Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(20):158-165
(http://derpharmachemica.com/archive.html)

Synthesis of Novel florescent colorants based on chromeno[2,3-d]pyrimidin-4-one derivatives and their application

K. A. Ahmed[*1,2], D. M. Masoud[3], H. M. Ahmed[1] and Mervat El-Sedik[1]

[1]Textile Research Division, National Research Centre, 12622 Dokki, Cairo, Egypt
[2]Quasim University-College of Sciences and Arts –Girls section, 111 in Oqlatu's Soqoor, Quasim- KSA
[3]Faculty of Science- Chemistry Department- Helwan University

---

ABSTRACT

Fluorescent dyes are important colored compounds used for different application one of them is textile coloration. The scientific literature includes fluorescent dyes studies for different purposes. This work aims to synthesize new fluorescent dyes based on chromeno[2,3-d]pyrimidin-4-one moiety , studying their photophysical properties and their ability to print polyester and polyamide fabrics. The printed fabrics with new fluorescent chromeno-pyrimidin-4-0ne dyes have high light fastness, excellent perspiration, washing and rubbing. The fluorescence quantum yield of the prepared dyes lie in the range from 0.10 to 0.90.

Keywords: chromeno-pyrimidin-4-0ne**,** dyes, photophysical properties, printing

---

INTRODUCTION

Fluorescent dyes are one of functional compounds which have ability to emit fluorescence. They have different structures most of them contain aromatic polycycles, heterocycles, and vinyl units. Recent researches represented that, fluorescent dyes were developed in many different fields such as applied chemistry, biochemistry, and other fields, such as, fluorescent probes [1, 2], biomedical diagnosis [3-5] and biological images [6] and textile coloration[7-11]. There are many types of fluorescent dyes are classified according to their chemical structure, e.g., coumarins perylenes, and xanthenes. The aim of this work is to synthesize novel fluorescent dyes based on chromeno- pyrimidin-4-0ne moiety from simple available material with high yield . The produced compounds have different wave length ranging from 353 to 423 nm. The synthesized dyes print polyester and polyamide fabrics giving greenish yellow color, the prints possess high color strength values and very good color fastness.

MATERIALS AND METHODS

Experimental:
Materials: The following materials were used in the study are reported here:
1- **Chemicals**: All Chemicals were purchased from Merck (Germany) and were used without further purification.
2- **Fabrics**: ● Polyamide 6 (PA) of 212 g/m2 supplied by El-Nasr Company for Spinning, Weaving and Knitting was treated with a solution containing 5 g/l soap at 50°C for 15 minutes, and then thoroughly washed and dried at room temperature.

● Polyester fabric (PE) knitted fabric of 150 g/m2,supplied by a private sector company, was treated with a solution containing 1 g/l non-ionic detergent at 70°C for 1/2 hour thoroughly washed and air dried at room temperature.

3- **Thickener**: Commercial synthetic thickener (acrylate copolymers) supplied by BASF Company

Synthesis:
A mixture of salicylaldehyde derivatives **1** (2 mole), cyano-N-methyleneacetohydrazide derivatives **2** (1 moles) and piperidine drops (catalyst) in ethanol or dimethylformamide solvent were refluxed for 1.5 hr. The reaction mixture was monitored by TLC. After the reaction was completed, the reaction mixture was cooled to room temperature . The precipitated product, was filtered off, dried and recrystallized

Printing paste: synthetic thickening agent (3.0 g), synthesized dyes (3a-h) (3.0 g) and water (94 ml) are mixed together to form the paste.

Printing method: polyester and poly amide fabrics are printed using silk screen printing technique, all prints are fixed at different temperature and time using thermo fixation technique.

Measurements:
Melting point: Melting points were taken on Electro thermal IA 9000 series digital melting point apparatus IR spectra: The IR spectra (KBr) were recorded on a Shimadzu CVT-04 spectrophotometer. The Infra-Red spectra of the synthesized dyes was measured using a Perkin Elmer/1650.FT-IR instrument 1H – NMR spectra: The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. 1H spectra were run at 300 MHz in deuterated dimethylsulphoxide (DMSO-d6).

