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A New Water-Soluble Zinc Azaphthalocyanine Containing Azo Groups: Synthesis, Characterization, Fastness and Antibacterial Properties on Cotton Fabric

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ABSTRACT

A novel water-soluble zinc azaphthalocyanine containing azo groups (Azo-ZnAzaPc) was synthesized and characterized using FT-IR, ^{1}H NMR, ^{13}C NMR, UV–vis, MS and elemental analysis. A dyeing experiment was performed on cationic cotton fabric with this dye via exhaustion process. The dyed fabric was examined for color fastness to light, water, washing, perspiration and rubbing according to ISO standards. Antibacterial properties of the fabric were evaluated against two types of bacteria: *Staphylococcus Aureus (S. Aureus)* and *Klebsiella Pneumoniae (K. pneumoniae)* according to ASTM E2149-01 and to AATCC 100 standards. Significant reduction of *K. pneumoniae* bacteria, rated as 95,91 %, was observed according to ASTM E2149-01 standard. Antibacterial activities and color fastness evaluation results of the azaphthalocyanine and of the similar phthalocyanine structure were presented for comparison.

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KEYWORDS
Azaphthalocyanine, antibacterial, cotton, azo group, color fastness

1. INTRODUCTION

Functional textiles have become extremely important in recent years. The use of antimicrobial finishes on textile materials grew year by year with increasing people sensitivity about the comfort and hygiene. Protective, decorative and technical textile products are created for a variety of applications in apparel, pharmaceutical, medical, engineering, agricultural and food industries. Some of the contemporary used antimicrobial agents in textiles and their types, characteristics, application methods are presented in literature [1-5]. Textile products, made from natural organic fibres especially such as cotton, wool, jute and flax, are susceptible to microbial attack [5-8].

Phthalocyanines (Pcs), predominantly the unsubstituted CuPc and its derivatives, are traditionally used as blue and green colorants for various applications including textile, paint, coating, printing ink, plastic materials. Detailed information about recent commercial uses of Pcs, provided by their unique properties were given in literature [9-12]. For instance, Pcs are known to be effective photosensitive substances and to have antimicrobial action against several species of bacteria [13]. Water soluble phthalocyanine compounds have a particularly good action against microorganisms [14]. That is mainly based on singlet oxygen generation as a result of photoactivation under irradiating with visible and /or infrared light in presence of oxygen and water [15-24].

Tetrapyrazinoporphyrazines and their metal derivatives, a group of azaphthalocyanines (AzaPcs), are the most widely studied class of aza-analogues of Pcs [25, 26]. AzaPcs differ from Pcs only in replacement of some of the benzene

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carbon atoms of Pc macrocyclic basic core by eight nitrogen atoms [27, 28]. Hence, they can be potentially used in practical applications in different fields similar to that of Pc [25, 29-31]. AzaPcs can be used as eco-friendly industrial textile colorants for controlling growth of microorganisms.

The aim of this study was to synthesize novel water-soluble Azo-ZnAzaPc structure and to investigate its antibacterial activities and color fastness properties on cotton fabric. Antibacterial efficiency of AzaPc on textile materials may depend on central metal ion and substituents at the peripheral benzene rings. Diamagnetic zinc metal atom coordinating to the center of Pc (or AzaPc) macrocycle lenghthens triplet state lifetime and ensures very high singlet oxygen quantum yield [26, 28, 32, 33]. The existence of an azo moiety in different types of compounds has caused them to show antibacterial and pesticidal activity [34-37]. Therefore, ZnAzaPc complex containing azo moieties was chosen to killing the bacteria on cotton fabric. The results of Azo-ZnAzaPc were compared with water-soluble zinc phthalocyanine containing azo groups (Azo-ZnPc structure) which were studied in our previous literature [14].

2. MATERIAL AND METHOD

2.1 Material

All used reagents and solvents were of analytical grade quality. Phenol and sulfanilic acid were supplied from Merck Chemical Company. Indosol E 50 Liq. was obtained from Clariant Chemicals and used as a cationic agent. Acetic acid and sodium carbonate were purchased from Merck Chemical Company. The bleached, hydrophilic 100 % cotton fabric was in single jersey knit structure (İzmir Basma Factory, Turkey), 260 g/m^2. Dyeing and cationization processes were carried out in Termal Laboratory Dyeing Machine (Turkey).

2.2 Method

2.2.1 Synthesis

Synthesis of the novel Azo-ZnAzaPc was performed according to the procedure stated in the literature [38,39].

