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Functional smart fabrics based on synthesized sub-phthalocyanine

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In Loving Memory of Late Professor Doctor ""Mohamed Refaat Hussein Mahran""

Abstract

In the present work, novel synthesis of subphthalocyanine chlorides was performed and used for dyeing polyester and wool fabrics. The chemical structure of subphthalocyanine was confirmed and evaluated using ^{1}H NMR, FTIR, element analysis and mass spectra. The morphological properties of fabrics before and after dyeing were studied using SEM and EDX measurements. The Color strength (K/S) measurements of the dyed fabrics and their color fastness to rubbing, washing, and perspiration, and light were investigated. Moreover, the UV protection measurement (UVP) was tested for the dyed fabrics. The results indicated that the dyed fabrics showed remarkable higher K/S value than un-dyed fabrics. The dyed of both polyester and wool fabrics showed improved UVP as 16.2 and 49.1 values compered to un-dyed fabrics 5.5 and 22.2, respectively. The results also indicated that, the fastness properties of dyed wool fabric and polyester have good to very good to perspiration rubbing, washing, light and rubbing fastness. This work provides simple and efficient process for dyeing of polyester and wool fabrics for smart functional fabrics.

Keywords: Subphthalocyanine, Dyes, UV protection, Color fastness, polyester Fabrics.

1. Introduction

The Natural and synthetic dyes are the two main categories of dyes. Natural materials including plants, animals, and minerals are the sources of the natural dyes. Chemicals are used in a laboratory to create synthetic dyes. Metals are also present in several artificial dyes. The textile industry requires a wide range of synthetic dyes, including sulphur, basic, acid, dispersion, reactive, direct, and vat dyes, to fulfil the increasing demand for quality, fastness, diversity, and color depth. The functional textile has grown largely due to its exceptional and valuable characteristics [1]. There is a considerable interest for production of functional fabrics in textile sector. Its application can cover valuable performance of textile possessing and products. One of the most use of nanotechnology of textiles allows becoming multifunctional and producing fabrics with special functions, including antibacterial, UV protection, self-cleaning, and mosquito repellent [1]. Silver nanoparticles conjugated with moringa aqueous extract was used to modify different fabric for mosquito repellent applications [2]. Polyaniline composite with aluminum and zinc nanoparticles was synthesized and applied to cotton fabrics for antimicrobial as well as UV protection application [3]. UV blocking treatment for cotton and wool fabrics are developed using functional synthesized and natural dyes [4–6]. Metal organic framework based on titanium was developed and applied on fabrics for mosquito repellent [7]. Zinc oxide (ZnO) micro-particles was applied into polyester fabrics for UV protection and results required optimum level of incorporation to the fabrics surface was from 3–5% ZnO that yield stable UV protection performance [8].

Phthalocyanine is an interesting class of material with versatile application in different fields such as in solar cell, photodynamic therapy, optical data storage, photovoltaics (OPVs), reverse absorbers, dyeing and printing [9–14]. The phthalocyanine dyes are one of the families of dyes which are obtained by the reaction of dicyanobenzene in the presence of metal atom such as copper, nickel, cobalt, etc. The phthalocyanine nucleus gives the molecule a good fastness performance. The most widely used dye in this family is copper phthalocyanine because of its high chemical stability [15–18].

Subphthalocyanines (SubPcs) are 14-electron aromatic dyes with a distinctive intrinsic curvature caused by a central sp3-Hybridized boron atom coupled to three isoindole units linked by azo-linkages [19]. After Meller and Ossko discovered SubPcs in

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1972 [18]. The chemistry of SubPcs has been largely pioneered by Torres, Bender, and others who have developed methodologies for their synthesis and functionalization [20]. This relatively new class of dyes has already shown promise in the fields of Cnops et al. recently utilized the SubPcs as both donor and acceptor materials by tuning frontier molecular orbital levels via synthetic alterations [21].