Mass spectra: Mass spectra were measured on a Varian MAT CH-5 spectrometer (70 eV).

Color strength measurements: The reflectance values of the fabric were measured using a Data Color SF 600+. Relative color strengths (K/S values) were determined using the Kubelka-Munk equation. K/S = (1-R) 2 /2R

Spectrophotometric measurements:
The absorption spectra were measured in 1, 4-dioxane solvent using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 10° standard observer in the ultraviolet-visible region between 200-700 nm. The steady-state fluorescence spectra were measured using JASCO FP-8300 spectrophotometer.

The instrument provides corrected excitation spectra directly; the fluorescence emission spectra were corrected for the characteristics of the emission monochromator and for the detection photomultiplier response. The fluorescence emission spectra were recorded by excitation at absorption maxima, the excitation spectra were recorded at fluorescence emission maxima. . The fluorescence quantum yields (qF) were measured.

The fluorescence quantum yields (Φ) were determined using the classical formula: $\Phi x = (As \times Fx \times n^2x \times \Phi s)/(Ax \times Fs \times n^2s)$ where A is absorbance at the excitation wavelength, F the area under the fluorescence curve, and n is the refractive index of the solvents used. Subscripts 's' and 'x' refer to the standard and to the sample of unknown quantum yield, respectively. Coumarin 6 in ethanol (Φ= 0.78) was taken as the standard [12].

Fastness properties measurements: Fastness to washing, rubbing, light and perspiration were assessed according to standard methods [13-16].

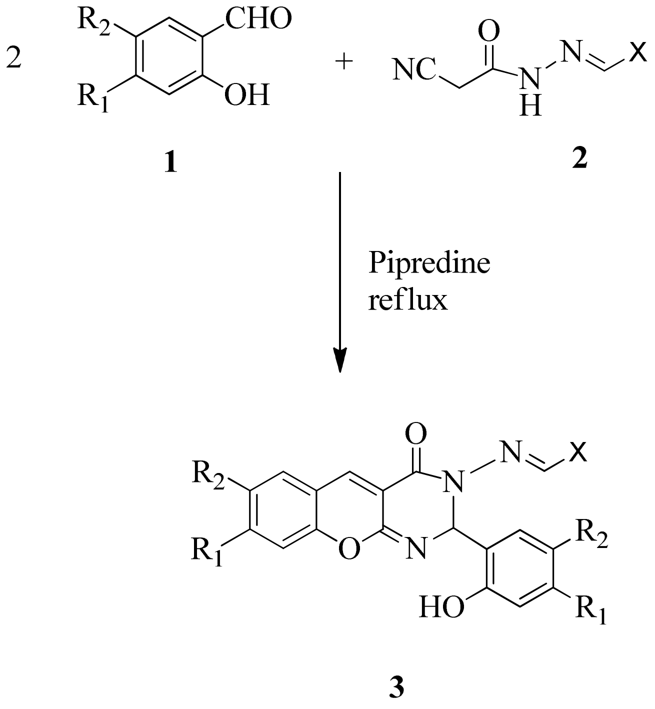
RESULTS AND DISCUSSION

Synthesis of **chromeno[2,3-d]pyrimidinanoe derivatives 3a-h**
In recent reports from our laboratory, we described the preparation of different novel fluorescent dyes [8-11] . In continuation of our work, the present article deals with a novel dyes based on chromeno[2,3-d]pyrimidin-4-0nes derivatives which prepared from low cost, available starting material.

