Synthesis and photoconductivity study of new bisazos containing hydrazone groups

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Abstract

Based on molecular design, three high photosensitive bisazos containing hydrazone groups were synthesized by reacting bis(2″-hydroxy-3″-chlorocarbonyl)-4,4′-biphenyl bisazo with various amines containing hydrazone groups. Characterization was made by elementary analysis, melting point, IR spectra and Raman spectra. The xerographic properties have been investigated in bilayer photoreceptor devices and all bisazos exhibit high photosensitivity. Study of spectral responses of the three bisazos containing hydrazone groups showed that the best photoconductivity was observed at about 690 nm and the maximum of absorption spectra was recorded at ~570 nm.   © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

The photoconductivity of azo compounds was first recognized in 1969 by Rau [1], who recorded strong photo-stimulated surface conductance with thin layers of 1-phebtlazo-2-naphthol. Several years later, Champ and Shattuck [2] reported that a commercially available bisazo pigment, Chlorodiane Blue [4,4′-bis(1″-azo-2″-hydroxy-3″-naphthanilide)-3,3′-dichlorobiphenyl], could photogenerate electron–hole (e–h) pairs in bilayer xerographic devices. The disclosure of the photoconductivity of azo compounds, as well as the ease of the synthesis, has obviously initiated an intense subsequent effort in the photoreceptor industry, where thousands of azo pigments of a variety of structures have been synthesized and screened for xerographic photoreceptor applications. But now computers and xerographic techniques developed so quickly that these xerographic photoreceptors hardly match their requirements and higher photosensitivity is further required. Many researchers are still attracted to find higher photosensitive materials.

Based on these studies of azo compounds, especially the photogeneration mechanism study of Umeda et al. [3] whose experiments showed that the photocarrier generation site lies on the molecular CGM/CTM (Charge Generation Materials/Charge Transporting Materials) interface formed by the

penetration of CTM from the CTL (Charge Transporting Layer) during the coating operation, we wondered whether these compounds, which had integrated the charge transporting group such as hydrazone group with the charge generation group into one molecular, have higher photosensitivity. With this in mind, we focused on the molecular design of azo compounds containing charge transporting groups for obtaining high photoconductivity.

Here we reported the syntheses of three new high photosensitive bisazos containing hydrazone groups (R^1, R^2 = H, phenyl, naphthalenyl) by reacting 4,4′-bis(1″-azo-2″-hydroxy-3″-chlorocarbonylnaphthalene)biphenyl with various amines containing hydrazone groups Fig. 1. The xerographic sensitivities of these bisazos were examined in bilayer xerographic devices using a common hole-transporting layer.

(X)=H, (m-)NO_2, (o-)CH_3, (p-)CH_3, (p-)Cl, (p)—CH=N—N$\langle^{R^1}_{R^2}$
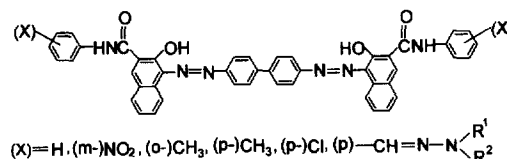
	R^1	R^2
Bisazo-1	phenyl	H
Bisazo-2	phenyl	phenyl
Bisazo-3	phenyl	naphthalenyl

Fig. 1. Structures of bisazos.

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2. Experimental details

2.1. Materials and equipment

Phenylhydrazine, N,N'-diphenylamine, N-phenyl-2-naphthamine, p-nitro-benzaldehyde, benzidine and 3-hydroxy-2-naphthalenecarboxylic acid were purchased in analytical grade. 1,1-Diphenylhydrazine and 1-phenyl-1-(2'-naphthalenyl)hydrazine were synthesized according to Ref. [4].

Elemental analyses were performed by Perkin-Elmer 240C Elemental Analyzer. Melting points were taken on a capillary melting point apparatus (Thomas Hoover) and were uncorrected. Infrared spectra were determined on NIC-5DX Fourier Transform Infrared Spectrometer and absorption spectra were recorded on DU-50 Spectrophotometer. Photoconductive properties were studied using a model GDT-II photoconductivity-measuring device.

