Arabian Journal of Chemistry (2009) **2**, 13–17

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Photochromic properties of 1,3,3-trimethylspiro-[indoline-2,3′-[3H]naphtho[2,1-b][1,4]oxazine] doped in PMMA and epoxy resin thin films

Abdullah M. Asiri [a,*], **Abood A. Bahajaj** [b], **Abdullah G. Al-Sehemi** [c], **Amerah M. Alsoliemy** [a]

[a] *Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah 21413, P.O. Box 80203, Saudi Arabia*
[b] *Chemistry Department, Faculty of Science, Hadhramout University of Science and Technology, P.O. Box 50512, Mukalla, Republic of Yemen*
[c] *Chemistry Department, Faculty of Science, King Khalid University, Abha, Saudi Arabia*

Received 10 July 2009; accepted 10 July 2009
Available online 6 August 2009

KEYWORDS

Spirooxazine;
Photochromism;
Polymer film;
Epoxy resin;
Photobleaching;
Photocoloration;
Kinetics;
Fatigue resistance

Abstract Irradiation of colorless 1,3,3-trimethylspiro[indoline-2,3′-[3H]naphtho[2,1-b][1,4]oxazine] SO doped in PMMA and epoxy resin with UV light (at 366 nm) results in the formation of an intensely colored zwitterionic photomerocyanine **PMC**. The reverse reaction was photochemically induced by irradiation with white light. Photocoloration and photobleaching reactions follow a first-order rate equation. It was found that photocoloration rate constant of **SO** in PMMA film is greater than that in epoxy resin. On the other hand, the photobleaching rate constant is almost identical in both matrices. Spirooxazine doped in epoxy resin shows much better fatigue resistance than that doped in PMMA.

1. Introduction

The IUPAC definition of photochromism is "a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra" (Bouas-Laurent and Durr, 2001). This transformation is usually induced by electromagnetic radiation in the ultraviolet wavelengths range, where a deeply colored specie B is generated from the uncolored or weakly colored specie A. The reverse reaction (bleaching) could be accomplished by thermal and/or photochemical effects. Various organic systems were found to show potential thermal and photochromic properties.

---

* Corresponding author.
E-mail address: aasiri2@kau.edu.sa (A.M. Asiri).

1878-5352 © 2009 King Saud University. All rights reserved. Peer-review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2009.07.009

Production and hosting by Elsevier

The widest and most important groups of such systems are those based on the reversible light-induced hexatriene/cyclohexadiene pericyclic reactions such as in fulgides (Yokoyama, 2000), diarylethenes (Hu et al., 2006), spiropyrans (Ubukata et al., 2007) and spirooxazines (Berkovic et al., 2000).

Spiropyrans and spirooxazines are much closed compounds in their photochromism. The photochromism of these colorless or weakly colored spiro compounds **SO** arises from the photo cleavage of the C–O spiro bond upon the UV irradiation. Such a cleavage results in the formation of an intensely colored zwitterionic open form known as photomerocyanine **PMC** which absorbs in the visible region. The reverse reaction (fading) proceeds thermally or under irradiation with white light. The immediate cleavage of the spiro carbon–oxygen bond upon UV irradiation results in the formation of a highly unstable intermediate cis–cisoid isomer (Glebov et al., 2006). This intermediate isomerizes to the more stable zwitterionic open form which in turn undergoes subsequent geometrical isomerism to give several quinoidal forms (Scheme 1).

Time-resolved absorption spectroscopy (Tamai and Miyasaka, 2000) and NMR studies (Berthet et al., 2006) reveal the coexistence of four geometrical isomers (TTC, CTT, CTC, and TTT) which are in thermal equilibrium at room temperature. Takahashi et al. (1988) has found that TTC isomer (trans–trans–cis isomer) is more stable in aliphatic hydrocarbons, while CTT and CTC are more stable in polar solvents. The recent interest in the photochromism of spiropyrans and spirooxazines is due to their fast coloration rate under UV irradiation, fast thermal fading, and excellent fatigue resistance. These criteria are indispensable for applications to optoelectronic devices, such as memories and switches, and nonlinear optics (Berkovic et al., 2000). Spiropyrans and spirooxazines have been recently used as nucleic acid hybridization probes (Guo et al., 2005).