The synthetic method was carried out as the following:
Preparation of bezylidine-2-cyanoacetohydrazide derivatives from reaction of aromatic aldehydes with cyanoacetamide followed by its cyclocondensation with salicylaldehyde derivatives as shown in **Chart 1**. The cyclocondensation process takes place via the condensation reaction of the carbonyl group of salicylaldehyde derivatives with methylene group of bezylidine-2-cyanoacetohydrazide then addition reaction of OH group of salicylaldehyde on the CN group of bezylidine-2-cyanoacetohydrazide.

Dyes structure of (3a-h) illustrated on the basis of elemental analysis and spectral data (Tables 1, 2 and 3); The mass spectrum of 3a(7-bromo-2-(5-bromo-2-hydroxyphenyl)-3-((4-methoxybenzylidene)amino)-2H-chromeno[2,3-

d]pyrimidin-4(3H)-one with the molecular formula : $C_{25}H_{17}Br_2N_3O_4$ (M^+ 579), and ^1H- NMR spectrum contained a single at 3.84 ppm, assignable to methoxy group, a multiplet at 6.72-8.61 ppm. assigned to aromatic protons, single at 9.1ppm assigned to methine group, and singlet at 11.4 ppm for hydroxyl group.



Dye no.	R_1	R_2	X
3a	H	Br	$4\text{-}OCH_3C_6H_5$
3b	H	Br	2- thiophene
3c	H	Br	$5\text{-}CH_3$- furfural
3d	H	Br	$4\text{-}NO_2C_6H_5$
3e	$N(C_2H_5)_2$	H	$4\text{-}OCH_3C_6H_5$
3f	$N(C_2H_5)_2$	H	2- thiophene
3g	$N(C_2H_5)_2$	H	$5\text{-}CH_3$-furfural
3h	$N(C_2H_5)_2$	H	$4\text{-}NO_2C_6H_5$

Chart 1

Table 1 Physical and analytical data of synthesized dyes 3a-h

Dye No.	Color	Yield %	m.p °C	Molecular Formula	M.W
3a	Yellow	93	220	$C_{25}H_{17}Br_2N_3O_4$	580.96
3b	Yellow	91	195	$C_{22}H_{13}Br_2N_3O_3S$	556.90
3c	Orange	90	188	$C_{23}H_{15}Br_2N_3O_4$	557.19
3d	Orange	92	223	$C_{24}H_{14}Br_2N_4O_5$	598.20
3e	Orange	95	212	$C_{33}H_{37}N_5O_4$	567.68
3f	Brown	91	156	$C_{30}H_{33}N_5O_3S$	543.68
3g	Orange	89	207	$C_{31}H_{35}N_5O_4$	541.64
3h	Orange	89	216	$C_{32}H_{34}N_6O_5$	582.65

Table 3 ^{1}H-NMR, and Mass spectra

Dye no	^{1}H-NMR (ppm)	Mass spectra (M^+)
3a	3.38 (s, 3H, OCH_3), 7.02-8.11 (8H, m, aromatic protons), 8.36 (s, H, benzyldenimin), 9.61(s, 1H, CH), 11.39 (s, 1H, OH)	579
3b	6.79-8.12 (8H, m, aromatic protons),), 8.32 (s, H, benzyldenimin), 9.61(s, 1H, CH),, 11.41 (s, 1H, OH)	555
3c	2.38 (s, 3H, CH_3), 6.87-8.66 (8H, m, aromatic protons),), 8.33 (s, H, benzyldenimin), 9.61(s, 1H, CH), 11.49 (s, 1H, OH)	556
3d	6.06- 8.66 (10H, m, aromatic protons), 8.30 (s, H, benzyldenimin), 9.61(s, 1H, CH), 11.50 (s, 1H, OH)	597
3e	1.15(s, 4H, $2CH_2$), 2.31 (s, 6H, $2CH_3$), 3.38 (s, 3H, OCH_3) 6.87-8.66 (8H, m, aromatic protons), 8.34 (s, H, benzyldenimin), 9.61(s, 1H, CH), 11.40 (s, 1H, OH)	566
3f	1.12(s, 4H, $2CH_2$), 2.33 (s, 6H, $2CH_3$), 6.79-8.19 (11H, m, aromatic protons), 8.40 (s, H, benzyldenimin), 9.61(s, 1H, CH),, 11.40 (s, 1H, OH)	542
3g	1.12(s, 4H, $2CH_2$), 2.33 (s, 9H, $3CH_3$), 6.06- 8.66 (10H, m, aromatic protons), 8.46 (s, H, benzyldenimin), 9.61(s, 1H, CH), 11.50 (s, 1H, OH)	540
3h	1.12(s, 4H, $2CH_2$), 2.33 (s, 6H, $2CH_3$), 6.06- 8.66 (10H, m, aromatic protons), 8.3 (s, H, benzyldenimin), 9.61(s, 1H, CH), 11.61 (s, 1H, OH)	581