Phthalocyanine and porphyrins are very colorful compounds. They have the potential to act as dye e.g in textile industry or in biological system, or as dye – photosensitizes in solar cells. Phthalocyanine compounds have a capable of advantages focused on dyeing textile fabrics that exhibit considerable biological activities such as antimicrobial and antioxidant activities based on their specific structures. There is not much work regarding of dyeing polyester and wool fabrics with subphthalocyanine compounds. Most widely working research in the mechanical, physical, and antibacterial properties of the textile fabric treated with some antibacterial dyes and stuffs were investigated [22–24]. This work tends to synthesis of subphthalocyanine chloride and dyeing polyester and wool fabrics with subphthalocyanine to produce smart functionalization dyed fabrics. Color strength, and fastness of the treated fabric to rubbing, washing and perspiration will be investigated. Ultra violet protection factor of these fabrics will be explored.

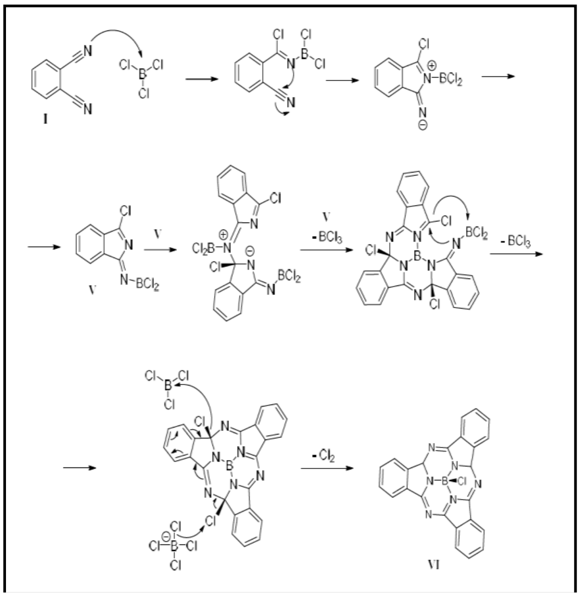
2. Experimental

2.1 Materials

Fabrics: Polyester (PET) 100% knitted fabric of 102 g/m2, supplied from private sector, Egypt. Wool 100% knitted fabrics of 165 g/m2, supplied from El-Mahal El –Qubra, Egypt Company.

2.2. Synthesis of Subphthalocyanine chloride (SubPcs)

A round dried flask evacuated with nitrogen gas, charged with a solution of phthalonitrile (Aldrich) (5.50 g, 42.9 mmol) in freshly distilled o-Dichlorobenzene (o-DCB) (100ml). The reaction mixture was evacuated with nitrogen three times and boron trichloride (BCl3) (Aldrich) (100 ml, 1M in heptane) was added to the solution, and the mixture was heated to reflux (70 °C) and stirred for 30 min. The heptane removed by distillation and the reaction mixture refluxed for additional 1.5 h. (180 °C). Cool the reaction and excess of BCl3 removed with a steam of nitrogen and the solvent removed until dryness under vacuum. The crude product washed with methanol (250 ml) by the means of revers Soxhlet extraction for 20 h. the remaining solid was washed with ethyl acetate (1 X 75 ml) and dried in vacuo which yielded the titled compound (3.09 g, 50%) as brown solid. The mechanism of the synthesized SubPcs was shown in (Scheme 1). M.P. > 250 °C; IR (KBr, ν, cm^{-1}); 3061 (C-H, aromatic), 1612 (-C=C-), 1564 (-C=N-), 1352 (-C-N-), 878 (B-Cl), 743 (B-N); ^1H NMR (500 MHz, $CDCl_3$): δ 7.94-7.96 (m, 6H), 8.89-8.91 (m, 6H) ppm. 13C NMR (500 MHz, CDCl3): δ 12.82, 123.97, 135.25, 148.67. HRMS (MALDI): m/z 431.09 [M+H+], calc. for (C24H12BClN6+): 430.09.



