Available online at www.sciencedirect.com

SCIENCE DIRECT®

Dyes and Pigments 72 (2007) 217–222

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Novel dyes derived from hydrazones. Part 4. Synthesis and characterizations of 2-{4-[(2*E*)-2-(1-arylylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile

Abdullah Mohamed Asiri*, Nahed A. Fatani

Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah 21413, P.O. Box 80203, Saudi Arabia

Received 2 March 2005; received in revised form 19 June 2005; accepted 17 August 2005
Available online 13 October 2005

Abstract

Novel tricyanovinyl derived from hydrazones have been prepared by the reaction of tetracyanoethylene and phenylethylidene hydrazone, and these dyes showed absorption in the region of 500–593 nm. The dyes showed pronounced solvatochromic effects as the polarity of the solvents increased. Some of the new dyes were studied to show the aggregation properties in solution as the concentration changed. Most of the dyes studied showed change in the absorption spectrum and hence the position of the maximum absorption bands.

The thermal stability of some of the prepared dyes was studied in polymethylmethacrylate film at 80 °C; the annulations on the aromatic group showed less thermal stability of the dyes.

Keywords: Donor–acceptor; Tricyanovinyl; Hydrazones; NLO chromospheres; Solvatochromism

1. Introduction

The electronic and structural properties of donor–acceptor substituted π-conjugated organic compounds are of considerable interest because of their applicability to electro-optic devices and data storage [1,2]. A wide variety of structural modifications on the donor–acceptor and π-conjugated moieties have been carried out [3,4]. Major research efforts have focused on developing NLO chromospheres possessing large molecular nonlinearity and good thermal stability as well as improved solubility and process ability. It is well known that the second order molecular nonlinear optical hyperpolarizability (β) increases with increasing donor and acceptor strengths and with increasing length of conjugation [5]. Many donor–acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzene, biphenyls, stilbenes, azobenzenes ferrocenyl and schiff bases [6–8]. In all these classes, benzene rings with or without the π-bridges have been employed as the conjugated moieties to connect donor and acceptor functional groups such as compounds **1–6**. However, optical studies on compounds containing more than two benzenoid rings are usually insoluble in most common organic solvents. We have recently [9], reported the synthesis of new NLO chromospheres based on pyrazoles as the donor groups, for example compound **7**. Also we have reported the synthesis of new tricyanovinyl based on hydrazones such as dyes **7**, **8** and **9** [10–12]. In this paper, we report on the synthesis and spectroscopic investigations of novel push–pull system based on hydrazones as donor groups.