Table 2: Elemental analysis and IR spectral data of synthesized dyes 3a-h

Dye no.	Elemental analysis						IR spectra	
	Calculated			found				
	C	H	N	C	H	N	C=O	O-H
3a	51.48	2.94	7.20	51.42	2.938	7.19	1679	3510
3b	47.25	2.34	7.51	47.21	2.31	7.49	1683	3523
3c	49.58	2.71	7.54	49.56	2.68	7.52	1687	3512
3d	48.19	2.36	9.37	48.11	2.29	9.35	1654	3490
3e	69.82	6.57	12.34	69.77	6.53	12.31	1669	3495
3f	66.27	6.12	12.88	66.24	6.11	12.85	1673	3488
3g	68.74	6.51	12.93	68.71	6.49	19.89	1677	3504
3h	65.96	5.88	14.42	65.93	5.87	14.40	1679	3498

The absorption and fluorescence properties

The absorption and fluorescence spectra were measured in 1, 4 dioxane solvent at room temperature and the fluorescence quantum yield are calculated for all the prepared dyes. The shape and the position of spectra are shown in Figures (1-8) and in Table 4. from this result we can observe that all compounds are absorbed in region 353-420 nm. There is no significant difference between the absorbance and emission of compounds 3a, 3b, 3c and 3d while the replacement of the bromine in coumarin ring with N, N diethylamino group showed the longest wavelength. The longest wavelength absorption band is characterized as intramolecular charge-transfer transition, as the bathochromic shift is caused by structural modification which increases electron-donating or -accepting ability.

The dyes exhibited fluorescence properties at room temperature. For all dyes 3a-h; the shape and position of the emission spectra were independent of the excitation wavelength, which confirms that only one species emits in each solution. Their fluorescence maxima were located at 408-464 nm shown in Table 4 . Compared with the absorption maxima of the dyes, the emission maximum was markedly shifted to the red shift for all compounds, and the Stokes shift (λ abs - λem) by 33-93 nm increased drastically. The prepared compounds have bluish and greenish fluorescence emission with the fluorescence quantum yield in the range between 0.10 to 0.90. It could be found that the value of fluorescence quantum yield for dyes possessing electron-donating group (N, N diethyl amino group) higher than dyes that contain electron-withdrawn group Br while compound **3e** has the highest fluorescence quantum yield (qF=0.90) due to the presence of electron donating groups (diethyl amine and anisole groups) which increasing the electron density of this compound whereas compound **3a** has the lowest fluorescence quantum yield (qF=0.1) due to the presence of electron withdrawing group (bromine).