Scheme 1: General mechanism of SubPc formation

2.3. Dyeing Process of polyester:

Dyeing process behavior of polyester fabrics with the synthesized dye (subphthalocyanines chlorides) was performed using Dyeing machine (Infra color dyeing supplied from India Company). Fabric sample (2g) was immersed in cups having 4 % of dye (subphthalocyanine) at 130 ºC and pH 4 for 60 min via the dyeing machine. After dyeing step, the dyed fabrics were picked up, rinsed with water, and treated with solution comprising 2 g/l sodium hydrosulfite and 2 g/l sodium hydroxide for 10 min at 60 ºC. The treated sample was rinsed thoroughly with water and neutralizing via acetic acid (1 g/L) for about 5 min at 40 ºC. The dyed fabrics samples were rinsed with cold water, washed in a bath containing 3 g/L detergent (Hostapal CV, Clariant) at 50 °C for 30 min, followed by rinsing with water and allowed to dry at room temperature [25].

2.4. Dyeing Process of wool

Dyeing process behavior of wool fabrics with the dye (synthesized subphthalocyanines chlorides) was performed. Amount of 4g fabric sample was immersed in cups containing 2% of subphthalocyanine at 90ºC and pH 5 for 60 min. After dyeing processes, the dyed fabrics were picked up and rinsed with warm water then cold water. The dyed fabric was treated with 3 g/L detergents (Hostapal CV, Clariant) at 50 °C for 30 min, then rinse with water. In the end, fabrics were dried at room temperature.

2.5. Characterization tools

1H and 13C NMR spectra were obtained on a Bruker AC-500 instrument. MALDI-TOF-MS spectra were performed using Bruker Reflex III instrument fitted with a nitrogen laser operating at 337 nm. UV/Vis spectra were measured with a Hewlett-Packard 8453 instrument. IR spectra were collected using KBr discs on a JASCO FT/IR 6100 Japan spectrometer (National Research Centre Cairo, Egypt). Fluorescence measurements were recorded with a Varian-Cary Eclipse fluorescence spectrophotometer. Melting points (mp) were measured in a Büchi Melting Point 504392-S apparatus and are uncorrected. Column chromatographic were conducted on silica gel (230-400 mesh, 0.040-0.063 mm, 60 Å) obtained from Merck. TLC analysis was carried out using fluorescent-indicating plates (aluminum sheets percolated with silica gel 60 F254, E. Merck). Most of the solvents employed in this work was distilled and kept under nitrogen gas over molecular sieves (3 and 4Å, respectively). The fabrics surface morphology was characterized using high resolution scanning electron microscope (FE-SEM QUANTA 250, accelerating voltage; 20KV) connected to energy dispersive X-ray unit to evaluate the elemental analysis of the surface.

2.6 Colour strength measurements (K/S)

The colorimetric analysis of the dyed fabrics was obtained via a spectrophotometer with pulsed xenon lamps as light source (Ultra Scan Pro, Hunter Lab DP-9000, USA). All measurements were achieved at different λ. Values. The color strength value (K/S) was evaluated by applying the KubelkaMunk (Eq. (1) [26].

$$k/S = \frac{(1-R)}{2R} - \frac{(1-R_0)}{2R_0} \quad (1)$$

1

Where: R and R0 are the Decimal fraction of the reflectance of the dyed and un-dyed fabrics, respectively, K is the Absorption coefficient and S is scattering coefficient.

2.7 Fastness properties.

The color fastness to washing of the dyed fabrics with synthesized SubPcs was assessed using the test method; ISO 105-C10:2006. Color fastness to rubbing was evaluated according to the test method ISO 105-X12:2016. Two synthetic perspiration solutions (acidic and alkaline) were prepared rendering to test method; ISO 105-E04:2013. The light fastness test in accordance with test method; ISO 105-B02:2014 was examined.