2. Results and discussion

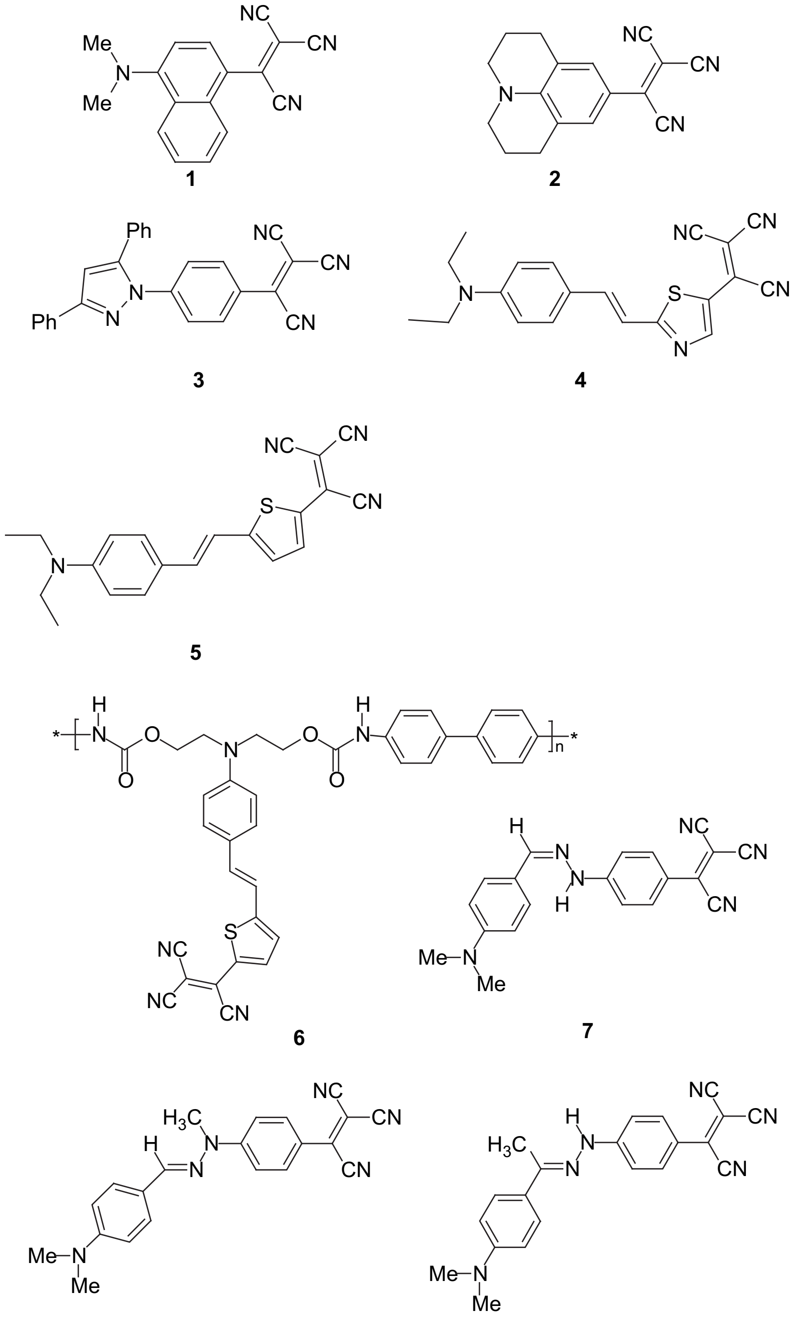
2.1. Synthesis of dyes

The new chromospheres **11** were prepared by direct tricyanovinylation of hydrazones and this was achieved by mixing together the appropriate hydrazones **10** and tetracyanoethylene

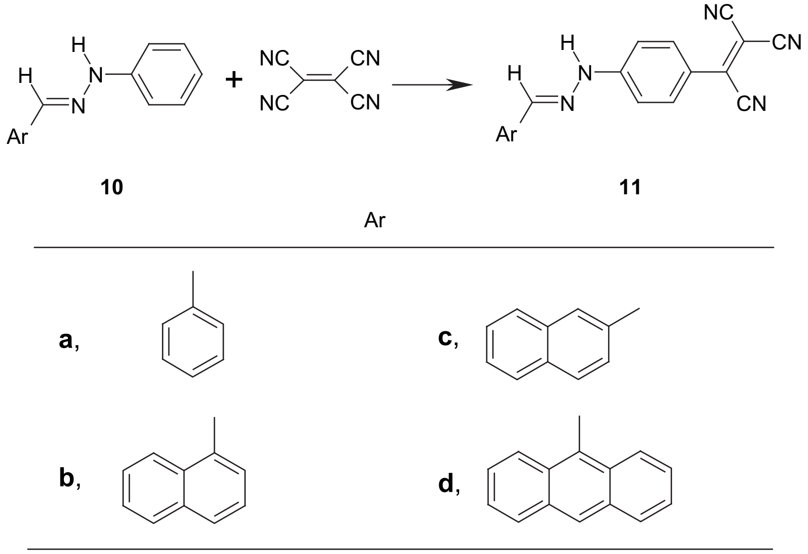
---

* Corresponding author. Tel.: +966 2 695 2293; fax: +966 2 695 2292.
E-mail address: aasiri2@kaau.edu.sa (A.M. Asiri).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.08.014



Scheme 1.



Scheme 1 (*continued*).

(TCNE), as shown in Scheme 1. All the prepared chromospheres were obtained as dark violet solids. The IR spectra of these new dyes exhibited three important absorption bands; the first band centered near 3200 cm^{-1} for the νNH absorption. The second band is a sharp absorption band in the region of 2215–2210 cm^{-1}, which was attributed to the cyano group absorption. The third is an absorption band in the region of 1609–1604 cm^{-1} ascribed for the C=N absorption. The tricyanovinylation undoubtedly takes place at a position *para* to the hydrazine group as evidenced from the ^{1}H NMR signals for the doublet two hydrogen. The oliefinc hydrogen of the synthesized dyes **11a–d** was located in the region of 8.19–9.13 ppm.