Table 4. Absorption (λA), excitation (λEx) and fluorescence (λF) maxima (nm) and fluorescence quantum yields (qF) of all compounds in dioxane

Compound No.	Absorption λA [nm]	Excitation λEx[nm]	Fluorescence λF[nm]	Stock shift	qF
3a	353	370	420	67	0.2
3b	353	368	408, 431	78	0.16
3c	353	392	442	89	0.13
3d	338	362	408, 431	93	0.10
3e	416	415	452	36	0.90
3f	423	417	456	33	0.43
3g	413	407	464	51	0.36
3h	420	406	456	36	0.25

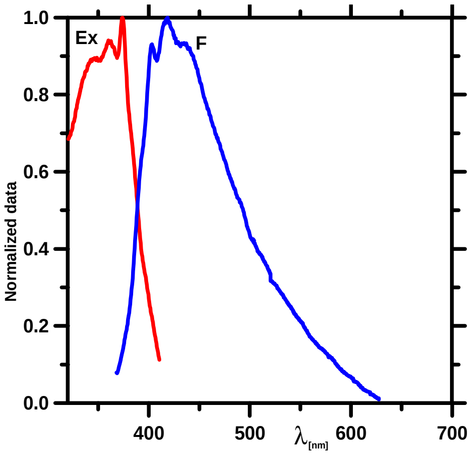


Figure 1. Excitation (Ex) and (F) fluorescence spectra of dye 3a

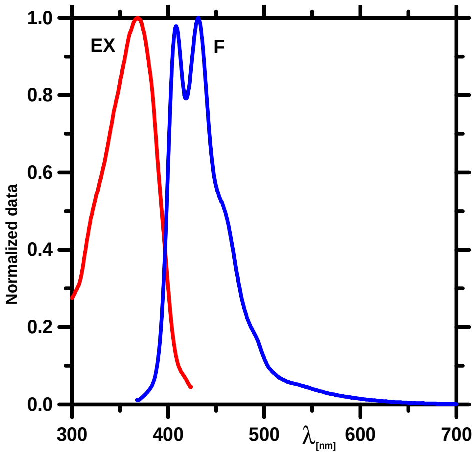


Figure 2. Excitation (Ex) and (F) fluorescence spectra of dye 3b

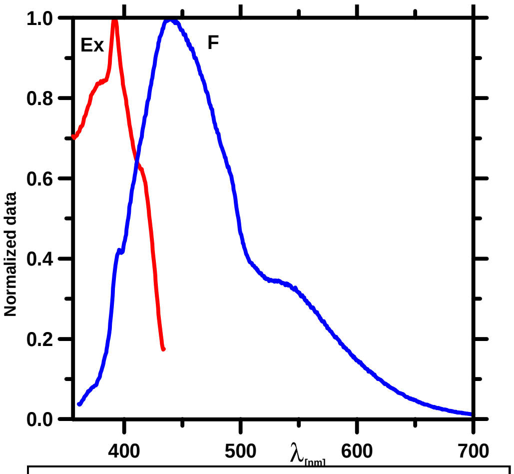


Figure 3. Excitation (Ex) and (F) fluorescence spectra of dye 3c

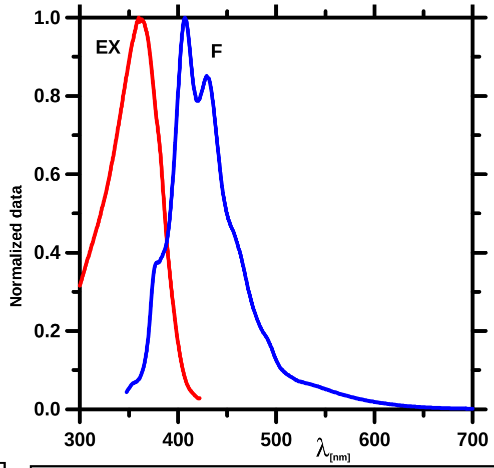