5-Chloropyrazine-2,3-dicarbonitrile and 4-[(4-hydroxyphenyl) azo] benzene sodiumsulfonate were prepared according to literature procedures [40,41].

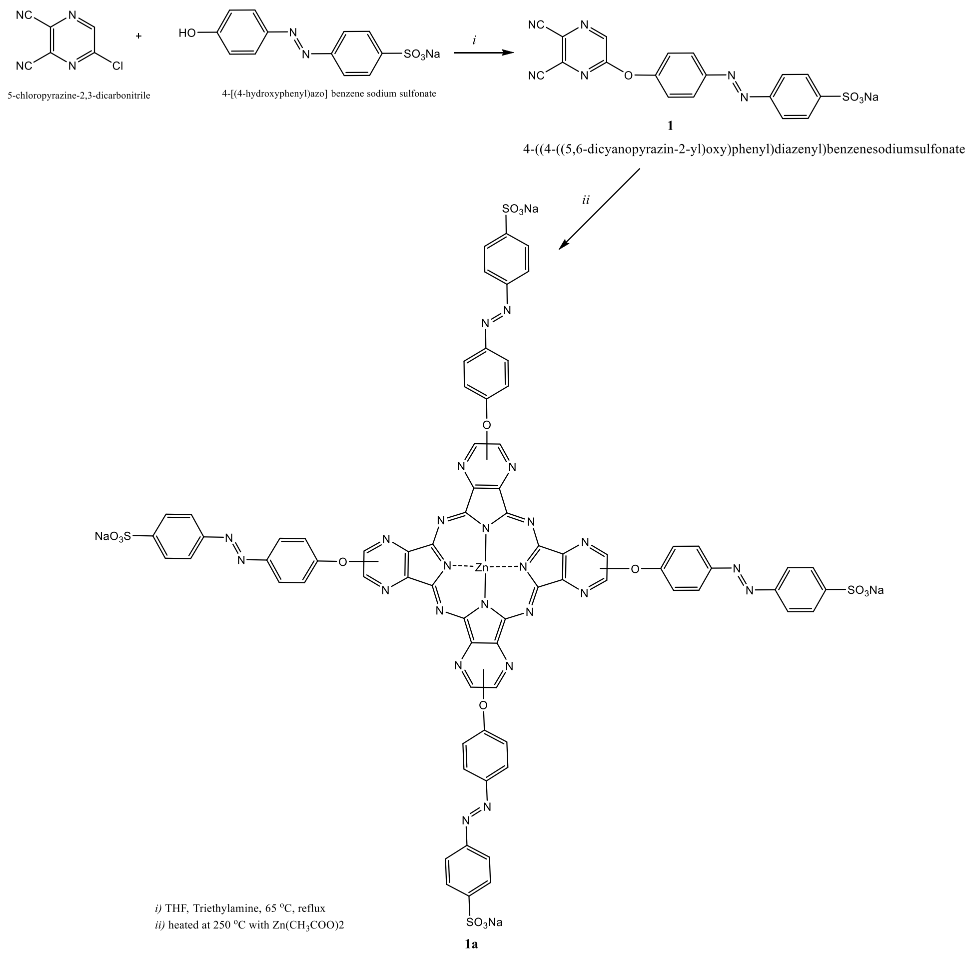

Figure 1. Synthesis of water soluble azaphthalocyanine containing azo groups.

4-((4-((5,6-dicyanopyrazin-2-yl)oxy)phenyl) diazenyl)benzenesodiumsulfonate (1)

5-Chloropyrazine-2,3-dicarbonitrile (0.5 g, 3.1 mmol) and 4-[(4-hydroxyphenyl) azo] benzene sodiumsulfonate (0.85 g, 3.1 mmol) were stirred in 15 ml of THF at 65 °C. Triethylamine (0.5 ml) was added to this solution and stirred at the 65 °C for 48 h. The orange precipitate was collected by filtration. The yield is 0.90 g (73%). m.p.: 244-245 °C. IR (ATR) υ_{max} (cm^{-1}): 3001 (CH, aromatic), 2241 (C≡N), 1560, 1536 (C=C aromatic), 1493, 1437, 1361, 1339, 1174, 1114, 1026, 1005, 864, 713. ^{1}H NMR (400 MHz, DMSO-d6): δ = 9.1 (s, 1H, Ar–H), 8.06-8.03 (d, 2H, Ar–H), 7.86-7.85 (d, 2H,Ar-H), 7.80-7.78 (d, 2H, Ar-H), 7.54-7.51 (d, 2H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): 113.92 (CN), 114.57 (CN), 122.67, 122.73, 124.95, 127.09, 127.22, 131.06, 142.19, 150.45, 151.54, 151.96, 153.93, 159.79. Calculated for C18H9N6O4NaS: C 50.47, H 2.12, N 19.62 %; found: C 50.40, H 2.22, N 19.18 %.

