ORIGINAL ARTICLE

Synthesis and spectral characterization of azo dyes derived from calix[4]arene and their application in dyeing of fibers

Serkan Elçin • Murat Muzaffer İlhan • Hasalettin Deligöz

Received: 28 May 2012/Accepted: 13 August 2012 © Springer Science+Business Media B.V. 2012

Abstract In this study, the synthesis and characterization of two new *upper rim* functionalized azocalix[4]arene dyes have been obtained by coupling calix[4]arene with different diazo compounds of 3,5-dicarboxyaniline and 4-aminobenzene sulphon amide. The characterization of these dyes has been carried out by elemental analysis, FT-IR and ¹H NMR spectra. The effect of varying dielectric constants of solvents on the absorption spectra of azocalix[4]arenes (1, 2, 3, 4) and commercial Isolan Gelb SGL (T) have been examined by UV–Vis spectrophotometer. These azocalix[4]arene dyes have also been used for dyeing textile fibers like cotton, wool, acetate, polyester and polyamide fibers. Their dyeing and fastness properties have also been discussed.

Keywords Calixarene · Azocalix[4]arene · Diazocoupling reaction · Solvent effect · Textile fibers dyeing · Fastness properties

Introduction

Calix[4]arenes, obtained from the oligomerization of phenol and formaldehyde, offer useful molecular scaffold for the construction of multivalent binding sites [1]. Over the past few decades, much effort has been devoted to the development of appropriate calix[4]arene chemosensors for the selective and sensitive detection of heavy metal ions

S. Elçin (\boxtimes) · H. Deligöz Department of Chemistry, Faculty of Science, Pamukkale

University, 20017 Denizli, Turkey e-mail: serel20@mynet.com

M. M. İlhan Deniz Textile Factory, Organized Industrial District, 20017 Denizli, Turkey because of their essential or deleterious roles [2, 3]. For instance, although Cu^{2+} is biologically important, its accumulation in the human body may induce hepatic cirrhosis or neurodegenerative diseases [4]. Moreover, they have effective binding properties for a particular set of cation and anions.

Chromogenic *cone* calix[4]dibenzothiacrown ethers containing nitrophenylazo groups have been used for their cation binding ability for the transition metal ions [5]. Chromogenic azocalix[4]arene was reported that it can be applied as the liquid crystal [6] and also as ionic and NLO sensors [7]. However, most of these studies were restricted to the investigation of absorption spectra of the azocalixarenes.

There were few reports in which macrocyclic calixarenes have been used as components for the preparation of azo dyes. Azocalixarenes were frequently reported as the coupling component for various diazotized aromatic amines [8].

A number of azocalix[4]arene derivatives have recently been prepared [9–13], and used for the recognition of metal ions and the discrimination of different types of amines, but scarcely explored for their pH sensing properties. Calix[4]arene was employed to prepare an azocalix[4]arene derivative with four carboxyl groups, namely 5,11,17,23-tetrakis(*p*-carboxy phenyl)azocalix[4]arene. Its pH sensing properties are virtually unknown. The conversion between azocalix[4]arene and its sodium salt was reversible accompanying an intriguing reversible color change [14, 15].

Nowadays, azo dyes and pigments represent the largest and most varied groups of synthetic organic colorants in use. More than half of dyes used commercially are azo dyes [16]. It has been known for many years that azo compounds are among the most widely used class of dyes due to their versatile application in various fields such as



Fig. 1 The structures of substituted azocalix[4]arene derivatives 1-4

dyeing of textile fiber, coloring of different materials, colored plastics, bio-medical studies and advanced application in organic synthesis [17–20]. There have been few reports including macrocycles such as crown ethers [21] and usage of calixarenes [22–25] as components for the preparation of azo dyes. However the researches on azocalix[4]resorcinarene dyes [26] are still on infancy.

The response of chromophoric calix[*n*]arenes to the presence of triester groups has been described previously [27]. Azocalix[4]arenes have been rendered chromophoric through reactions with diazonium salts to generate azo compounds. Previous reports of chromophoric phenylazocalix[*n*]arenes included a description of the autocatalytic nature of azo bond formation [28], the selectivity for binding to metals [29], spectral properties of the azophenol–quinine–hydrazone tautomerization [30] and detection of amines with a chromophoric calix[8]arene [31].