2.2. Synthesis of amines containing hydrazone groups

Amine-1: The reaction scheme is noted in Scheme 1. Around 0.1 mol of phenylhydrazine was dissolved in alcohol and quantitative acetic acid was added. Under room temperature, to the solution 0.1 mol of p-nitro-phenylaldehyde solved in alcohol was added and the reaction was kept for 5 h. After filtration the crude phenylhydrazone (a1) (Cald for $C_{13}H_{11}N_3O_2$: C 64.72, H 4.60, N 17.42; Found: C 64.12, H 4.55, N 17.11) was recrystallized from alcohol. The red phenylhydrazone (a1), 230 g of stannic chloride and 800 ml of hydrochloric acid were refluxed at room temperature for 24 h. After filtration the red filtrate was alkalified using hydroxy natriate solution and the precipitate was separated. The amine containing phenylhydrazone groups (b1) was recrystallized from alcohol in yellow crystal (Anal. Cald for $C_{13}H_{13}N_3$ (b1): C 71.91, H 4.76, N 13.24; Found: C 69.87, H 4.77, N 12.98).

Another two amines were synthesized analously. Amine-2: Using 1,1-diphenylhydrazine instead of the phenylhydrazine. Anal. Cald for $C_{19}H_{15}N_3O_2$ (a2): C 71.91, H 4.76, N 13.24; Found: C 71.86, H 4.31, N 13.22. Cald for $C_{19}H_{17}N_3$ (b2): C 79.41, H 5.96, N 14.62; Found: C 78.13, H 5.02, N 14.10. Amine-3: The phenylhydrazine was substituted by 1-phenyl-1-(2'-naphthalenyl)hydrazine. Anal. Cald for $C_{23}H_{17}N_3O_2$ (a3): C 75.19, H 4.66, N 11.44; Found: C 75.12, H 4.48, N 11.32. Cald for $C_{23}H_{19}N_3$ (b3): C 81.87, H 5.68, N 12.45; Found: C 80.98, H 5.55, N 12.01.

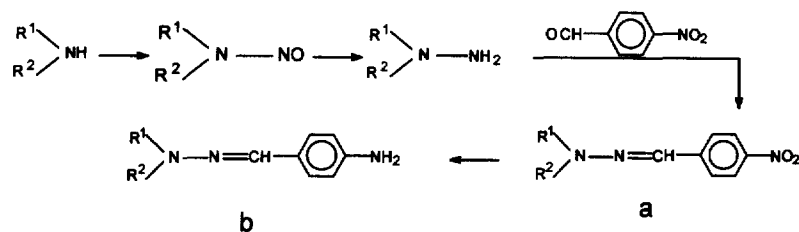### 2.3. Synthesis of bisazos containing hydrazone groups

Bisazo-1: As noted in Scheme 2, 19 g of 4,4'-biamino biphenyl was dissolved in 80 ml of 36% hydrochloric acid and approximately 900 ml of water in a three-necked reaction flask. After being cooled to 2°C, 50 ml of the nitrous natriate solution (15 g nitrous natriate and 50 ml of water) was dropped in. At lower than 5°C, the reaction was kept for another 1 h. Then the solution was filtered. Under room temperature, the filtrate was added to the 3-hydroxy-2-naphthalenecarboxylic acid solution (500 ml of water, 40 g of 3-hydroxy-2-naphthalenecarboxylic acid, 34 g of hydroxy natriate and 30 ml of acetic acid). The whole solution was stirred for 1 h and then kept over night. Purplish red azo (c) (Cald for $C_{34}H_{22}N_4O_6$: C 70.10, H 3.81, N 9.62; Found: C 69.98, H 3.78, N 9.54) was filtered out, washed with 500 ml of water, 1000 ml of alcohol and a great deal of water and then dried in 80°C. The dried azo (c), 500 ml of chlorobenzene, 80 ml of dichloro sulfone and some N,N'-dimethyl formamide (DMF) were placed in a flask and heated to reflux for 1 h. After filtration azo (d) (Cald for $C_{34}H_{20}N_4O_4Cl_2$: C 65.92, H 3.25, N 9.04; Found: C 64.88, H 3.30, N 8.76) was washed with tetrachloromethane and dried in 110°C. 12.39 G of the dried azo (d), 500 ml of chlorobenzene, a little pyridine and 8.45 g of Amine-1 (b1) were placed in a flask and heated to reflux for 1 h. After filtration the blue-violet product was washed with alcohol, water and DMF successively. Anal. Cald for $C_{60}H_{44}N_{10}O_4$: C 74.35, H 4.58, N 14.46; Found: C 73.91, H 4.13, N 13.61.