Synthesis of zinc azaphthalocyanine (1a)

Compound (**1)** with zinc acetate (0.5 mmol) were mixed and heated at 250°C for 20 min. After cooling, the blue product was washed with common solvents (ethanol, choloroform, ether). The yield is 0.90 g (73%). m.p.> 300 °C (dec). IR (ATR) υ_{max} (cm^{-1}): 3001 (CH, aromatic), 1626, 1594 (C=C aromatic), 1477, 1343, 1299, 1216, 1178, 1119, 1031, 1006, 848, 716.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.09 (s, 1H, Ar–H), 8.06-8.03 (m, 2H, Ar–H), 7.84-7.73 (m, 2H, Ar-H), 7.53-7.51 (m, 2H, Ar-H), 6.93-6.91 (m, 2H, Ar-H). Calculated for C72H36N24O16Na4S4Zn: C 48.62, H 2.14, N 18.9 %; found: C 48.91, H 2.32, N 18.8 %. UV/Vis (DMSO): λ_{max} /nm 357, 578, 637

2.2.2 Cationization and dyeing procedure

Cationization and dyeing processes were performed according to literature [14]. Cotton fabric was cationized with the assistance of a cationic auxiliary (Indosol E 50 Liq, 5% concentration) at 60°C for 20 min. in acidic media (via acetic acid, pH-5) by using exhaustion method (1:10 liquor ratio). The Azo-ZnAzaPc was solubilized at 80°C for 45 min. in alkali media (via sodium carbonate, pH 10) then applied to cationic cotton fabric for 3% dye concentration during 90 min. Then it was *sequentially* neutralized with acetic acid, washed with water thoroughly and air-dried.

2.2.3 Antibacterial activity measurements

Antibacterial activities of Azo-ZnAzaPc on cotton fabric were measured according to ASTM E2149-01 and to AATCC 100 test methods against Gram-positive *S. aureus* and Gram-negative *K. Pneumoniae* bacteria, not applied special irradiation procedure with infrared or visible light lamp.

2.2.4 Color fastness measurements

Cotton fabrics were tested according to ISO 105-X12 for crockfastness, ISO 105-B02 for lightfastness, ISO 105-CO6 for washfastness, ISO 105-E04 for perspiration fastness, and ISO 105-E01 for water fastness.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

The synthesis route of the new water soluble azaphthalocyanine (M:Zn) substituted with azo dye can be seen in Figure 1. 5-Chloropyrazine-2,3-dicarbonitrile and 4-[(4-hydroxyphenyl) azo] benzene sodiumsulfonate were prepared according to literature procedures [40, 41].

The synthesis of pyrazine compounds is the most important stage in these reaction series. For this purpose, compounds **1** were synthesized by treating 5-Chloropyrazine-2,3-dicarbonitrile with 4-[(4-hydroxyphenyl) azo] benzene sodiumsulfonate in THF using Triethylamine as the base for nucleophilic aromatic substitution at 65 ºC for 24 h. Pure products were precipitated and no further purification was necessary. In the FT-IR spectrum, formation of compound 1 was indicated by the appearance of a sharp CN band at 2241 cm^{-1}. In the ^{1}H NMR spectrum of compound 1, aromatic peaks appeared at 9.1 ppm as a singlet, at 8.06-8.03, 7.86-7.85, 7.80-7.78 and 7.54-7.51 ppm as four doublets. NMR and elemental analysis data indicate highly pure products.

Finally, azaphthalocyanine was obtained from by heated starting pyrazine compounds with corresponding metal salt for 20 min. FT-IR spectrum of the AzaPc **1a** signified the cyclotetramerisation of compound **1** with the disappearance of the CN peak at 2241 cm^{-1}. In the ^{1}H NMR spectrum, formation of compound **1a** was indicated by aromatic peaks appearing at 9.09 as a singlet, at 8.06-8.03, 7.84-7.73, 7.53-7.51 and 6.93-6.91 ppm as four multiplets.