In our recent works [32-34], preparation of many azocalix[*n*]arenes were described and synthesized by reacting carbocyclic amines or heterocyclic amines with a calix[*n*]arene. The absorption spectra and ability of prepared azocalix[*n*]arenes was discussed by considering both the effect of varying pH and solvents.

This study aims the synthesis of water-soluble azocalix [4]arene derivative to develop as a novel calix [4]arene dyes that contain an azophenol moiety to provide colour (Fig. 1). Moreover, fastness properties and other absorption characteristics of these dyes is determined throughout this study. Syn-thesized dyes can be used as a dyestuff for cotton, wool, acetate, polyester and polyamide fibers.

All solvents and compounds are commercially graded

Experimental

General

Melting points were measured using an Electrothermal IA9100 digital melting point apparatus in capillaries sealed under nitrogen and were uncorrected. ¹H NMR spectra were referenced to tetramethylsilane at 0.00 ppm as internal standard and were recorded on a Bruker 400 MHz spectrometer at room temperature (25 ± 1 °C). IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. UV–Vis spectra were obtained on a Shimadzu 1601 UV–Vis recording spectrophotometer. The elemental analysis was performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).

Solvent of crystallization was retained in some of the analytical samples and affected by the elemental analysis. In such cases, best fits between the analytical values and appropriate fractional increments of solvents were used.

Preparation of the ligands

p-tert-Butylcalix[4]arene and calix[4]arene were synthesized as described previously [35, 36]. Commercial Isolan Gelb SGL was purchased from Dystar, 100 % nylon knitted fabric, 100 % wool woven fabric (SDC Wool Abradant Fabric-BS EN ISO 12947-1: 1999-Certificate Of Conformity No: 0690-Stock Code: 2016).

Preparation of substituted azocalix[4]arenes (1-4)

Diazotisation of the various carbocyclic amines was affected with concentrated HCl. A typical procedure was that described below used for aniline derivatives. 5,11,17,23-Tetrakis(3,5-dicarboxyphenyl)azocalix[4]arene (1), 5,11, 17,23-tetrakis(4-sulphonylphenyl)azocalix[4] arene (2), 5,11, 17,23-tetrakis(4-sulphonylamidophenyl)azocalix[4]arene (3) and 5,11,17,23-tetrakis(4-carboxyphenyl)azocalix[4]arene (4) were obtained using the same method in 64–87 % yield. The obtained compounds were purified by crystallization using the same solvent (DMF–H₂O) and then analyzed.

All of the azocalix[4]arenes **1–4** were soluble in water, 10 % HCl, 10 % NaOH, EtOH, acetic acid, acetone, acetonitrile, DMF and DMSO.

The synthesis of 5,11,17,23-tetrakis(3,5-dicarboxyphenyl)azocalix[4]arene (1)

A solution of 3,5-dicarboxyphenyldiazonium chloride, prepared from 3,5-dicarboxy aniline (1.75 g, 9.67 mmol), sodium nitrite (1.33 g, 19.34 mmol) and concentrated HCl (1.65 mL) in water (5 mL), was added slowly to a cold (5 °C) solution of calix[4]arene (1.0 g, 2.36 mmol) and sodium acetate trihydrate (4.00 g, 29.24 mmol) in H₂O–DMF (13 mL, 5:8 v/v) to give a dark brown suspension. After keeping for 2 h at room temperature, the suspension

was acidified with aqueous HCl (50 mL, 0.25 %) and the mixture was then warmed to 60 °C for 30 min. After then it was cooled 50 mL ethyl acetate was added into the mixture. The crude product gave a pale brown solid, which was filtered and washed with ethyl acetate. After then the resulting solid was recrystallized from MeOH-EtAc (50 mL, 5:2 v/v). Yield, 2.17 g (77 %), mp 270 °C (dec.). [Found: C: 60.68 %; H: 3.29 %; N: 9.28 %]; $C_{60}H_{40}N_8O_{20}$ requires C: 60.41 %; H: 3.38 %; N: 9.39 %. FT-IR (KBr) v (cm⁻¹): 3082 (COOH), 1701 (C=O), 1452 (N=N). ¹H NMR (CDCl₃, 25 °C) δ_{H} : 3.18–4.02 (8H, d AB, Ar*CH*₂Ar), 6.64–7.93 (12H, m, Ar*H*–N=N), 8.48 (8H, s, Ar*H*-calix), 10.02 (4H, s, Ar–O*H*), 13.20 (8H, s, –COO*H*).