Bisazo-2: 12.39 g the dried azo (d), 500 ml of chlorobenzene, a little pyridine and 11.49 g of Amine-2 (b2) were placed in a flask and heated to reflux for 1 h. After filtration the blue-violet product was washed with alcohol, water and DMF successively. Anal. Cald for $C_{72}H_{52}N_{10}O_4$: C 77.11, H 4.68, N 12.50; Found: C 76.97, H 4.69, N 12.41.

Bisazo-3: 12.39 g of the dried azo (d), 500 ml of chlorobenzene, a little pyridine and 13.50 g of Amine-3 (b3) were placed in a flask and heated to reflux for 1 h. After filtration the blue-violet product was washed with alcohol, water and DMF successively. Anal. Cald for $C_{80}H_{56}N_{10}O_4$: C 78.66, H 4.62, N 11.47; Found: C 76.54, H 4.78, N 10.98.

2.4. Preparation of bilayer photoreceptor devices and measurement of photoconductivity

The xerographic properties of the synthesized bisazos were studied in bilayer devices (Fig. 2a). Onto the cleaned alu-

Scheme 1. Reaction scheme of amines containing hydrazone groups.
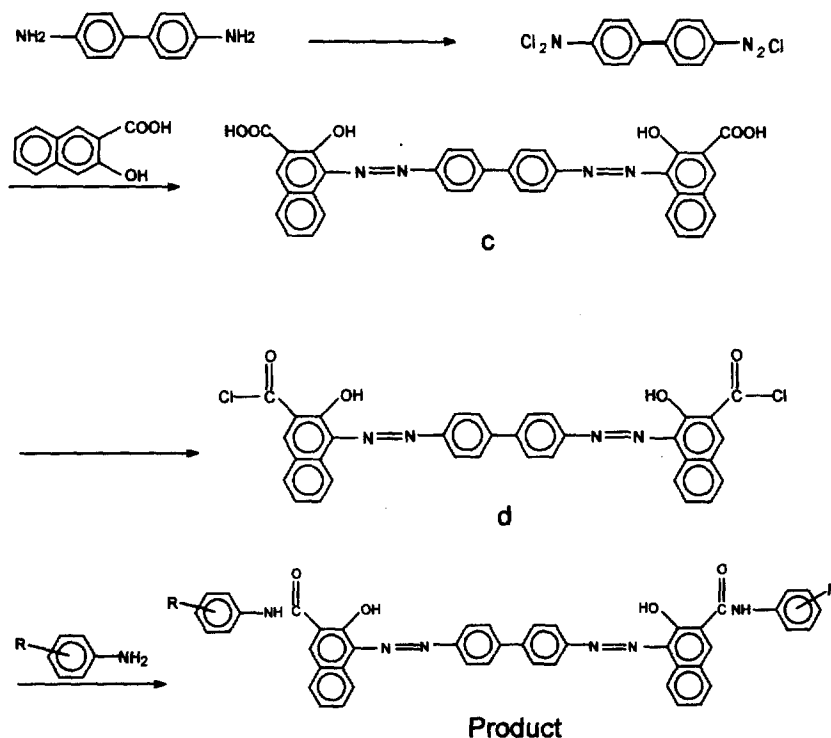
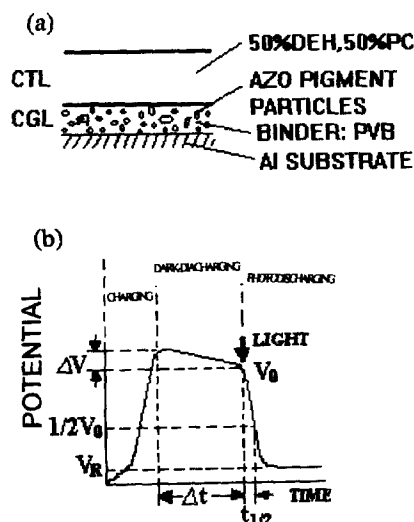Scheme 2. Reaction scheme of bisazos containing hydrazone groups.