2.2. Electronic absorption properties

The electronic absorption spectra of the new chromospheres are characterized by an intense, low-energy band that is dependent on the nature and the position of the subsistent on the aromatic rings (Table 2). Dye **11a**, which contains no substitution on the phenyl ring, showed absorption band at 523 nm in chloroform. A substitution of phenyl group by 1-naphthyl and 2-naphthyl groups, e.g. dyes **11b** and **11c** generally showed a bathochromic shift of 12 nm compared with the phenyl dye **11a**, in addition to substitution of the phenyl group with 9-anthryl group, e.g. dye **11d** caused a bathochromic shift of 20 nm compared to dye **11a** (Table 1).

2.3. Solvatochromism

The dyes were measured in various solvents having different polarity. Generally increasing the solvent polarity gave a bathochromic shift of the maximum absorption bands of dyes **11a–d**. In non-polar solvents for instance in ether dye **11d** showed the most solvatochromic shift with absorption maxima at 524 nm while in the DMF the maxima is at 593 nm (Table 1). The solvatochromic effect can be estimated from the difference between the absorption maxima in polar and non-polar solvents, e.g. $\Delta\lambda$ (Table 1). Figs. 1–3 showed the visible absorption spectra of tricyanovinyl hydrazone dyes **11b–d** in various solvents. The solvent's effects can be rationalized on the basis of the dipole formed by charge migration from the nitrogen to the acceptor tricyanovinyl (Scheme 2).

Table 1
The effects of solvents on the absorption maxima of dyes **11a–e** and **12**

Dye no.	λ_{max}							ε_{max}	$\Delta\lambda$
	CH_3COCH_3 20.7[a]	CH_3CN 37.5[a]	CH_3COOH 6.15[a]	$CHCl_3$ 4.8[a]	$(C_2H_3)_2O$ 4.33[a]	$C_6H_5CH_3$ 2.43[a]	$(CH_3)_2NCHO$ 36.7[a]		
11a	525	522	520	523	516	507	558	45 662	51
	333		316	317	315		318	10 564	
11b	529	528	528	535	522	517	570	21 145	53
	353	354	350	354	350	354	359	5568	
11c	529	527	527	535	522	516	570	29 249	54
	340	340	349	342	350	350	354	11 231	
11d	540	535	527	543	524	519	593	21 062	74
	407	405	407	411	405	407	411	9406	

$\lambda = \lambda_{max}$ DMF; λ_{max} toluene.

[a] Dielectric constant.

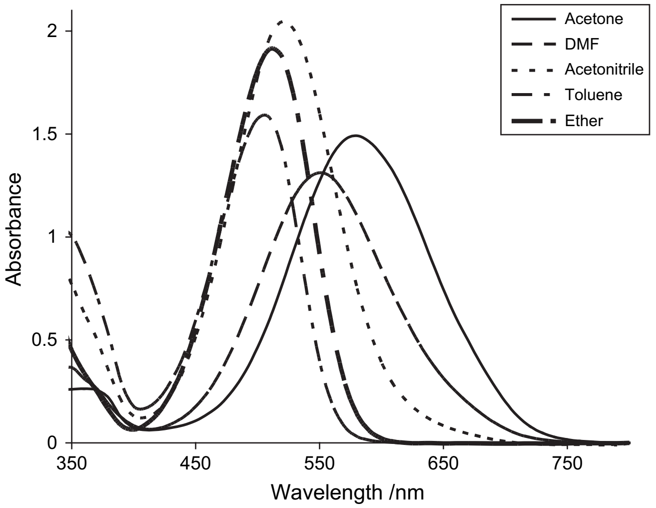


Fig. 1. Effects of solvents on electronic spectra of dye **11b**.