Figure 4. Excitation (Ex) and (F) fluorescence spectra of dye 3d

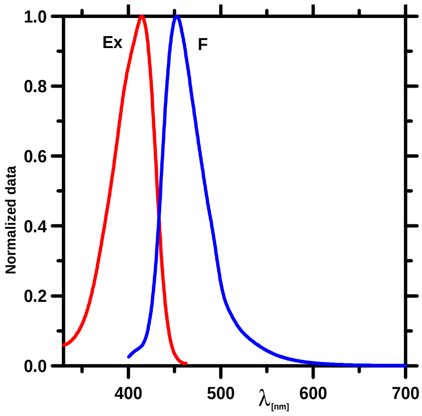


Figure 5. Excitation (Ex) and (F) fluorescence spectra of dye 3e

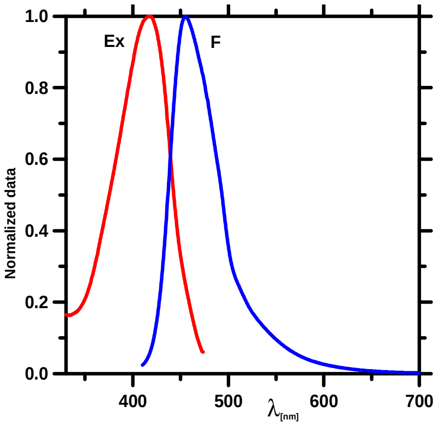


Figure 6. Excitation (Ex) and (F) fluorescence spectra of dye 3c

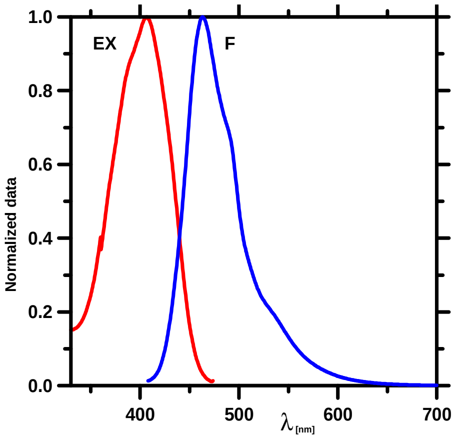


Figure 7. Excitation (Ex) and (F) fluorescence spectra of dye 3g

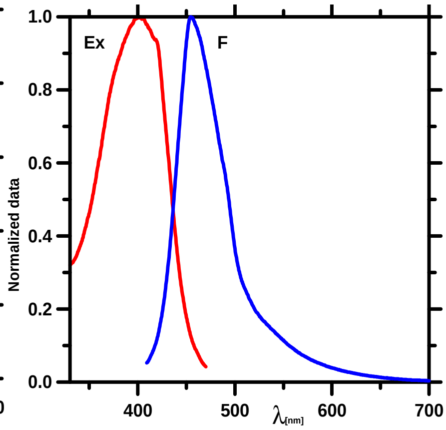


Figure 8. Excitation (Ex) and (F) fluorescence spectra of dye 3h

Effect of fixation temperature

Figures 9 and 10 represent, the effect of fixation temperature on the color strength printed polyester and polyamide respectively using the synthesized dyes (3a-h), fixation times was 3 minutes. The K/S of the all prints increases by increasing the fixation temperature from 150, 170 to 190°C of all dyes 3a-h.