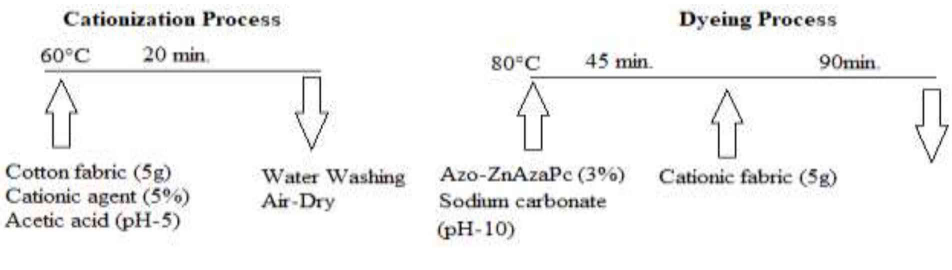

Figure 2. Cationization and dyeing process conditions.

Compound **1** is nonsymmetrical and consequently four constitutional isomers of compound **1a** may be formed. For this reason the [1]H NMR spectrum of compound **1a** have broad with unresolved splittings signals. The best evidence for the azaphthalocyanine macrocylic is their UV/vis spectra in solutions. The newyl synthesized AzaPc **1a** showed two strong absorption peaks, one of these in the UV region at 357 nm (B band) and the other in the visible region at 637 nm (Q band) in DMSO, respectively. The UV/Vis spectrum of the newly synthesized AzaPc **1a** are shown in Figure 3.

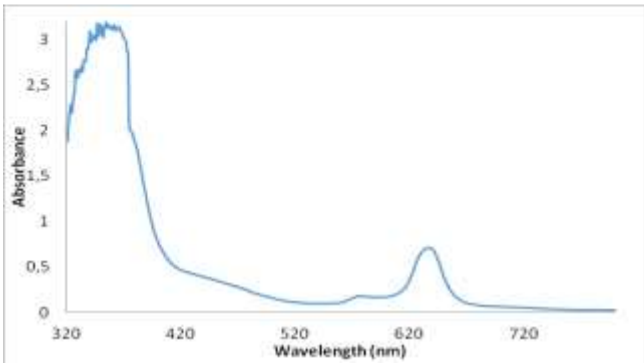

Figure 3. UV/Vis spectrum of AzaPc **1a**.

3.2 Cationization and dyeing of cotton fabric

The Azo-ZnAzaPc dye has low solubility in water because of having a large aromatic structure, so it was need to apply solubilization step with alkali media before dyeing step. Changing of the substituted sulfonic acid moiety of Azo-ZnAzaPc to sulfonates (negative ions) with sodium carbonate ensured high solubility in water. The pretreatment cationization process was required for improving affinity of cotton to the large aromatic dye structure due to forming electrostatic interactions between cationic groups of cotton and sulfo groups of the dye. It was thought that chemical bonding procedure was similar to direct dyes.

3.3 Color fastness assessments

Color fastness values of the dyed fabrics with the Azo-ZnAzaPc and Azo-ZnPc at 3% dye concentration were given in Table 1-4. For the dyed fabric with Azo-ZnAzaPc: Perspiration (Table 1), water (Table 2) and washing fastness (Table 3) gray scale ratings were good (grade 4-5, 5) leading to high commercially acceptable levels. Modarete light fastness level (grade 3) was observed in according to the wool scale rating. It was slightly better than the result of the dyed fabric with Azo-ZnPc (grade 2). Unlike the Pc, nitrogen atoms in the AzaPc's macrocyclic basic core may be the reason of higher light fastness result. The dyed fabric with Azo-ZnAzaPc exhibited medium wet rubbing (grade 3) and good dry rubbing (grade 4) fastness results. They were slightly less than the Pc's values (wet grade 3-4; dry grade 4-5) The reason may be less electrostatic interactions between dye and fibre. Thus, more dye migration can be occured on fibre.

Table 1. Perspiration fastness values of the dyed fabrics.

Color fastness to perspiration *Azo-ZnAzaPc*		**Colour change**	Staining					
			Acetate	Cotton	Nylon	Polyester	Acrylic	**Wool**
	Acidic	**4**	5	4-5	4-5	5	5	5
	Alkaline	**4**	5	4-5	4-5	5	5	5
Azo-ZnPc	**Acidic**	**4-5**	4-5	4-5	4-5	4-5	4-5	5
	Alkaline	**4-5**	4-5	4-5	4-5	4-5	4-5	5

Table 2. Water fastness values of the dyed fabrics.

