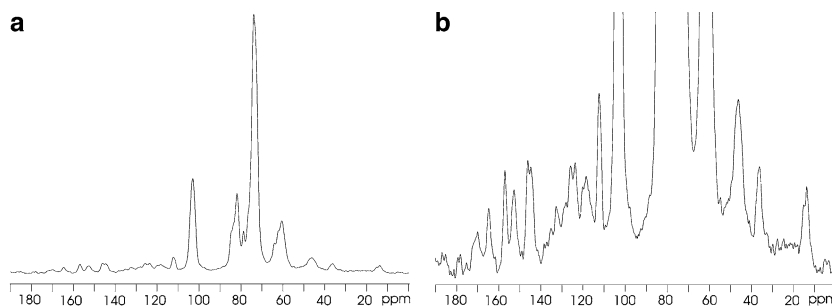


Fig. 3 (a) ^{13}C CP MAS NMR spectrum in the solid state of Dye 3/ β -cyclodextrin complex, (b) spectrum amplified

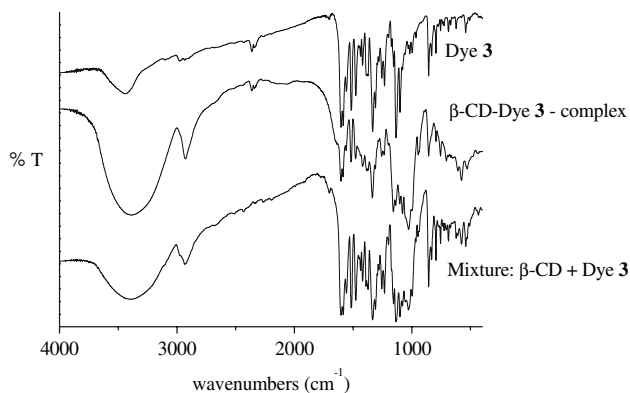
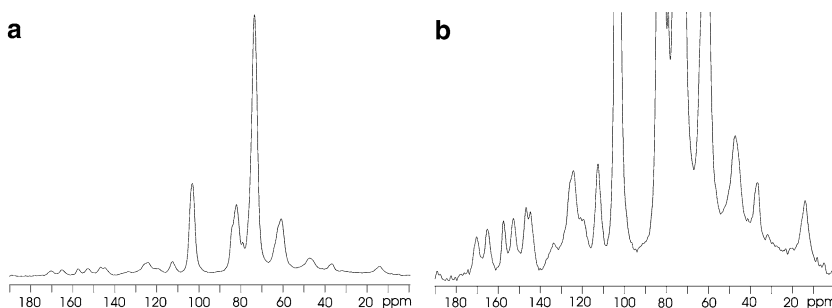


Fig. 4 FT-IR spectra of Dye 3, its β -CD inclusion complex and a mechanical mixture of the two structures

Analysis (TGA) and Differential Temperature Analysis (DTA).

In Figs. 6 and 7 the DTA–TGA curves of the Dye 3 and its mixture with β -cyclodextrin (ratio 1:2) are reported.

In both cases DTA curves show a signal due to the melting of the dye at 210 °C. An intense exothermic signal is shown for the free dye at 225 °C whereas in the mixture a signal due to the decomposition is evidenced at 275 °C. Probably the melted dye give rise to a complex formation. In Fig. 8 the TGA–DTA curves of the milled mixture are reported. The signal due to the dye melting is absent whereas an exothermic signal due to the decomposition of the dye is shown at 250 °C. Thermal data point out the absence of free dye

after the milling procedure. The presence of an excess of β -cyclodextrin can not be excluded.

The whole set of thermal and spectral data, point out the existence in the solid state of dye- β -cyclodextrin complexes.

Dyes/ β -cyclodextrin complexes in solution

Likewise important is the presence of complexes in solution.