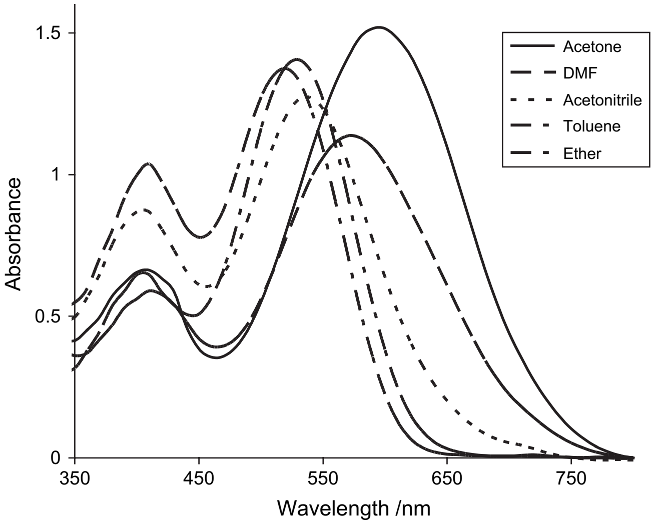


Fig. 3. Effects of solvents on electronic spectra of dye **11d**.

2.4. Thermal stability

The dyes were tested for their stability against the exposure to heat in polymethylmethacrylate matrix at 80 °C. A thin film of poly(methylmethacrylate) (PMMA) doped with dyes **11a–b** was prepared from a solution of the polymer and the dyes in chloroform (dye contents around 3%), and then the film was casted on a glass substrate. After drying at room temperature, the film was further dried under vacuum. The films were pealed from the glass and the absorption spectra were measured before heating, then the films were heated in an oven set at 80 °C, at intervals for which the absorption spectra were measured. The total heating period was 200 min.

Fig. 4 showed the effects of heating for different time intervals on the degradation of some of the dyes prepared. Also the extents of the degradation (calculated from $(A^0 - A_t) \times 100/A^0$) of the dyes **11a–d** are shown in Table 2. It is noteworthy to say that, the parent dye **11a** is the less stable dye on heating at 80 °C since 93% of the dye content was decomposed. On the other hand, dye **11b** is the more stable dye relative to the studied dyes.

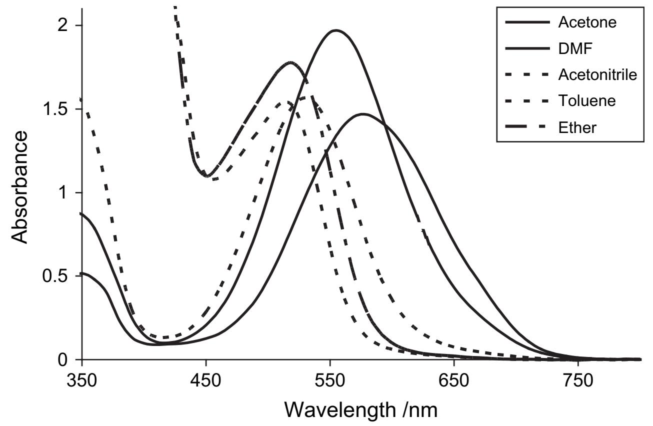


Fig. 2. Effects of solvents on electronic spectra of dye **11c**.

2.5. Aggregation properties

The ability of certain dyes to form associates (aggregates) is called aggregation [13,14]. Until recently, the association of identical molecules of dyes (formation of homogeneous aggregates) was usually investigated using the absorption spectroscopy. The change of the position and the shape of the absorption maxima with the change in the concentration of the dyes are usually appreciable. Table 3 shows the aggregation effects on the absorption properties as the concentrations of the dyes **11a–d** change in DMF. From the data presented in Table 3, it can be seen that decreasing the concentration of the dyes showed a bathochromic shift and hence the formation of new absorption band, due to the formation of dimers of the dye in solution.

3. Experimental

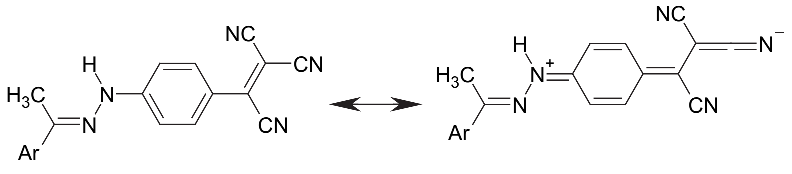
3.1. General

Melting points were recorded on a Thomas–Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer, ^{1}H NMR were recorded in $CDCl_3$ on a Bruker DPX 400 spectrometer using TMS as internal standard. UV–visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

3.2. Synthesis of hydrazones

3.2.1. General procedure

Equimolar quantities of phenylhydrazine and the aldehydes were boiled in ethanol for 3–6 h. The precipitated hydrazones



11 **11'**

Scheme 2.

were filtered, washed and dried. The pure hydrazones were obtained after recrystallization from ethanol. The physical data are summarized in Table 1.