2. Experimental

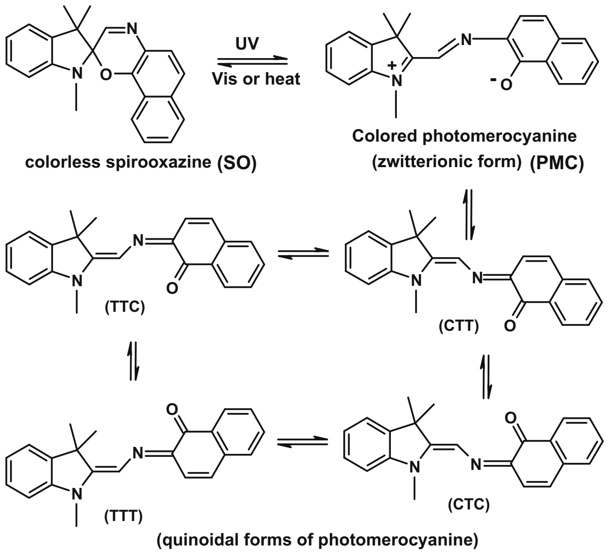
1,3,3-Trimethylspiro[indoline-2,3′-[3H]naphtho[2,1-b][1,4]oxazine] was prepared according to the general procedure reported previously (Tan and Chen, 2005). The films were prepared as follows: 2.23 g of PMMA (Aldrich product) was dissolved in 20 mL of chloroform and warmed to ensure complete dissolution. The solution was then cooled. Two blank films were prepared by taking 0.3 mL of the above-mentioned solution and spread over a quartz plate. These plates were covered and left overnight in the dark. About 1 mg of spirooxazine **SO** was added to the remaining solution and mixed well. Then 0.3 mL of the mixture was added to each of the quartz plates which were then covered and left overnight in the dark. The epoxy resin film was prepared as follows: 10 mL of epoxy resin (diglycidyl ether of bisphenol A) and 1 mL of diamine hardener were added and mixed thoroughly to ensure complete dissolution. Two blank films were prepared by taking 0.3 mL of the above-mentioned solution and spread over each quartz plate. To the remaining mixture, a solution of 2 mg of **SO** dissolved in 15 mL of chloroform was added and mixed. Then 0.3 mL of the mixture was added to each of the quartz plates which were then covered and left overnight in the dark.

Ultraviolet and visible spectra were measured using Perkin–Elmer lambda EZ210 spectrophotometer. Photocoloration (at 366 nm) was carried out using Blak–Ray lamp model UVL-56 and photobleaching was carried out using a tungsten filament lamp. Two fresh films of **SO** in PMMA and epoxy resin were annealed for 3 h at 75 °C. The fatigue resistant of the annealed **SO** doped PMMA and epoxy resin films was carried out by photocoloring and photobleaching **SO**, consecutively for 9 cycles. In each cycle, the film was irradiated with UV lamp for 30 min and photobleached with white light for 20 min.

3. Results and discussion

3.1. Photocoloration

1,3,3-Trimethylspiro[indoline-2,3′-[3H]naphtho[2,1-b][1,4]oxazine] **SO** doped in PMMA polymer film was irradiated with mercury lamp (366 nm) and the photocoloration process was followed spectrophoto-metrically by monitoring the absorption of the intense purple colored open form



Scheme 1 Photochemical reactions of spiroindolinenaphthooxazine.

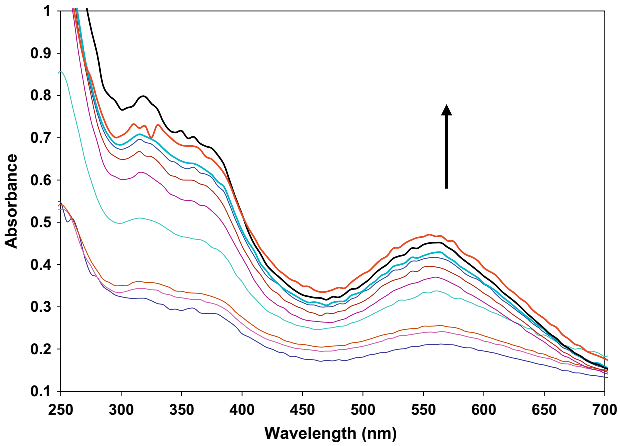


Figure 1 Photocoloration of SO doped in PMMA polymer film. The arrow direction indicates the increase of absorbance with increasing exposure time (s), 0; 20; 40; 100; 120; 140; 200; 240; 280; 340; 520; 560; 600.