The existence in solution of dye/ β -cyclodextrin complexes is studied by means of ESI-MS technique. Due to a very low solubility in aqueous phase, ESI-

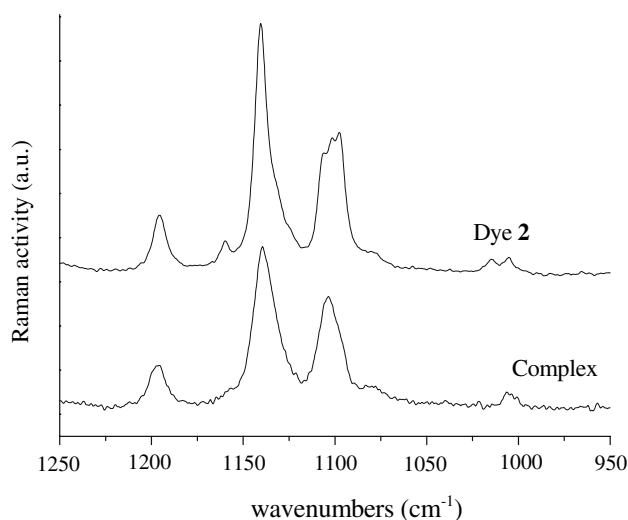


Fig. 5 Raman spectra of Dye **2** and its β -CD inclusion complex: a detail

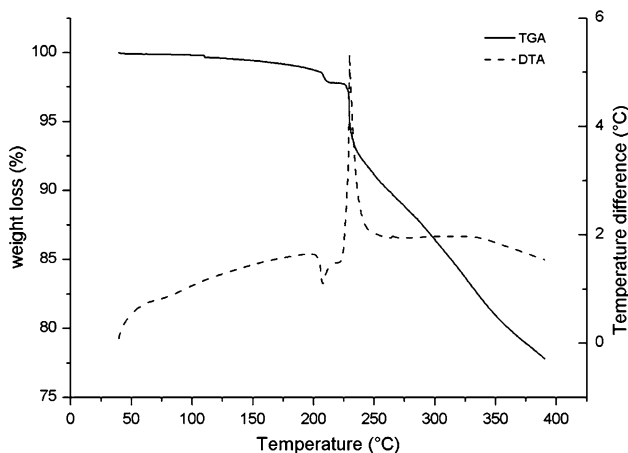


Fig. 6 DTA-TGA of Dye **3**

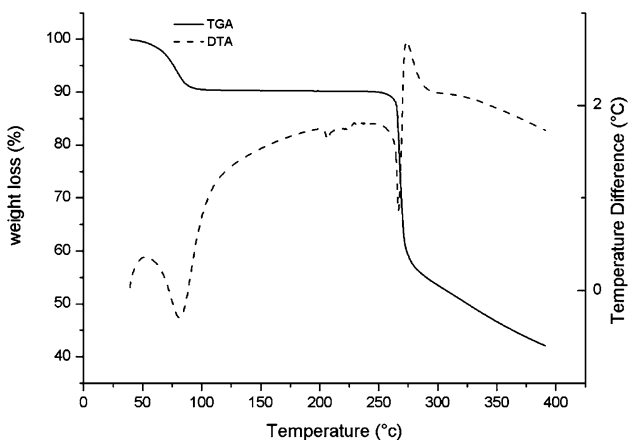


Fig. 7 DTA-TGA of a mixture β -cyclodextrin/Dye **3**

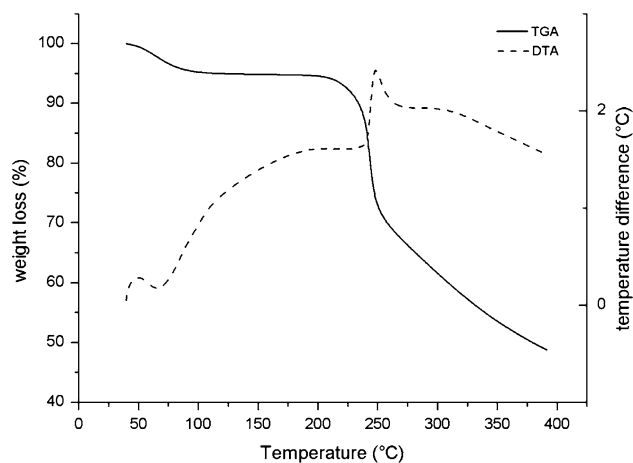


Fig. 8 DTA-TGA of complex β -cyclodextrin-Dye **3**

MS spectra are recorded in a water/methanol (20/80) solution containing a 2×10^{-4} M ammonium acetate buffer. In Fig. 9 the ESI-MS spectrum (1400–1500 amu range) of a solution containing dye **2** (1×10^{-5} M) and β -cyclodextrin (1×10^{-4} M) is reported. Signals at (+) 1462 and (+) 1479 m/z confirm the presence in solution of the dye **2**/ β -cyclodextrin complex coordinating H^+ or NH_4^+ , respectively.