3. Results and discussion

3.1. Synthesis and characterization of the dye (SubPcs)

As part of our ongoing efforts to create privileged class molecules [27] and our particular interest in the use of the simple methods for heterocyclic synthesis, we present herein a simple synthesis of Subphthalocyanine chloride (SubPcs) [28]. We initiated our studies with a classical, well-known synthesis of SubPc (Fig. 2).

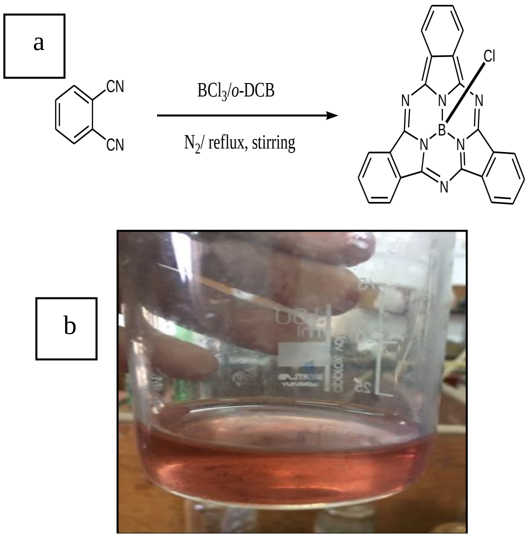


Figure 2. (a) Synthesis procedure of subphthalocyanine and (b) image indicated the color of the prepared subphthalocyanine in DMF.

The synthesized Subphthalocyanine chloride (SubPcs) was confirmed using 1H NMR (500 MHz, CDCl3): as indicated in figure (2a). The results displayed the two multiple peaks δ ppm 7.94-7.96 (m, 6H) and 8.89-8.91 (m, 6H). On the other hand FTIR (figure 2b) indicated new peaks at 878 and 743 cm^{-1} for the new (B-Cl) group and (B-N) respectively, in addition to well characterized peaks at 3061 (C-H, aromatic), 1612 (-C=C-), 1564 (-C=N), and 1352 cm^{-1} (-C-N). These results confirmed the successful synthesis of subphthalocyanine chloride.

3.2. Characterization of treated fabrics

3.2.1. FTIR

Characterization of the reactive functional groups of untreated and treated polyester and wool fabrics samples was achieved using FT-IR as displayed in Fig. 4. FTIR spectrum for blank polyester fabric indicates characteristics peeks at 1710 cm^{-1} related stretch vibration of carbonyl (-C=O) of ester group [29]. The peaks at 1240 cm^{-1} related to C-O group and peak at 1407 cm^{-1} corresponding to aromatic ring. The peak at 2956 related to symmetric stretching vibration of CH_2 groups and 1330 cm^{-1} associated to H-O-C symmetric bending vibration. The FTIR of wool fabrics showed band at 1631 related to carbonyl C=O of amide groups. The peak at 3276 cm^{-1} related to vibration of NH combined with OH groups. The spectra of treated fabrics showed no new peaks representing the subphthalocyanine unit; this may be due to the very low concentration of the coated layer.

3.2 .2. Scanning electron microscope (SEM):

As we know before, Scanning electron microscope was used to determined and study the surface characteristics of fabrics. Fig. (5) represented the polyester and wool fabrics before and after dyeing with subphthalocyanine. Fig. (5a) represent the untreated polyester fabric which appeared as smooth surface, whereas the dyed polyester fabrics (Fig. 5b) appeared with coated layer with some spots which indicate the deposition of subphthalocyanine layer with non-uniform structure. The morphology of wool fabric surface before and after dyeing with subphthalocyanine was represented in Fig. 5c and 5d, respectively. The blank wool fabric surface appear as fish peel with smooth structure [30]. The treated wool fabric have some deposition and coating layer of subphthalocyanine. Fig (5d) indicated also one cutted yarn that filled with dyeing material which indicated the successful treatment process of the selected fabrics.