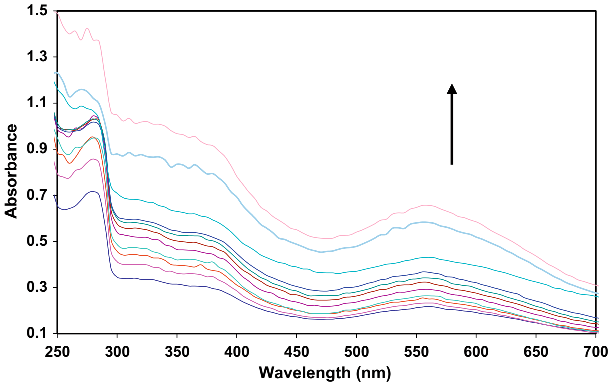


Figure 2 Photocoloration of SO doped in epoxy resin polymer film. The arrow direction indicates the increase of absorbance with increasing exposure time (s), 0; 20; 40; 60; 100; 140; 180; 220; 300; 480; 540.

photomerocyanine **PMC** at its $\lambda_{\max}$ (555 nm) at intervals of time as shown in Fig. 1.

The film of **SO** doped in an epoxy resin was similarly treated. The resulting **PMC** has its $\lambda_{\max}$ at 560 nm (Fig. 2). The observed red shift of the absorption band of **PMC** in epoxy resin compared to that in PMMA film is a result of increasing the polarity of the medium. It is well known that this absorption band shows a bathochromic shift as the solvent polarity increases (Chu, 1983; Shin et al., 2000; Kopelman et al., 2008; Lafuma et al., 2003) which represents a positive solvatochromism.

Kinetics of spiropyrans and spirooxazines have been studied in solutions (Chu, 1983; Shin et al., 2000; Kopelman et al., 2008; Lafuma et al., 2003), in phospholipid bilayers (Wohl and Kuciauskas, 2005), in solid polymer matrices (Fua et al., 2007; Lin and Chiu, 2003) and in the crystalline state (Bénard and Yu, 2000). They show, in general, first-order rate dependence, especially in solutions (Shin et al., 2000; Kopelman et al., 2008). However, in polymer matrices deviation from the simple first-order reaction was observed. Such nonlinearity of the first-order plots was attributed to several factors such as the effects of the polymer matrix on the photochromic compound, the presence of more than one conformer or the dye that might be confined in the solid polymer matrix (Rappon and Ghazalli, 1995).

The integrated form of the first-order rate law for the photocoloration process is:

$$\ln\frac{(A_\infty - A_0)}{(A_\infty - A_t)} = kt$$

where k is the rate constant, A_∞, A_t, and, A_0 are the absorbance of the **PMC** at infinite time, at time t, and at zero time, respectively. Plot of $[\ln(A_\infty - A_0)/(A_\infty - A_t)]$ against time gives a straight line with slope equals as shown in k (Fig. 3). From the graph the apparent first-order rate constant (k) for the photocoloration of spirooxazine **SO** doped PMMA and epoxy resin films was found to be $0.0040\ \mathrm{s}^{-1}$ and $0.0021\ \mathrm{s}^{-1}$, respectively. It is clear that the photocoloration of **SO** in PMMA is almost twice faster than that in epoxy resin. This could be attributed to the larger free volume of the PMMA compared to that of epoxy resin which offers a large space for the dye to undergo isomerization. Another factor could be the possible hydrogen bonding between the epoxy resin and the spirooxazine which stabilizes the latter.