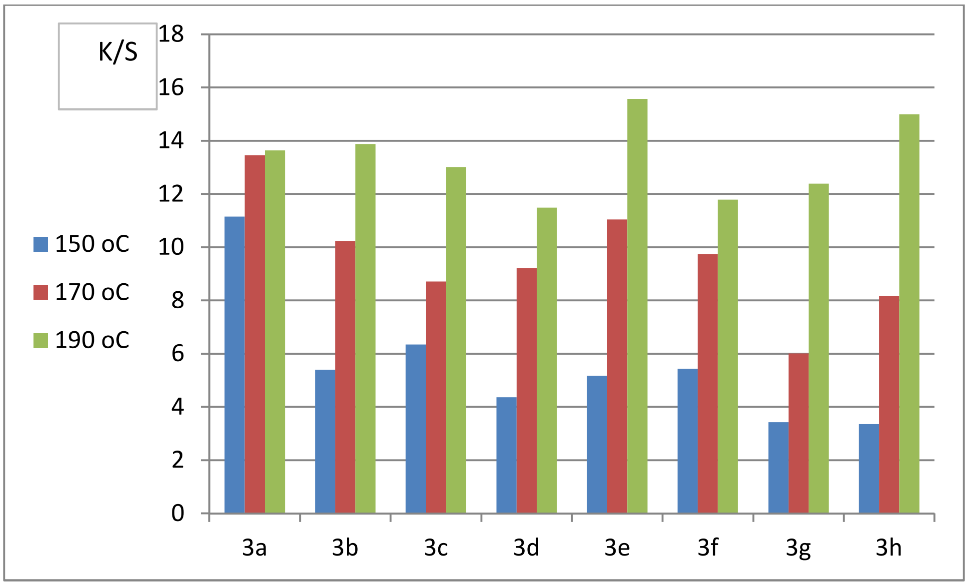


Figure 9: Color strength values for Silk screen printed polyester fabrics using synthesized dyes 3a-h, at 150, 170, 190 °C fixation temperature

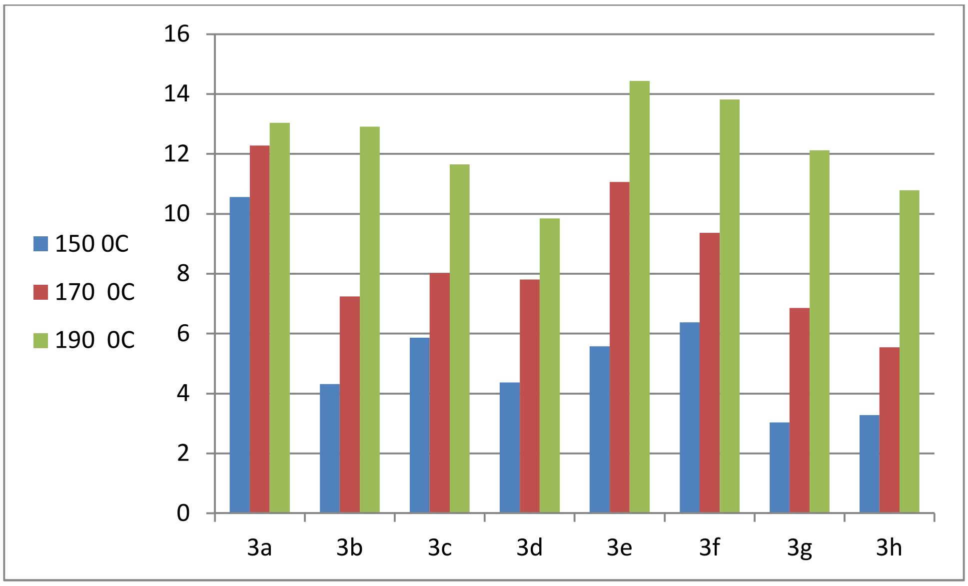


Figure 10: Color strength values for Silk screen printed polyamide fabrics using synthesized dyes 3a-h, 150, 170, 190 ^{o}C fixation temperatures

Fastness properties

Table 5 represents the fastness properties of silk screen printed fabrics using the synthesized dyes (3a-h). Given the evaluation of the experimental results, It was found that in both fabrics printed with new fluorescent chromeno-pyrimidin-4-0ne dyes, high level light fastness, excellent level perspiration, washing, rubbing were obtained. The printed polyester and polyamide using dye no. 3e possess highest color strength value and this may be attributed to presence of (diethyl amine and methoxy groups) within its molecular structure. Also prints with dye no 3d, which possess lowest (K/S) value. This may be due to presence of three electron with drawing groups (two-bromine atoms and nitro group) with its structure.