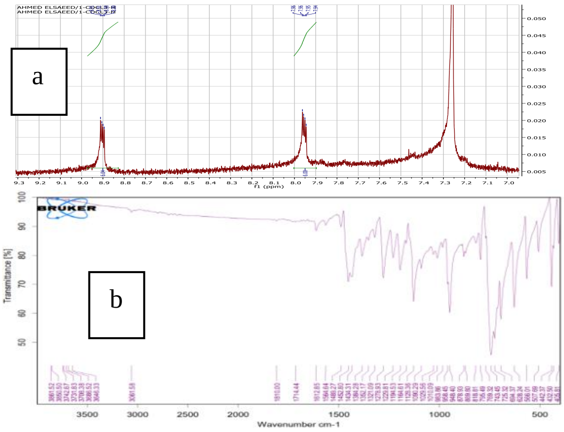


Figure 3. (a) 1H NMR and (b) FT-IR for SubPcs, respectively.

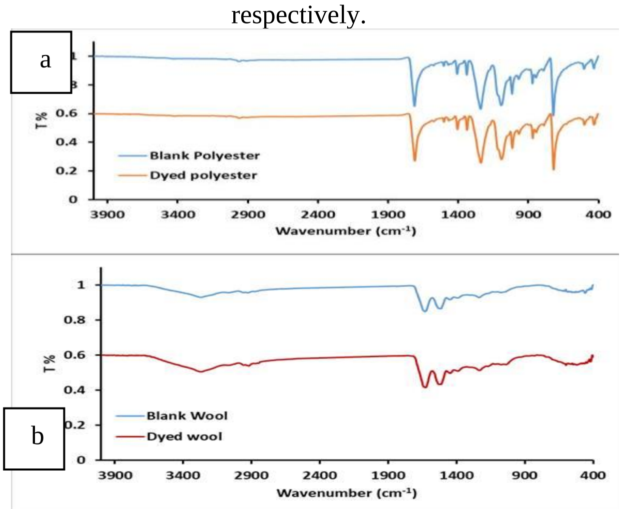


Figure 4. FTIR of blank and treated a) polyester and b) wool fabrics, respectively.

The elemental analysis of the polyester and wool fabrics after treatment with subphthalocyanine was evaluated using EDX measurement as presented in Fig 6. The blank polyester fabrics contains only carbon and oxygen elements, while wool fabrics containing carbon, oxygen, sulfur and nitrogen [31]. The two treated fabrics displayed boron, nitrogen and chloride elements with varying concentration representing the chemical composition of subphthalocyanine unit coated on the fabrics surface. This experiment confirmed the successful dyeing of the synthesized subphthalocyanine on the selected fabrics.

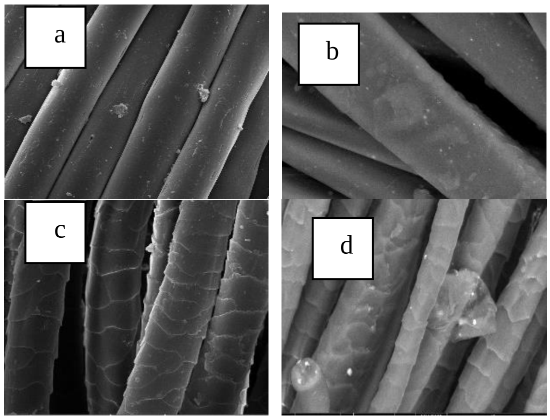
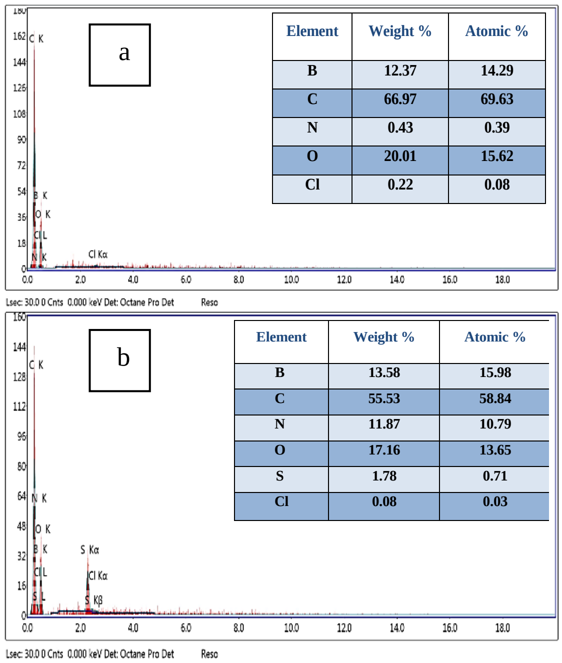