Fig. 2. (a) A cross-section of a bilayer xerographic device; (b) Schematics of the photoinduced discharge curve.

minum substrate the CGL (Charge Generation Layer) was made by coating the CGM solution (10 ml cyclohexanone and 10 ml butanone solvent of 0.1 g poly(vinylbutyral) (PVB) and 0.1 g bisazo) and dried at 70°C for 4 h. The thickness was ~ 0.7 μm, estimated from ELEKTKO-PHY-SIK MINITEST 2000 thin-film-measuring apparatus. Then the CTL was obtained by coating the CTM solution (10 ml 1,2-dichloroethane and 10 ml chloroform solvent of 0.2 g N,N'-diethyl-p-phenylaldehyde biphenylhydrazone (DEH) and 0.2 g polycarbonate (PC)) with the thickness of ~ 23

μm. The resulting bilayer device was dried at 80°C for more than 12 h.

Xerographic measurements were made on a GDT-II model photoconductivity measuring device, using a 5-W, 24-V incandescent lamp as a light source. In the measurement, the surface of the bilayer device was negatively charged in the dark, as soon as the lamp was lit, charge carriers were generated in the CGL and injected into the CTL. During the exposure, the surface potential decreased, then the photoinduced discharge curve (PIDC) of the device was recorded [5]. From PIDC (Fig. 2b), we obtained $\Delta V_1\%$ (the percentage of potential discharge after 1 s of exposure), $t_{1/2}$ (the time from the original potential to half under exposure), and $E_{1/2}$ (the product of $t_{1/2}$ multiplied by I (intensity of light)). The $E_{1/2}$ can indicate photosensitivity. The smaller the $E_{1/2}$, the higher the photosensitivity.

3. Results and discussion

3.1. Physical properties, infrared spectra and absorption spectra of bisazos

Table 1 shows the physical properties of the product bisazos. All bisazos containing hydrazone groups are blue-violet solids that do not melt even at 300°C. As indicated in Table 1, they exhibit characteristic C=O stretching at ~ 1740 cm⁻¹ and characteristic C=N stretching at ~ 1610 cm⁻¹ in the infrared spectra, while in Raman spectra N=N stretching is

Table 1
Physical properties, infrared data and Raman data of bisazos

Product azo	R¹	R²	M.p. (°C)	Infrared spectra (cm⁻¹)		Raman spectra (cm⁻¹)	
				C=O	C=N	N=N	Intensity ratio [a]
1	Phenyl	H	>300	1739	1609	1593.11	1.6/1
2	Phenyl	Phenyl	>300	1739	1607	1592.61	1.6/1
3	Phenyl	Naphthalenyl	>300	1740	1607	1592.36	1.6/1