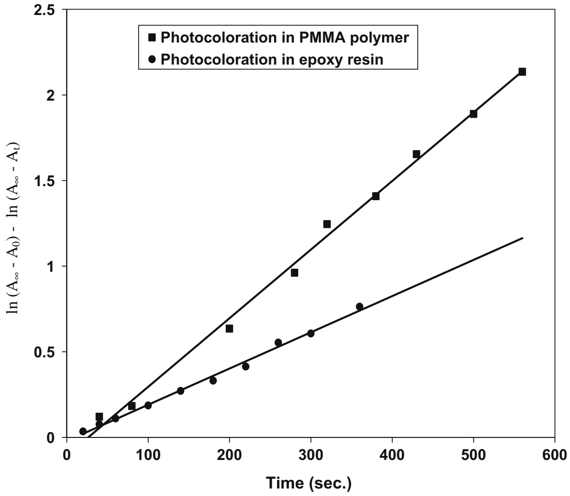


Figure 3 First-order plot of the photocoloration of SO doped in PMMA and epoxy resin.

3.2. Photobleaching

Spiropyrans and spirooxazines are known (Lafuma et al., 2003) to be thermally reversible photochromic compounds. This thermal reversibility is due to the sigma bond cleavage of the spiro C–O single bond. The open form photomerocyanine reverts thermally to the closed form spiro compound. The rate of thermal fading of photomerocyanine to spiro form was found to decrease with increasing solvent polarity (Lafuma et al., 2003) and metal complexation (Kopelman et al., 2008; Zhang et al., 2008). This trend was attributed to the stabilization of the polar zwitterionic photomerocyanine through complexation and hydrogen bonding.

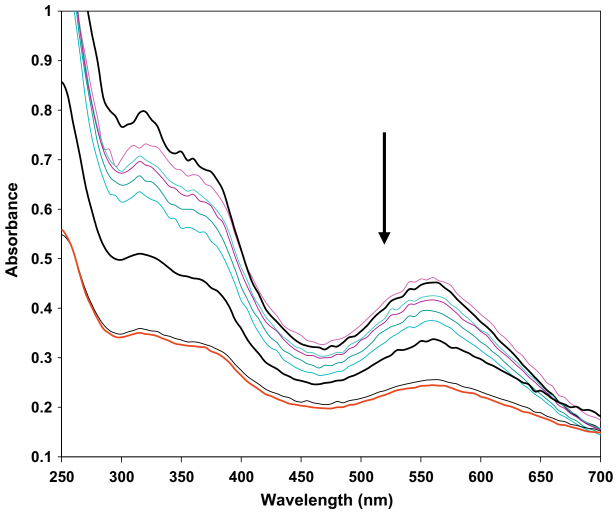


Figure 4 Photobleaching reaction of PMC in PMMA polymer film. The arrow direction indicates the decrease of absorbance with increasing exposure time (s), 0; 20; 100; 120; 200; 240; 280; 340; 560.

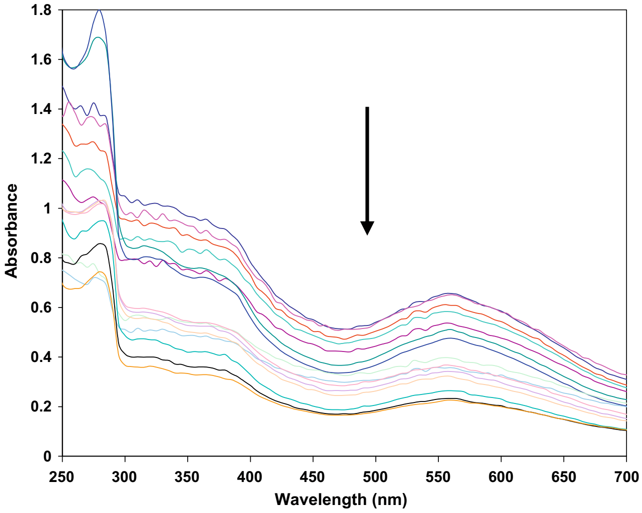


Figure 5 Photobleaching reaction of PMC in epoxy resin film. The arrow direction indicates the decrease of absorbance with increasing exposure time (s), 0; 20; 40; 60; 80; 140; 180; 320; 400; 440; 500; 540; 680; 720.

Photobleaching and thermal fading of **PMC**–**SO** follow simple first-order rate law. When the open form **PMC** was irradiated with white light, it was converted to the colorless spirooxazine **SO**. Thus, the purple color gradually disappeared with time. Figs. 4 and 5 show the absorption spectrum of the photobleaching reaction of photomerocyanine **PMC** doped in PMMA and epoxy resin polymer films, respectively.