Figure 5: SEM of (a) un-dyed polyester fabric, (b) dyed polyester fabrics, c) un-dyed wool fabrics and d) dyed wool fabrics.



(a)

Element	Weight %	Atomic %
B	12.37	14.29
C	66.97	69.63
N	0.43	0.39
O	20.01	15.62
Cl	0.22	0.08

(b)

Element	Weight %	Atomic %
B	13.58	15.98
C	55.53	58.84
N	11.87	10.79
O	17.16	13.65
S	1.78	0.71
Cl	0.08	0.03

Figure 6. EDX of (a) dyed polyester and (b) dyed wool, respectively

3.3. Color strength results:

The innovations of synthesized dyes based on sub-phthalocyanine have been made due to increased need for bright dyes. The main aim of this work was to show the dyeing ability of the phthalocyanine compounds. The present work focused on synthesis of sub-phthalocyanine and its dyeing properties on polyester and wool fabrics. Fig. 7a showed, color strength results of un-dyed and dyed polyester fabric with synthesized dye. From results, the colors of the fabrics dyed with the phthalocyanine dyes were observed getting higher color strength values than un-dyed fabrics. The color strength increased from about 0.18 to 1.2 K/S. The results indicated the ability of the synthesized sub-phthalocyanine for dyeing polyester fabrics and produce fabrics with brown yellow color shads.

Fig. 7b showed, color strength results of un-dyed and dyed wool fabric with synthesized dye. The dyed wool fabrics showed remarkable higher K/S value than un-dyed wool fabrics with the same trend of polyester fabrics. Fig 7c represent the polyester fabric before and after dyeing with subphthalocyanine.

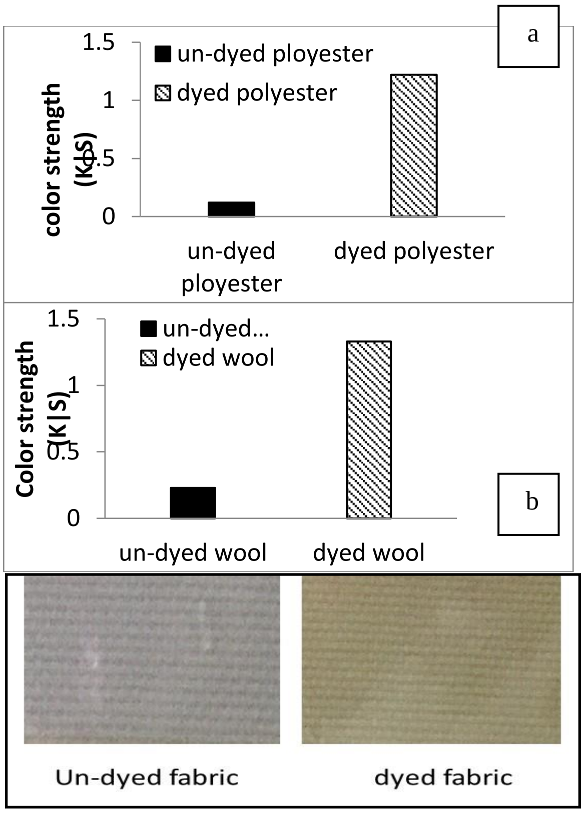


Figure 7: Color strength of (a) polyester (b) wool fabrics treated with subphthalocyanine, and (c) images of polyester before and after dyeing

3.4. UVP measurements:

Fabrics are the most convenient and natural way for protecting the human body from harmful and external environmental factors. Nowadays, the market focused in fabrics which can be presented suitable protection against Ultraviolet irradiation (UV) is growing rapidly and continuously. Based on the radiation intensity, the penetration degree and the corresponding harm resulted from the numerous wavelengths can cause human skin illnesses. So that, functional dyed fabrics which are resist to UV radiation are very importance matters.