The synthesis of 5,11,17,23-tetrakis(4-sulphonylphenyl)azocalix[4]arene (2)

Azocalix[4]arene **2** was prepared as Morita et al. method [14], using 4-amino benzene sulphonic acid in water/HCl (5/1.65 mL) and obtained as a dark yellow solid, which was filtered and washed with water and MeOH, and dried. The final solid was recystallized from DMF/H₂O (104 mL, 8:5 v/v) mixture that gave a pale brown product. Yield (64 %), mp. 250 °C (dec.) (Lit. mp >230 °C (dec.)).

The synthesis of 5,11,17,23-tetrakis(4sulphonylamidophenyl)azocalix[4]arene (3)

Azocalix[4]arene **3** was prepared as described above, using 4-aminobenzene sulphonamide in water/HCl (5/1.65 mL) and obtained as a pale brown solid, which was filtered and washed with ethyl acetate, and then dried. The resulting solid was recystallized from MeOH-EtAc (50 mL, 5:2 v/v) mixture that gave a dark yellow product. Yield (81 %), mp. 290 °C (dec.). [Found: C: 53.79; H: 3.98; N: 14.89; S:11.02]; C₅₂H₄₄N₁₂O₁₂S₄ requires C: 53.97 %; H: 3.83 %; N: 14.52 %; S:11.08 %. FT-IR (KBr) v (cm⁻¹): 3258 (NH₂), 1332 (S–NH₂), 1466 (N=N), 1165 (S=O). ¹H NMR (CDCl₃, 25 °C) $\delta_{\rm H}$: 3.72 (4H, s, Ar*CH*₂Ar), 4.44 (4H, s, Ar*CH*₂Ar), 7.82 (8H, s, Ar*H*-calix), 7.86–7.92 (16H, m, Ar*H*–N=N), 10.03 (4H, s, Ar–O*H*), 11.80 (8H, s, Ar-N*H*₂).

The synthesis of 5,11,17,23-tetrakis(4carboxyphenyl)azocalix[4]arene (4)

Azocalix[4]arene **4** was prepared as Morita et al. method described [14], using 4-amino benzoic acid in water/HCl (5/1.65 mL) and obtained as a red solid, which was filtered and washed with water and MeOH, and then dried. The resulting solid was recystallized from DMF/H₂O (104 mL, 8:5 v/v) mixture that gave a dark brown product. Yield (87 %), mp. 290 °C (dec.) [Lit. mp >250 °C (dec.)].

Dyeing of fibers (nylon and wool)

0.5 % of Azocalix[4]arene dye was dissolved in a neutral or slightly alkaline solution in dyeing baths and then 5 mL of 30 % aqueous NaCl or Na₂SO₄ solution was added. The scoured fiber hunk (3.5 g) was then added to the dyeing bath and its temperature was maintained at (\sim 90 °C) for 30 min. The dyed hunks were then removed by rinsing with cold water and drying.

Studies for fastness properties [37]

It is essential to colored fibers under such conditions as rubbing exposure, washing, perspiration etc. during their subsequent use and test their standing in such conditions. Because these conditions usually result in alteration in depth, or in hue, or in brightness of the fibers. Some of the parameters that have been studied were as follow:

Fastness to washing (as per IS: 764-1979)

Pair of dyed and undyed specimen was immersed in 0.5 % commercial detergent solution and was agitated for 30 min at 60 °C. The specimens were removed were rinsed three times with water and then dried. Change in color was assessed using the standard gray scale, where a rating of 5 is considered as excellent and 1 is poor.

Fastness to water (as per IS: 767-1988)

Pair of dyed and undyed specimen was immersed in water for 30 min, thereafter water was drained and the hunks were dried separately and the change in color of the dyed hunks and the staining of the undyed hunks were assessed by means of the standard grey scale, where a rating of 5 is considered as excellent and 1 is poor.

Fastness to perspiration (as per IS: 971-1983)

Both acidic and alkaline solutions were used in this test. The tests were carried out in dry atmosphere at 38-40 °C in glass test tube. The change in color of the dyed specimen and staining of the undyed specimen were assessed.

Rubbing test

The rubbing fastness test was carried out using a crockmeter in accordance with ISO105-X12:2006.