The integrated form of the first-order rate law for the photobleaching process is

$$\ln\frac{A_t}{A_0} = -kt$$

where k is the rate constant, A_0 is the absorbance of the **PMC** at zero time and A_t is the absorbance at time t. Plot of $[\ln(A_t - \ln(A_0)]$ against time gives a straight line with slope equals $(-k)$. Fig. 6 shows the simple first-order plots of the photobleaching reaction of **PMC** doped in PMMA and epoxy resin polymer films, respectively. The apparent first-order rate constant (k) for the photobleaching of spirooxazine **SO** doped in PMMA equals 0.0012 s^{-1} and that for **SO** doped in epoxy resin equals 0.0013 s^{-1}. The rate of photobleaching reaction of **PMC** in both films is almost the same. We found that the reaction rate for the photobleaching process is slower than that of the photocoloration process in both matrices. This is expected because PMMA and epoxy resin are both polar and could form hydrogen bond with photomerocyanine and thus stabilize the latter which results in the retardation of photobleaching rate.

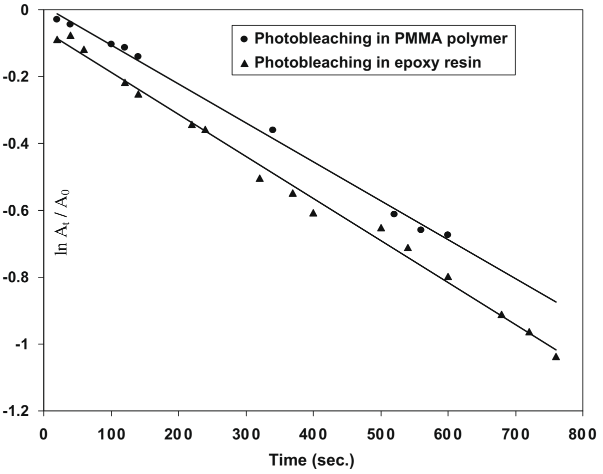


Figure 6 First-order plot of the photobleaching reaction of PMC in PMMA and epoxy resin films.

3.3. Photochemical fatigue resistance of spirooxazine in PMMA and epoxy resin polymer films

One of the indispensable properties that should be fulfilled by a photochrome to be used as a data-storage medium is its high resistance to photochemical degradation. The fatigue resistance of spirooxazine **SO** doped in PMMA and epoxy resin polymer films is reported as the changes in A_n/A_0 with UV/visible irradiation cycles numbers, A_0 and A_n are the absorbance of the open form **PMC** at its $\lambda_{\max}$ obtained on the first and nth cycles, respectively (Fig. 7). As it is clear from Fig. 7, the fatigue resistance of spirooxazine doped in epoxy resin is much better than that of spirooxazine doped in PMMA. Similar results were reported with fulgides (Bahajaj and Asiri, 2005, 2006; Lafond et al., 2002; Lessard et al., 2003). This was attributed to the decrease of available polymer-free volume due to increasing cross-linkage in the epoxy resin (Lessard et al., 2003).

4. Conclusion

The photochromic properties of 1,3,3-trimethylspiro[indoline-2,3′-[3H]naphtho[2,1-b][1,4] oxazine] **SO** doped in epoxy resin and PMMA films were investigated. Kinetics of photocoloration and photobleaching reactions were followed spectrophoto-metrically. Irradiation of colorless spirooxazine **SO** doped in PMMA and epoxy resin with UV light (366 nm) results in the formation of the intensely colored zwitterionic photomerocyanine **PMC**.

The reverse reaction was photochemically induced by irradiation with white light. It was found that the visible absorption band is red shifted of the **PMC** doped in epoxy resin compared to that doped in PMMA. Such a bathochromic shift

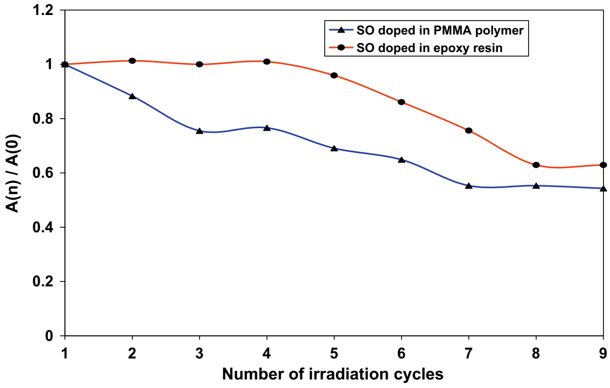


Figure 7 Photochemical fatigue resistance of SO doped in PMMA and epoxy resin polymer films.