Table (1): UVP values of un-dyed and dyed for both polyester and wool fabrics.

Fabrics type	UVP values
Un-dyed polyester	5.5
Dyed polyester	16.2
Un-dyed wool	22.2
Dyed wool	49.1

Table 1 showed UVP values for dyed polyester and wool fabrics. According to Melbourne Australian⁄New Zealand slandered (As⁄ NZS-4399-1996) [32], fabrics can be classified according to their UVP values, UV rating gets minimum +15 provide acceptable protection for human body skin from harmful UV rays.

From results, we found dyed polyester fabric gets (16.2) which is minimum acceptable protection value. On the other side, dyed wool fabric gets (49.1) which is excellent protection resist values. It can be summarized that, dyed of both polyester and wool (16.2-49.1) fabrics gets higher UVP values compered to un-dyed fabrics (5.5-22.2) respectively. The increased values of UVP may be due to the presence of aromatic subphthalocyanine with oscillating resonance ability of electrons and its color which may prevent the penetration of UV irradiations.

3.5. Fastness properties of the treated fabrics:

Color fastness is the most important feature that must be set to show the quality of the dyed materials. Fastness is defined as the strength of the color against many factors during the production and use of the textile material. So that, evaluation of dye fastness properties of the treated fabrics was considered of most importance for the textile market. It is well known that, fabric and dyestuffs types have a certain effect on the whole color strength and fastness results of all dyed fabrics.

Table 2, showed the fastness of dyed fabrics of polyester and wool fabrics for rubbing, washing, perspiration and light fastness. From the results, one can found that dyed polyester and wool fabrics get values from good to v. good (4 to 4-5) in rubbing, washing and perspiration according to fastness standards. In addition to that, the dyed polyester and wool fabrics get excellent value (6) in light fastness. It can be concluded that, the dyeing of wool and polyester fabrics with the synthesized subPC can greatly enhance the fastness properties of fabrics withe good to excellent fastness for rubbing, washing, perspiration and light fastness.

Table 2: Fastness properties of the dyed fabrics toward rubbing, washing, perspiration and light.

Material	rubbing		Washing				perspiration								Light
							Acid				Alkaline				
	Dry	wet	St.	st.*	St.**	alt.	St.	st.*	St**	alt.	St.	st.*	St**	alt.	
Dyed polyester	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6
Dyed wool	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6

Alt.: alteration; St.: staining on cotton; St.*: staining on wool and St**: staining on polyester

4. Conclusion

Synthesis of subphthalocyanine chlorides was successfully performed and produce 50% yield product. The elucidation of chemical structure of the obtained subphthalocyanine was explored using H-NMR, ^{13}C, Mass spectra and FTIR. The utilization of the prepared subphthalocyanine as dyestuff for dyeing of polyester and wool fabrics was performed. The dyed fabrics were investigated using SEM, EDX and FTIR spectra. These reported results indicated the synthesized dye have ultra violet properties which produced functionality dyed fabrics. The dyed fabrics showed remarkable high color strength value than un-dyed fabrics. The dyed polyester and wool fabrics showed enhanced UVP as 10.2, 49.1 values compered to un-dyed fabrics 5.5, 22.2 respectively. The dyed polyester and wool fabrics showed values from good to very good in rubbing, washing and perspiration fastness. The dyed polyester and wool fabrics showed excellent value in light fastness.

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