Chlorinated water test (as per TS 837 EN ISO 105-E03/ April 2006)

Pair of dyed and undyed specimen was immersed in 20 ppm chlorinated water for 30 min, thereafter water was

drained and the hunks were dried separately and the change in color of the dyed hunks and the staining of the undyed hunks were assessed by means of the standard grey scale, where a rating of 5 is considered as excellent and 1 is poor.

Results and discussion

Synthesis and characterizations

The aim of this study was to synthesize novel water-soluble azocalix[4]arene dyes using 3,5-dicarboxy aniline, 4-aminobenzene sulphonic acid, 4-aminobenzene sulphonamide and 4-aminobenzoic acid. Two new (1 and 3) and two literature (2 and 4) azocalix[4]arene dyes was achieved by diazo of natrium nitrite using concentrate hydrochloric acid as the coupling in DMF at room temperature for 30 min under nitrogen according to previous papers [14, 32, 38, 39]. The purification of these azocalix[4]arenes for characterization required column chromatography on silica gel using ethyl acetate as an eluent and gave in quantitative (64-87 %) yield.

The formulations and molecular structures of azocalix[4]arene dyes (1-4) was given in Fig. 2. These molecular structures were also supported by the data obtained from micro analysis, where in the percentage of C, H and N from the analysis conform the calculated values. The structures of these novel compounds were fully characterized using spectroscopic methods (FT-IR and ¹H NMR) and elemental analysis. Synthesized dyes (1-4) and the commercial dye (Isolan Gelb SGL (T)) had a dyestuff structure for cotton, wool, acetate, polyester and polyamide fibers.

The FT-IR spectra of azocalix[4]arene dyes **1** and **3** showed a weak band within the range $3,350-3,250 \text{ cm}^{-1}$ corresponding to –OH. The low value reveals that the –OH groups were involved in intramolecular H-bonding, a weak band or shoulder located at $3,082 \text{ cm}^{-1}$ was assigned to dicarboxylic acid for dye **1** and appearance of band in the region $1,332-1,165 \text{ cm}^{-1}$ confirmed the presence of S–NH₂ and S=O groups for dye **3**, respectively. Asymmetrical stretching vibration of the N=N group leading to the band located in the 1,466–1,452 cm⁻¹ region.

These compounds (1 and 3) were examined in solution by high-resolution NMR. The ¹H NMR spectrum showed broad peak at $\delta = 10.02-10.03$ ppm (–OH), singlet peak for methylene bridge protons (–CH₂–) at $\delta = 3.18-4.02$ to 3.72-4.44 ppm, singlet from $\delta = 7.82-8.48$ ppm for aromatic protons (ArH-calix), singlet from $\delta = 6.64-7.93$ to 7.86-7.92 ppm for aromatic protons (ArH–N=N), singlet peak for carboxylate protons (–COOH) at $\delta = 13.20$ ppm, singlet peak for sulphonyl amide protons (–SO₂NH₂) at $\delta = 11.80$ ppm. The obtained datas were according to the literature [14, 32, 38, 39]. The absorption spectra of azocalix[4]arene dyes

Synthesized azocalix[4]arene dyes were capable of absorbing light in the chromophore groups and color compounds. The basic difference of other similar compounds structure was in water resolutions and their fastness properties in textile material. These azocalix[4]arene dyes cotton, wool, acetate, polyester and polyamide fibers' dyeing ability were studied dyeing ability. Some dyes dyed nylon and wool fibers properly. Nylon and wool dyeing of these dyes examined with the commercial dye (**T**) and in a comparative analysis of the comparative values of the dyed and color fastness. In addition, the resulting water-soluble azocalix[4]arene dyes were investigated acidic–basic media on the absorption properties and in varying solvents.

Solvatochromic effects

Solvatochromism is the ability of a chemical substance to change color due to a change in solvent polarity. Generally, the ground state for almost all molecules is less polar than the excited state so that a polar solvent will tend to stabilize the excited state more than the ground state. Hence with the increase in polarity of the solvent a bathochromic shift is observed. The absorption spectra of azocalix[4]arenes 1–4 were recorded in various solvents at a concentration of $\sim 10^{-4}$ to 10^{-6} M, the results are summarized in Table 1.