was attributed to the higher polarity of epoxy resin compared to PMMA. Photocoloration and photobleaching reactions follow a first-order rate equation. It was found that photocoloration rate constant of **SO** in PMMA film is greater than that in epoxy resin. On the other hand, photobleaching rate constant is almost identical in both matrices. This was attributed to the higher stability of the zwitterionic photomerocyanine **PMC** in both matrices compared to the colorless closed spirooxazine **SO**. Spirooxazine doped in epoxy resin shows much better fatigue resistance than that doped in PMMA.

Acknowledgements

The authors wish to thank King Abdul Aziz City for Science and Technology (KACST) for funding this research work via Grant No. At-27-68.

References

Bahajaj, A.A., Asiri, A.M., 2005. Pigment Resin Technol. 34, 275.

Bahajaj, A.A., Asiri, A.M., 2006. Opt. Mater. 28, 1064.

Bénard, S., Yu, P., 2000. Chem. Commun., 65.

Berkovic, G., Krongauz, V., Weiss, V., 2000. Chem. Rev. 100, 1741.

Berthet, J., Delbaere, S., Carvalho, L.M., Vermeerscha, G., Coelhob, P.J., 2006. Tetrahedron Lett. 47, 4903.

Bouas-Laurent, H., Durr, H., 2001. Pure Appl. Chem. 73, 639.

Chu, N.Y.C., 1983. Can. J. Chem. 61, 300.

Fua, S., Hub, W., Xieb, M., Wanga, G., Lia, Y., Duanmua, Q., Tiana, J., Liu, Y., 2007. Physica B 400, 198.

Glebov, E.M., Vorobyev, D.Yu., Grivin, V.P., Plyusnin, V.F., Metelitsa, A.V., Voloshin, N.A., Minkin, V.I., Micheau, J.C., 2006. Chem. Phys. 323, 490.

Guo, H., Zou, W.X., Ji, Q., Meng, J.B., 2005. Chin. Chem. Lett. 16, 751.

Hu, H., Pei, J., Xu, D., Qi, G., Hu, H., Zhang, F., Liu, X., 2006. Opt. Mater. 28, 904.

Kopelman, R.A., Paquette, M.M., Frank, N.L., 2008. Inorg. Chim. Acta 361, 3570.

Lafond, C., Bolte, M., Lessard, R.A., 2002. Proc. SPIE 4833, 584.

Lafuma, A., Kimmes, S.C., Quinn, F.X., Sanchez, C., 2003. Eur. J. Inorg. Chem., 331.

Lessard, R.A., Lafond, C., Dererian, G., Gardette, J.L., Rivaton, A., Bolte, M., 2003. Proc. SPIE 5216, 139.

Lin, J.-S., Chiu, H.-T., 2003. J. Polym. Res. 10, 105.

Rappon, M., Ghazalli, K.M., 1995. Eur. Polym. J. 31, 233.

Shin, T.W., Cho, Y.S., Huh, Y.D., Lee, K.D., Yang, W., Park, J., Lee, I.J., 2000. J. Photochem. Photobiol. A: Chem. 137, 163.

Takahashi, H., Murakawa, H., Sakaino, Y., Ohzeki, T., Abe, J., Yamada, O., 1988. J. Photochem. Photobiol. A: Chem. 45, 233.

Tamai, N., Miyasaka, H., 2000. Chem. Rev. 100, 1875.

Tan, Ting-feng, Chen, Pei-li, Huang, Hua-ming, Meng, Ji-ben, 2005. Tetrahedron 61, 8192–8198.

Ubukata, T., Takahashi, K., Yokoyama, Y., 2007. J. Phys. Org. Chem. 20, 981.

Wohl, C.J., Kuciauskas, D., 2005. J. Phys. Chem. B 109, 21893.

Yokoyama, Y., 2000. Chem. Rev. 100, 1717.

Zhang, Z., Zhang, C., Fan, M., Yan, W., 2008. Dyes Pigments 77, 469.