Table 5 Fastness properties of silk screen printed Polyester and polyamide fabrics, using the synthesised dyes 3a-h at 190 ^{o}C

Dye No.	Fabric		**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**
Wash fastness	polyester	*Alt.	5	5	5	5	5	5	5	5
		*St.	5	5	5	5	5	5	5	5
	polyamide	Alt.	5	5	5	5	5	5	5	5
		St.	5	5	5	5	5	5	5	5
Rubbing fastness	polyester	Dry	5	5	5	5	5	5	5	5
		Wet	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	polyamide	Dry	5	5	5	5	5	5	5	5
		Wet	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Perspiration fastness	polyester	Acidic	5	5	5	5	5	5	5	5
		Alkali	5	5	5	5	5	5	5	5
	polyamide	Acidic	5	5	5	5	5	5	5	5
		Alkali	5	5	5	5	5	5	5	5
Light fastness	Polyester		5-6	7-8	6-7	7-8	5-6	7-8	7-8	5-6
	polyamide		5-6	7-8	5-6	7	6-7	7-8	5-6	7-8

**Alt.=Alternation, *SC= Staining on cotton*

CONCLUSION

- The dyes are prepared from simple, cheap and lab available materials and produce high yield.
- The new chromeno[2,3-d]pyrimidin-4-0ne dyes are succeed as fluorescent dyes which have bluish and greenish fluorescence emission with the fluorescence quantum yield in the range between 0.10 to 0.90.
- All prints using prepared dyes possess bright colors, high color strength values, very good light fastness as well as improved overall fastness properties

REFERENCES

[1] T. Ueno and T., Nagano *Nature Methods* **2011**, 8, 642– 645,
[2] N. Shuangmu Zhuo, P.T. C. So *and* H. Yu, *Nature Methods* **2011**, 8, 642–645.
[3] C.-H. Quek and K. W. Leong, *Nanomaterials*, **2012**, 2, 92-112.

[4] V. M. Yashchuk, S. M. Yarmoluk, V. Yu. Kudrya, M. Yu. Losytskyy V. P. Tokar, V. M. Kravchenko, V. B. Kovalska, A. O. Balanda, and D. V. Kryvorotenko, *Advances in Optical echnologies*, **2008**, 2008 , Article ID 908246, 11 pages http://dx.doi.org/10.1155/2008/908246.
[5] X. Yi, F. Wang, W. Qin, X. Yang, J. Yuan, *International Journal of anomedicine*, **2014**, 9(1), 1347—1365
[6] J. O. Escobedo, O. Rusin, S. Lim, and R. M. Strongin, *Curr Opin Chem Biol*. **2010,** 14(1), 64.
[7] K.A. Ahmed, M. M. El-Molla, M.S.A. Abdel-Mottaleb, Mohamed S. Attia and M.S. El-Saadany, *Research Journal of Chemical Sciences*, **2013** 3(4), 3-18.
[8] Galal Elgemeie, Kawther Ahmed, Ebtsam Ahmed, Maher Helal, Doaa Masoud, *Pigment and Resin Technology*, **2015,** 44(2), 87-93.
[9] G.H. Elgemeie, K.A. Ahmed, E.A. Ahmed, M.H Helal, DM Masoud, *Pigment and Resin Technology*, **2015**, 44(3), 165-171.
[10] M. S. Attia, Kawther A. Ahmed,Soad A. Elsaadany, ,Mohamed M. El-Molla,M. S. A. Abdel-Mottaleb, *J. of fluorescence January* **2015**, 25 (1), 119-125.
[11] G.H. Elgemeie, K.A. Ahmed, EA Ahmed, M.H. Helal, D.M. Masoud " *Pigment and Resin Technology*, **2015**, 45(4), 217 - 224.
[12] G.A. Reynolds, and K.H. Drexhage, *Optics Communications*, **1975**, 13(3), 222-225.
[13] AATCC, Technical Manual, Method, 36, (**1972**), 68, (1993).
[14] AATCC, Technical Manual, Method, 8, (**1989**), 68, 23, (1993).
[15] AATCC, Technical Manual, Method,15, (**1989**), 68, 30, (1993).
[16] AATCC, Technical Manual, Method, 16A, (**1989**), 68, 33, (1993).