An analogous experiment with Dye **3** gave rise to a weak signal at 1631 (Dye **3** + β -cyclodextrin + Na^+). A MS/MS experiment on the (+) 1631 (precursor ion) showed a product ion at (+) 1157 corresponding to the sodium- β -cyclodextrin ion. The data point out the presence of the complexes in water/methanol solutions.

Dyeings

Possible uses of dye/ β -cyclodextrin interactions in textile chemistry are evaluated. β -Cyclodextrin, interacting with dyes, can behave as vehicle suitable to replace the surface active agents, therefore giving rise to a lower environmental impact. Dyeing tests are planned to evidence: (a) the general use of dyes **2** and **3** in the dyeing of different textile substrates, (b) the ability of β -cyclodextrin, used as additive in the dyeing baths or as previously prepared complexes, to give rise to specimens with uniform, intense and stable colouration. Results evaluation is made using Tristimulus Colorimetry [10]. The higher the ΔE values the more intense are the colouration of goods. Comparison of ΔE values give rise to a correct evaluation only within samples dyed with the same dye. Samples with high colouration uniformity show low $\sigma_{\Delta E}$ values. Best samples show high ΔE and low $\sigma_{\Delta E}$ values.

ΔE values, reported in Table 2, show higher values for dye **2** than for dye **3**. The dyeing uniformity is also

Fig. 9 ESI-MS(+) spectrum of a mixture of Dye 2 and β -cyclodextrin

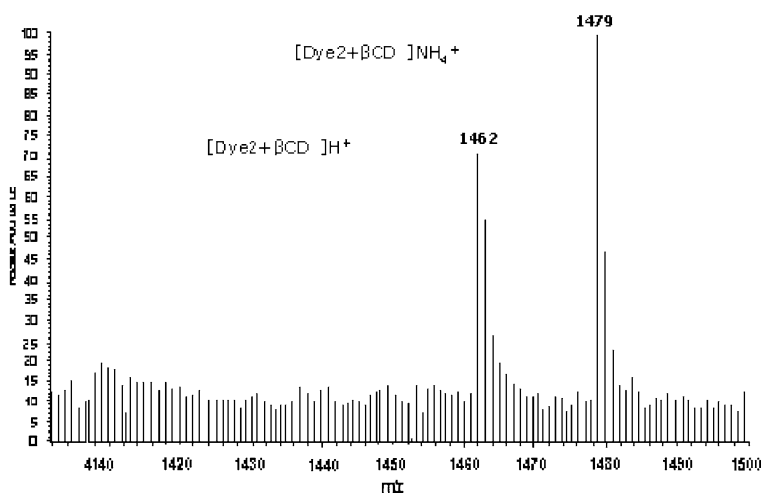


Table 2 $\Delta E \pm \sigma_{\Delta E}$ values

	Dyeing	Cotton	Nylon	Blend	PET
Dye 3	1	10.0 ± 1.0	18.0 ± 2.4	20.1 ± 1.4	29.0 ± 0.8
	2	21.7 ± 1.7	45.7 ± 5.4	25.6 ± 0.8	36.7 ± 0.5
	3	10.0 ± 1.0	26.0 ± 3.7	20.6 ± 0.8	31.5 ± 0.4
Dye 2	4	50.0 ± 1.0	63.0 ± 0.9	54.8 ± 0.8	52.5 ± 0.4
	1	58.7 ± 1.7	74.3 ± 0.2	62.6 ± 0.2	83.1 ± 0.4
	2	51.7 ± 3.5	74.3 ± 0.4	62.7 ± 0.1	82.8 ± 0.4
	3	67.0 ± 2.5	73.4 ± 0.2	62.8 ± 0.8	82.9 ± 0.4
	4	69.2 ± 0.2	76.1 ± 0.1	63.0 ± 0.9	83.2 ± 0.2