Color fastness to water	**Colour change**	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	**Wool**
Azo-ZnAzaPc	**4**	5	4-5	4-5	5	5	5
Azo-ZnPc	4-5	5	5	5	5	5	5

Table 3. Washing fastness values of the dyed fabrics.

Color fastness to	**Colour**	Staining

		Acetate	Cotton	Nylon	Polyester	Acrylic	**Wool**
	4	5	4-5	5	5	5	5
	4-5	4-5	4-5	4-5	4-5	4-5	5

Table 4. Lightfastness and crockfastness values of the dyed fabrics.

	Light Fastness	Rubbing Fastness	
		Wet	**Dry**
Azo-ZnAzaPc	3	3	4
Azo-ZnPc	2	3-4	4-5

3.4 Antibacterial activity assessments

K. pneumoniae and S. Aureus are both pathogenic bacteria species. *S. Aureus* bacterium is a facultatively anaerobic, Gram-positive coccus causes a multitude of infections such as lung infections (pneumonia, influenza-associated), skin infections (mostly moderately severe, rarely necrotizing fasciitis), bone infections (e.g., osteomyelitis), blood infections (bacteremia, septicemia), indwelling medical device associated infections (e.g., endocarditis), specific toxin-related diseases (toxic shock syndrome, food-borne illness) [42-44]. *K. pneumoniae* bacterium is a Gram-negative, nonmotile, encapsulated, rod-shaped bacillus, can cause serious infections in some parts of human body such as blood (bacteremia or septicemia), brain (meningitis), heart (endocarditis), skin (cellulitis, soft tissue infections), urinary tract (urinary tract infections) [44, 45].

The antibacterial activity results were given in Table 5. It was observed that the Azo-ZnAzaPc dye was effective on *K. pneumoniae* bacteria but not has significant impact on *S. aureus* bacteria. Good antibacterial action was obtained according to the dynamic shake flask test method (ASTM E2149-01) against *K. pneumoniae* bacteria, 95,91 %.

Antibacterial action on cotton fabric dyed with Azo-ZnPc at 1% concentration are markedly higher than the cotton fabric dyed with Azo-ZnAzaPc at 3% concentration. Significant reduction of *K. pneumoniae* and *S. aureus* bacteria, rated as 99,74 % and 99,99 % respectively, had been observed according to AATCC 100 test method. Therefore, it can be said that the presence of AzaPc macrocyclic basic core instead of Pc caused decreasing in antibacterial activity. It may be due to lower singlet oxygen production capacity of the Azo-ZnAzaPc.

4. CONCLUSION

Novel Azo-ZnAzaPc structure was synthesized. This structure was used as a dyestuff in textile colouration for the first time in this study, thereby being achieved the production of eco-friendly antibacterial textile material via only coloration without any additional finishing process. Dyeing properties, color fastnesses and antibacterial activities on cotton fabric were investigated. Good antibacterial action against *K. pneumoniae* bacteria, rated as 95,91 % according to ASTM E2149-01 test standard was observed. Despite of moderate light fastness (grade 3) and wet crockfastness values; perspiration, water, washing and dry crockfastness values were at commercially acceptable levels (range from grade 4 to 5). Uniformly green coloured fabric can be promissing used for antibacterial technical textile productions in variety fields such as military, healthcare, work/uniforms, domestic products, sports apparel, especially in medical textiles.

As well as coloration ability, this new azaphthalocyanine structure’s other possible properties/uses such as textile bleaching agents, photoinactivators for controlling growth of microorganisms, catalysts for oxygen reduction, materials for electrochromic displays, media for optical data storage with large memory capacity, inhibitors of thermal degradation of polymers, photosensitizers for photodynamic therapy of cancer..etc. may be worthwhile to study.

Table 5. Antibacterial activity test results of the dyed cotton fabrics with Azo-ZnAzaPc at 3% dye concentration and with Azo-ZnPc at 1% dye concentration.

	Microorganisms	Test Method	Reduction (%), 24h
Azo-ZnAzaPc (3 %)	*S. aureus* (Gr +)	AATCC 100	4,64
		ASTM E2149-01	27,22
	K. pneumoniae (Gr -)	AATCC 100	61,26
		ASTM E2149-01	95,91
Azo-ZnPc (1 %)	*S. aureus* (Gr +)	AATCC 100	99.99
	K. pneumoniae (Gr -)	AATCC 100	99.74

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