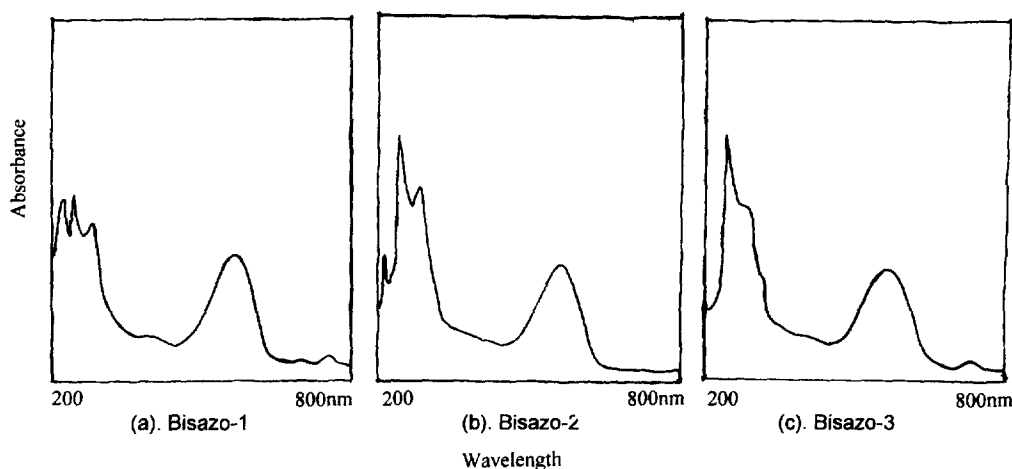[a] The ratio of N=N Raman intensity to the aromatic Raman intensity at ~1170 cm⁻¹.

Fig. 3. Absorption spectra of bisazos in CHCl₃.

recorded at ~1590 cm⁻¹. In Raman spectra, another feature which should be given attention is that the ratio of N=N Raman intensity to the aromatic Raman intensity at ~1170 cm⁻¹ is about 2 to 1 as compared with common bisazos without hydrazone groups, whose ratio is from about 3 to 1 to about 4 to 1. It can be explained by the introduction of more aromatic cycles in product bisazos through the hydrazone moiety.

The solubility of product bisazos in organic solvents are very poor while they are soluble in 98% sulfuric acid. Fig. 3, which depicts typical absorption spectra of these bisazos in CHCl₃ (10^{-5} g l⁻¹), shows that the absorption covers most of the visible region (450–650 nm). Absorption spectra of various bisazos are similar and the max is unchanged at ~570 nm. It indicates that the max is not sensitive to the electronic effects exerted by the various hydrazone groups. Very similar results have been obtained for common photosensitive bisazos without hydrazone groups [6,7].

3.2. Xerographic properties of bisazos containing hydrazone groups

The xerographic properties of all three bisazos containing hydrazone groups were examined in bilayer xerographic devices consisting of CGLs of various bisazos and a CTL (Fig. 2a). The CTL contains 50% by weight of a hole-trans-

porting molecule, DEH, in polycarbonate matrix with ~23 μm thickness while the CGL is ~0.7 μm and the concentration of bisazos in the CGL is 50% by weight. Thus, the geometry of all xerographic devices examined is held to be the same, enabling the xerographic properties of various bisazos to be compared. The photoconductive data are showed in Table 2. Bisazo-1 (R¹ = phenyl, R² = H) exhibited a value of $t_{1/2}$ as low as 0.313 s and a low $E_{1/2}$, 9.375 lux s, as well as a low dark decaying value, 51.2 V s⁻¹, which indicate good photoconductivity. It was reported [3,8–11] that hole-transporting molecules actually penetrate into the CGL during the CTL overcoating step and that the sites for the photogeneration of e–h pairs are at the boundaries of excitons that are residing on the surfaces of pigment particles in the CGL. In other words, e–h pairs are actually generated in the 'bulk' of the CGL between the exciton of the pigment and the hole-transporting molecule. It was also reported [10] that, for a given azo pigment, one may be able to increase its sensitivity if its effective surface area for photogeneration is increased. Bisazo-1 (R¹ = phenyl, R² = H) contained two phenylhydrazone groups in the molecule. That just shows that the e–h pairs can be generated at all the surfaces of pigment particles of Bisazo-1 in the CGL, resulting in good photoconductivity of bisazo pigment. However, other studies of photosensitive bisazo pigments showed that the substituents in the anilide ring of naphthanilide had effect on the