Table 3 Washing fastness values

	Dyeing	Cotton	Nylon	Blend	PET
Dye 3	1	<i>D</i> : 3/4	<i>D</i> : 4	<i>D</i> : 5	<i>D</i> : 5
		<i>S_s</i> : 4/5	<i>S_s</i> : 4/5	<i>S_s</i> : 5	<i>S_s</i> : 5
	2	<i>S_w</i> : 2/3	<i>S_w</i> : 5	<i>S_w</i> : 5	<i>S_w</i> : 5
		<i>D</i> : 1/2	<i>D</i> : 3	<i>D</i> : 5	<i>D</i> : 5
Dye 2	3	<i>S_s</i> : 3	<i>S_s</i> : 4	<i>S_s</i> : 5	<i>S_s</i> : 5
		<i>S_w</i> : 2/1	<i>S_w</i> : 4/5	<i>S_w</i> : 5	<i>S_w</i> : 4/5
	4	<i>D</i> : 3	<i>D</i> : 5	<i>D</i> : 5	<i>D</i> : 5
		<i>S_s</i> : 3/4	<i>S_s</i> : 5	<i>S_s</i> : 5	<i>S_s</i> : 5
Dye 2	1	<i>S_w</i> : 3	<i>S_w</i> : 5	<i>S_w</i> : 5	<i>S_w</i> : 5
		<i>D</i> : 2/3	<i>D</i> : 5	<i>D</i> : 5	<i>D</i> : 4/5
	2	<i>S_s</i> : 3	<i>S_s</i> : 5	<i>S_s</i> : 5	<i>S_s</i> : 4/5
		<i>S_w</i> : 2	<i>S_w</i> : 5	<i>S_w</i> : 5	<i>S_w</i> : 3/4
Dye 2	3	<i>D</i> : 1	<i>D</i> : 2	<i>D</i> : 4/5	<i>D</i> : 5
		<i>S_s</i> : 4	<i>S_s</i> : 1/2	<i>S_s</i> : 5	<i>S_s</i> : 5
	4	<i>S_w</i> : 2	<i>S_w</i> : 2	<i>S_w</i> : 4/5	<i>S_w</i> : 5
		<i>D</i> : 1/2	<i>D</i> : 1/2	<i>D</i> : 4/5	<i>D</i> : 5
Dye 2	1	<i>S_s</i> : 4/5	<i>S_s</i> : 1/2	<i>S_s</i> : 4/5	<i>S_s</i> : 5
		<i>S_w</i> : 2/3	<i>S_w</i> : 2/3	<i>S_w</i> : 4/5	<i>S_w</i> : 5
	2	<i>D</i> : 1	<i>D</i> : 2	<i>D</i> : 5	<i>D</i> : 5
		<i>S_s</i> : 3	<i>S_s</i> : 2	<i>S_s</i> : 5	<i>S_s</i> : 5
Dye 2	3	<i>S_w</i> : 2	<i>S_w</i> : 2	<i>S_w</i> : 4/5	<i>S_w</i> : 5
		<i>D</i> : 1/2	<i>D</i> : 3	<i>D</i> : 5	<i>D</i> : 5
	4	<i>S_s</i> : 4	<i>S_s</i> : 1/2	<i>S_s</i> : 5	<i>S_s</i> : 5
		<i>S_w</i> : 2	<i>S_w</i> : 2	<i>S_w</i> : 5	<i>S_w</i> : 4/5

D: degradation, *S_s*: staining on the same fibre, *S_w*: staining on wool

better for dye **2**. The use of dye **3** complex (dyeing **4**) show more interesting results as high ΔE and low $\sigma_{\Delta E}$ values.

Fastness to washing are reported in Table 3. Fastness to washing are displayed with an empiric scale ranging from 1 (worst value) to 5 (best value) [11].

Very good fastness values are reported for PET fibre. For nylon and cotton fibres low fastness values are measured with disperse dye **2**. The presence of reactive groups in dye **3** systematically enhance fastness to washing properties. This effect can be related to the reaction between reactive chlorotriazine moiety and reactive site of nylon and cotton fibres. Washing fastness are not strongly influenced by dyeing conditions, as presence of surface active agents or β -cyclodextrin, being obtained in all cases a good diffusion of dyes into the fibres.

Conclusions

Dyes/ β -cyclodextrin complexes were evidenced both in solid state and in solution.

β -Cyclodextrin easily substituted the surface active agents, normally used in industrially dyeing processes, without loss in dyeing quality. Colour properties (intensity and uniformity) were enhanced when complexes were employed. Reactive-disperse dye **3** showed better fastness to washing than dye **2** as a consequence of a reaction with nylon 6 and cotton fibres.

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