The choice of solvent is based on polarity/dielectric constant. The electronic absorption spectra of these dyes (1–4) exhibited one absorption band in the range 300–500 nm corresponding to π - π * and n- π * transitions. The visible absorption spectra of the dyes were found to exhibit strong solvent dependency but did not show expected regular variation with the polarity of the solvent [8]. In consideration of the results reported in Table 1, we did not find any regular bathochromic or hypsochromic shift except that all dyes in all solvents show the negative solvatochromism with respect to dichloromethane.

As an example, absorption spectra of azocalix[4]arenes **1–4** and commercial **T** dyes, in different solvents, was shown in Fig. 3. Strong evidence for the existence of these compounds in an equilibrium was provided by the *isosbestic points* in the visible spectra of, for example, compound **1** in different solvents. This equilibrium may exist between tautomeric forms. The equilibrium depends on the basicity of the solvents used; in proton accepting solvents such as DMSO, DMF, acetonitrile, methanol and acetic acid, the compounds displayed a red shift of λ_{max} . The effect of concentration of the compound on absorption maxima was examined. The λ_{max} of all compounds did not change with compound concentration which also indicates that azocalix[4]arenes exist in their tautomeric form in all solvents used.



Fig. 2 Diazo-coupled substituted azocalix[4]arene derivatives 1-4

Table 1 Influence of solvent on λ_{max} (nm) of azocalix[4]arene (1–4) and commercial (T) dyes

Dyes	DMSO	DMF	MeCN	MeOH	AcOH	MeOH + HCl	MeOH + KOH
1	379.80	382.84	356.32	365.10	348.78	348.34 465.39 ^(s)	375.75 482.20 ^(s)
2	364.87	363.99	-	359.80	-	346.97 489.99	386.90 490.10 ^(s)
3	374.83	368.67	358.56	363.03	345.61	348.02 483.57	383.95 496.91 ^(s)
4	382.75	369.77	366.49	365.39	356.10	356.15 496.34 ^(s)	382.86 518.29 ^(s)
Т	442.01	438.49	382.91 423.34	430.11 340.17 ^(w)	441.15 337.21 ^(w)	444.16 337.30 ^(w)	431.96 336.50 ^(w)

s Shoulder, w weak

Effect of acid and base

The effect of acid and base on the absorption of the azocalix[4]arene dye solutions was investigated and the results were shown in Fig. 4. With the addition of base (0.1 M sodium hydroxide), the λ_{max} of the dyes showed a hypsochromic shift along with a shoulder at longer wavelength. The λ_{max} of the compounds in methanol also showed slightly hypsochromic effects with addition of acid (50 % acetic acid). The azocalix[4]arenes (1–4) may exist in four possible tautomeric forms, namely an azo–enol and keto–hydrazo form was shown in Fig. 5.

Dyeing and fastness properties

The structural and physical properties of the azocalix[4]arene dyes 1-4, revealed that they may be classified as direct dyes for the dyeing of cotton, silk, and wool. It was observed that with the increase in dye concentration from 0.20 to 0.45 M there was an increase in reflectance, after which there is negligible effect on reflectance with increase in concentration of azocalix[4]arene dyes. It suggested greater availability of dyestuff onto fiber even at low concentration. The effect of varying the concentration of salt from 1.0 to 5.0 % was assessed on dyed fibers. The result showed that 3.0-5.0 % of aqueous salt did not have much effect on the reflectance of the fibers. When the fibers were dyed at various pH between 3.0 and 10.5 and its effect was studied by the reflectance measurements. At a lower pH the dyeing was incomplete, whereas the dyeing capacity was maximum between pH 6.5 and 8.0, but beyond pH 8, the dyeing capacity decreased gradually.

The fastness properties of dyed fibers to washing, water, perspiration and light were summarized in Table 2. The results showed that fastness level was in between 3 and 5 indicating very slight alteration in the shade or lose in depth of the dyes. Light fastness results were found to be 5–6, which indicates slight color loss of dyed fibers.