Table 2
Xerographic data of bisazos

Wavelength (nm)	Surface potential (V)	Dark decaying (V s^{-1})	V_R (V)	ΔV (%)	$t_{1/2}$ (s)	$E_{1/2}$ (lux s)
(a) Bisazo-1 ($R^1 = phenyl$, $R^2 = H$)						
570	906	49.6	164	71.41	0.375	11.25
605	937	51.2	171	72.38	0.313	9.38
679	992	56.0	171	73.59	0.313	9.38
762	890	33.6	171	66.25	0.500	15.00
772	937	23.2	164	40.92	1.250	37.50
(b) Bisazo-2 ($R^1 = R^2 = phenyl$)						
570	937	33.6	171	52.00	0.928	28.13
605	890	32.8	164	53.72	0.875	26.25
679	914	36.9	179	59.15	0.625	18.75
762	937	26.4	195	32.95	2.000	60.00
772	898	23.2	195	15.97	3.625	108.75
(c) Bisazo-3 ($R^1 = phenyl$, $R^2 = naphthalenyl$)						
570	976	43.2	156	64.91	0.562	16.88
605	937	40.0	148	63.81	0.625	18.75
679	890	38.4	140	65.15	0.563	16.88
762	1000	32.8	203	47.60	1.063	31.88
772	992	28.0	179	20.13	2.500	75.00

photosensitivity of bisazo pigments [6,7,9]. For the bisazos of which the central aromatic moiety is benzine, neither a electron-releasing group, such as methoxy, nor a electron-withdrawing group, such as nitro, promotes high xerographic sensitivity. Bisazo-1 uses benzine as central aromatic moiety and hydrazone groups are electrons donors, leading to a limit on the increase of the photosensitivity. As data (Table 2a) showed, interaction of both effects—an increase in photocarrier generation sites and a withdrawal of electrons by hydrazone groups—on Bisazo-1 causes its high photoconductivity.

Similar results were obtained for Bisazo-2 ($R^1 = R^2 = phenyl$) (Table 2b) and Bisazo-3 ($R^1 = phenyl$, $R^2 = naphthalenyl$) (Table 2a) and both of them exhibited a good photosensitivity.

3.3. Spectral response

The spectral responses were obtained by analyzing the xerographic data at various wavelengths. The absorption spectra of product bisazos in the solvent of $CHCl_3$ and plots of the spectral sensitivities are given in Figs. 3 and 4. Our data show a strange phenomenon that the spectral responses are not parallel to their absorption spectra. The three bisazos have higher photosensitivity from 570 nm to 705 nm and the best is observed at about 690 nm but the maximum of the spectral absorption is recorded at ~ 570 nm though there also exhibits absorption at 690 nm. That is to say that the highest photogeneration efficiency is not obtained at the maximum of absorption spectra. Wondering whether the absorption spectra shift to red and near-IR in solid, the absorption spectra of solid-Bisazo films (Fig. 5) were also determined. The
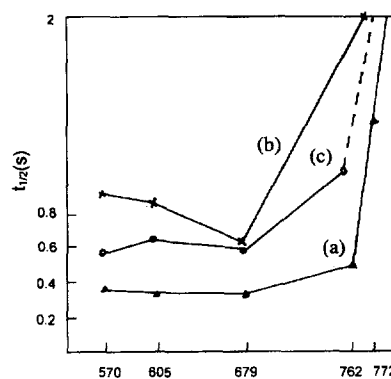
Fig. 4. Plots of the spectral sensitivity.

solid-Bisazo films were obtained by coating CGM solution on cleaned glasses. Compared to these, we also recorded the absorption spectra of the solid-Bisazo films with a CTL on it (CTM solution was coated on the solid-Bisazo films and the solvent was moved). Though the absorption spectra of the solid-Bisazo films shifted a little to red as compared with those obtained in $CHCl_3$, the maximum is observed still at ~ 570 nm but not at about 690 nm. It means that this unconformity between absorption spectra of product bisazos and their spectral sensitivities is caused neither by the solvent effect nor by the effects of charge-transporting materials on CGL. That is to say that the energy of the light at ~ 570 nm is too high for these bisazos that e–h pairs migrate faster and have much more chances for the combination so that the photogeneration efficiency cannot be satisfied. However, the

(a)