3.2.2. Benzaldehyde phenylhydrazone **11a**

Melting points 150–152 °C, yield 93%, R_f 0.61 (9:1), ^{1}H NMR (CDCl$_3$): δ 6.82 (t, 1H), 7.13 (d, 2H), 7.27 (d, 2H), 7.40–7.67 (m, 5H), 8.17 (s, 1H).

3.2.3. 1-Naphthaldehyde phenylhydrazone **11b**

Melting points 72–74 °C, yield 91 %, R_f 0.74 (8:2), ^{1}H NMR (CDCl$_3$): δ 6.89 (bs, 1H, NH), 7.16–7.82 (m, 7H, naph-H), 7.84 (s, 5H, Ph-H), 8.0 (d, 1H, CH).

3.2.4. 2-Naphthaldehyde phenylhydrazone

Melting points 222–224 °C, yield 88 %, R_f 0.58 (8:2), ^{1}H NMR (CDCl$_3$) δ 7.91 (2H), 7.69 (2H), 7.26 (2H), 7.07 (2H), 6.85 (1H), 2.16 (3H), 9.5 (1H, NH).

3.2.5. Anthracene-9-carbaldehyde phenylhydrazone

Melting points 199–202 °C, yield 21 %, R_f 0.35 (9:1), ^{1}H NMR (CDCl$_3$): δ 7.31–7.63 (m, 14H, Ph-H), 9.13 (s, 1H, CH=N).

3.3. Synthesis of tricyanovinyl derivatives **11a–e**

3.3.1. General procedure for the reaction of TCNE with hydrazones

A solution of aromatic amine (10 mmol) and TCNE in DMF (25 ml) was stirred at 60–90 °C for 8 h. The solvent was removed and the residual solid was collected and recrystallized from toluene–chloroform mixture.

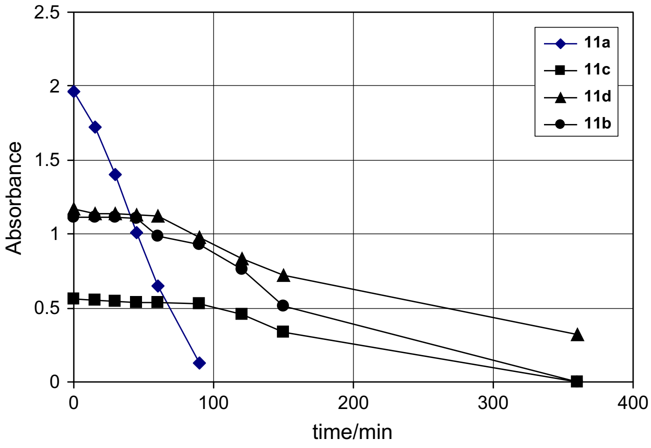


Fig. 4. Thermal stability of dyes **11a–d**.

3.3.2. 2-{4-[2-Benzylidenehydrazino]phenyl}ethylene-1,1,2-tricarbonitrile **11a**

Melting points 285–288 °C, yield 76%, R_f 0.13 (petroleum ether:ethyl acetate, 8:2); UV–vis (acetone): λ_{max} (nm) 525, 333; IR ν (cm^{-1}): 3272 (sec. NH), 2211 (CN), 1613 (C=N), 1345 (C–N); ^{1}H NMR (CDCl$_3$): δ 7.42–8.13 (m, 11H, Ar-H + CH + NH + Ph-H). ^{13}C NMR (CDCl$_3$): δ 111.85, 113.31, 114.14, 115.65, 117.5, 121.41, 127.14, 128.89, 130.21, 132.96, 136.54, 137.1 144.19, 162.55.