Washing fastness measurement of the treated dyed fabrics was carried out according to the standard method IS: 764-1979. After washing process in these series, azocalix[4]arene **1** showed the highest improvement in



Fig. 3 Absorption spectra of azocalix[4]arene (1-4) and commercial (T) dyes

wash fastness properties, which can be attributed to the presence of both carboxylic acid and hydroxyl groups in the dye molecule. The presence of these groups in the azocalix[4]arene 1 caused the easy hydrolysis of the adsorbed dyes on fibers and then being converted into water solubilized dye. The dyes on polyamide surface which are soluble in water can removed easily by the washoff treatment. Therefore, the dye remaining on the surface of the fabric can be eliminated. This property in this group of dyes improves the wash fastness of the dyeing processes and also its brightness in this group of dyes [40]. In comparison to used commercial dyes, the synthesized dyes had good washing fastness properties on polyamide fabrics. The color change of dyed fabrics with commercial Isolan Gelb SGL (T) against to washing was 4-5, while the synthesized dyes had good wash fastness.

All dyed samples showed similar high rubbing fastness values (Tables 2, 3). These results indicated that the used dyes had moderate to good rubbing fastness values, which could be related to the polar groups in dye's molecular structure like the washing fastness. The dyed fabrics with commercial dye

(T) had relatively better rubbing fastness than the dyed fabrics with synthesized dyes (1–4).

Measurement of color fastness to perspiration has been carried out with the dyed fabrics in contact with adjacent fabrics (i.e., cotton and nylon) in alkaline and acidic solutions containing histidine. The dyed fabrics were subsequently drained and placed under constant pressure. The specimens were then placed in an incubator for 4 h at 37 °C. After drying, change in color of the dyed fabrics and staining of the adjacent fabrics has been evaluated with Gray Scales. Results showed that the synthesized and commercial dyes had good perspiration fastness values on polyamide fabrics in both different solutions containing alkaline and acidic media (Tables 2, 3).

Conclusions

In conclusion, the present paper was reported on the synthesis, characterization, absorption spectra and the industrial application of a series of water-soluble azocalix[4]arene



Fig. 4 Effect of acid and base absorption spectra of dyes



Fig. 5 The azo-enol and keto-hydrazo tautomer form of azocalix[4]arene dye 1

Table 2 Nylon dyeing fastness values of 1 and T

Applied fastnesses	Trash and color change values of multifibre													
	Acetate		Cotton		Nylon		Pes		Acrylic		Wool		Color change	
	Т	1	Т	1	Т	1	Т	1	Т	1	Т	1	Т	1
40 °C Washing fastness		4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
60 °C Washing fastness		4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Water fastness	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Alkaline perspiration F.	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Acidic perspiration F.	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
								1						
Wet rubbing fastness	4/5							4/5						
Dry rubbing fastness								4/5						
20 ppm Fastness to chlorinated water								3/4						

Table 3 Wool dyeing fastness values of 1 and T

Applied fastnesses	Trash and color change values of multifibre													
	Acetate		Cotton		Nylon		Pes		Acrylic		Wool		Color change	
	Т	1	Т	1	Т	1	Т	1	Т	1	Т	1	Т	1
40 °C Washing fastness		4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
60 °C Washing fastness		4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Water fastness	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Alkaline perspiration F.	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Acidic perspiration F.	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Т							1						
Wet rubbing fastness	4/5							4/5						
Dry rubbing fastness	4/5							4/5						
20 ppm Fastness to chlorinated water								4/5						

compounds. The perspiration fastness and water fastness of all the synthesized dyes were found to be good and very good. The azocalix[4]arene dyes were all stable up to 245 °C as DTA/TG data and hence can be effectively used in almost all kinds of inks.

We synthesized a new class of supramolecular chromogenic azocalix[4]arene dyes (1–4) and a commercial Isolan Gelb SGL (T) having -N=N- group as well as -COOH and $-SO_3H$ group to enable it to exhibit both coloring and binding properties. The effects of solvent and substituent do not exhibit expected regular variation in bathochromic shift. These azocalix[4]arenes are direct dyes which can be considered as a good candidate for dyeing cotton, silk, and wool fibers because of easy dyeing process just because they don't require after treatment process and they posses good fastness properties.

The substituted azocalix[4]arenes 1-4 showed solvatochromic effects because of the increased polarity of the azocalix[4]arene dyes. On the other hand, the tautomeric equilibrium and dissociation of substituted azocalix[4]arenes need to be considered in the future. Further studies to explore their complexing abilities with various metal ions in solution and solid state are underway.

Acknowledgments Authors thank to the Research Foundation of Pamukkale University for the financial support (BAP, 2010FBE011) and Deniz Textile Factory.

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