(a). Bisazo-1   (b). Bisazo-2   (c). Bisazo-3

Wavelength

(b)

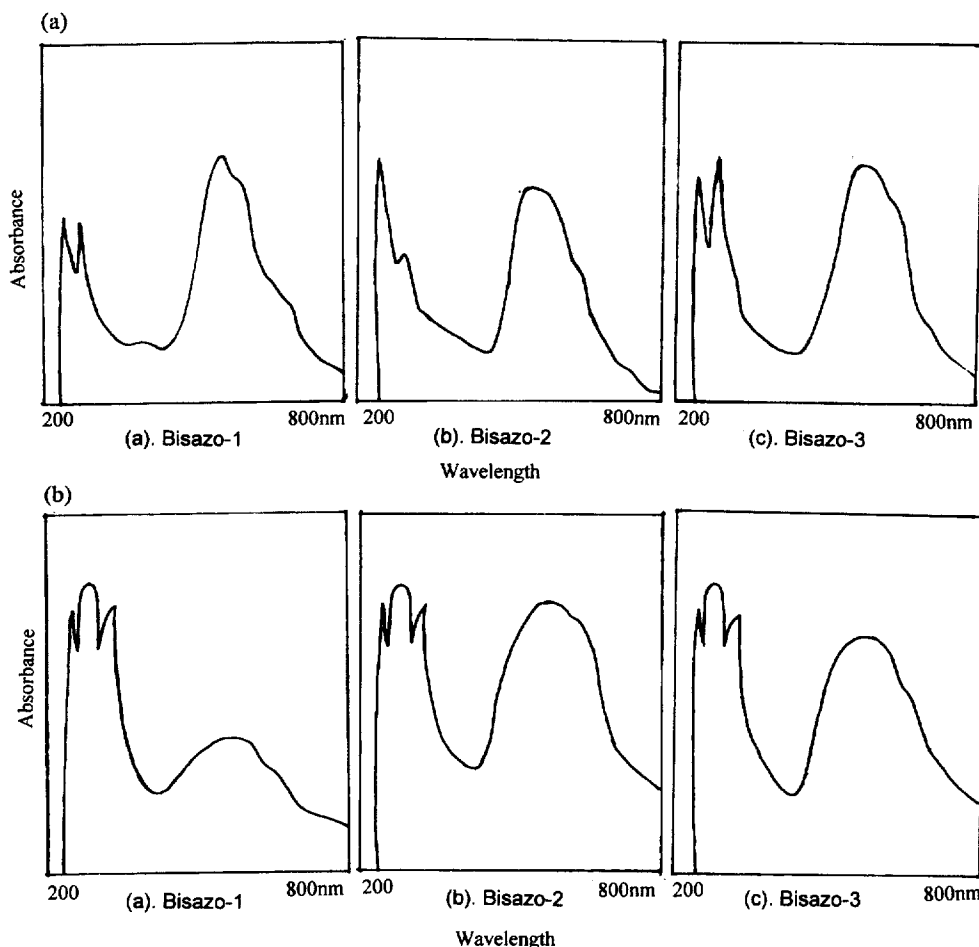(a). Bisazo-1   (b). Bisazo-2   (c). Bisazo-3

Wavelength

Fig. 5. Absorption spectra of solid-Bisazo films on cleaned glasses. (a) Uncoating a CTL on it; (b) Coating a CTL on it.

light of 690 nm has lower energy and just can excite the bisazos to obtain the highest photogeneration efficiency.

4. Conclusions

In this work, three new bisazos containing hydrazone groups were synthesized and characterized. Xerographic measurements show that all three bisazos have high photosensitivity and this coincides with previous photogeneration mechanism study of bisazos. The absorption data show that these bisazos absorb in the visible region. The absorption wavelength of the CGL is red shifted as compared with their $CHCl_3$ solvent, but the maximum at ~ 570 nm is unchanged. Investigation of spectral responses on bisazos containing hydrazone groups showed that the best photosensitivity was found at about 690 nm and the maximum of absorption spectra was recorded at ~ 570 nm.

Acknowledgements

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