3.3.3. 2-{4-[2-(1-Naphthylmethylene)hydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile **11b**

Melting points 275–277 °C, yield 93%, R_f 0.32 (6:4); UV–vis (acetone): λ_{max} (nm) 529, 353; IR ν (cm^{-1}): 3271 (sec. NH), 2213 (C–N), 1655 (C=N); ^{1}H NMR (CDCl$_3$): δ 7.22–8.0 (m, 13H, naph-H + Ph-H + CH + NH).

3.3.4. 2-{4-[2-(2-Naphthylmethylene)hydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile **11c**

Melting points > 300 °C, yield 89%, R_f 0.29 (petroleum ether:ethyl acetate 8:2); UV–vis (acetone): λ_{max} (nm) 529, 340; IR ν (cm^{-1}): 3270 (sec. NH), 2210 (CN), 1628 (C=N), 1328 (C–N); ^{1}H NMR (CDCl$_3$): δ 6.89 (bs, 1H, NH), 7.22–8.84 (m, 11H, naph-H + Ph-H), 8.0 (d, 1H, CH). ^{13}C NMR (CDCl$_3$): δ 111.85, 112.81, 113.39, 115.65, 117.5, 120.21, 122.86, 123.0, 123.57, 126.52, 127.13, 127.98, 128.10, 128.57, 129.35, 136.02, 137.21, 139.10, 144.29, 162.5.

3.3.5. 2-{4-[2-(9-Anthrylmethylene)hydrazino]phenyl}-ethylene-1,1,2-tricarbonitrile **11d**

Melting points 248–250 °C, yield 64%, R_f 0.13 (petroleum ether:ethyl acetate 8:2); UV–vis (acetone): λ_{max} (nm) 540, 407; IR ν (cm^{-1}): 3281 (NH), 2215 (CN), 1661 (C=N),

Table 2
The extent of decomposition of dyes **11a–b** and **12**

Compound no.	% Degradation
11a	93
11b	54
11c	64
11d	72

Table 3
The effects of concentration on the absorption of dye **11c**

Dye no.	Concentration							
	1×10^{-4}		4×10^{-5}		2×10^{-5}		1×10^{-5}	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
11a	558	45 662	564	45702.5	569	47 970	571	48 330
11b	570	31 777	580	33682.5	583	34 975	583	33 870
11c	570	29 249	577	31 090	579	31 725	581	31 970
11d	579	18 842	602	12 640	602	20 670	603	20 000

1339 (C–N); ^{1}H NMR ($CDCl_3$): δ 7.19–9.10 (m, 14H, Ar-H + Ph-H + CH + NH).

Acknowledgments

We thank King Abdul Aziz City of Science and Technology (KACST) for their financial support to N. Fatani by the grant No. PG-67-8.

References

[1] Boyd RW. Nonlinear optics. New York: Academic Press; 1992.
[2] Marder SR, Sohn JE, Stucky GD. Materials for nonlinear optics: chemical perspectives. In: ACS symposium series 455. Washington, DC: ACS; 1991.
[3] Marder S, Gorman CB, Tiemann BG, Cheng LT. J Am Chem Soc 1993;115:3006.
[4] Wang Y-K, Shu C-F, Breitung EM, McMahon J. J Mater Chem 1999;9:1449 and references therein.
[5] Williams DJ. Angew Chem Int Ed Engl 1984;23:690.
[6] Singer KD, Sohn JE, King LA, Gordon HM, Katz HE, Dirk CW. J Opt Soc Am B 1989;6:1339.
[7] Shu C-F, Wang Y-K. J Mater Chem 1998;8:833.
[8] Asiri AM. Appl Organometal Chem 2001;15:907.
[9] Asiri AM. J Saudi Chem Soc 2001;5:193.
[10] Asiri AM. J Saudi Chem Soc 2003;7:77.
[11] Asiri AM, Ismail IMI, Al-Amry KA, Fatani NA. Dyes Pigments 2005;67:111.
[12] Asiri AM, Ismail IMI, Al-Amry KA, Fatani NA. Dyes Pigments 2006; 71:102–7.
[13] James TH. The theory of the photographic process. 4th ed., London; 1977.
[14] Tatikolov AS, Ponterini G, Krasnaya ZhA. Int J Photoenerg 2000;2:17.