Coloration of Glasses with Organic Reactive Dyes

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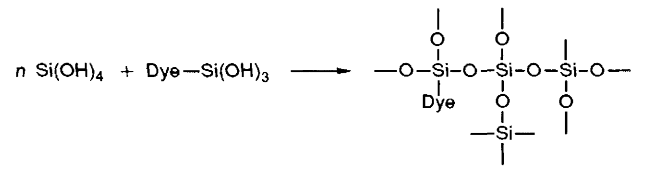
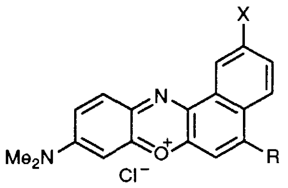
The transparent coloration of glasses has been successfully achieved by coating glass surfaces (to a thickness of 0.2 μm) with phenoxazinium and phenazinium dyes with a terminal triethoxysilyl group by the sol–gel coloured coating method.

The so-called sol–gel processing has attracted much attention for the preparation of advanced inorganic materials, such as glasses and ceramics, and is particularly important for thin coatings on glass substrates.[1,2] The sol–gel method is of interest for the preparation of coloured glasses using organic dyes and pigments. However, this coloration process was not possible for anthraquinone and naphthoquinone dyes because of their low solubility in the silica sol solution.[3]

We have now prepared some phenoxazinium and phenazinium dyes, **1** and **2**, with a terminal triethoxysilyl group

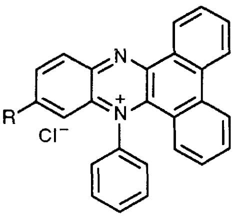


Scheme 1



1

a; X = R = H
b; X = OH, R = H
c; X = H, R = NH[CH$_2$]$_3$Si(OEt)$_3$
d; X = OH, R = NH[CH$_2$]$_3$Si(OEt)$_3$



2

a; R = H
b; R = NH[CH$_2$]$_3$Si(OEt)$_3$

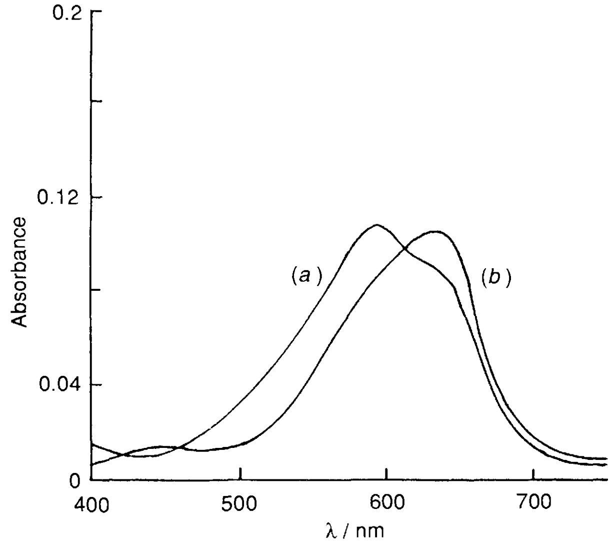


Fig. 1 Absorption spectra of dye **1c** (*a*) in sol–gel coating layer (thickness: 0.2 μm) prepared from Si(OEt)$_4$ and (*b*) in water

connected directly with a network of Si–O matrix gels in the sol–gel processing, as shown in Scheme 1. Reaction of the corresponding phenoxazinium derivatives, **1a** and **1b**, and the phenazinium derivative, **2a**, with aminopropyltriethoxysilane in refluxing EtOH for 30 min gave dyes **1c**, **1d** and **2b** with a terminal triethoxysilyl group in 20–30% yield [**1c**, λ_{max} 628 nm (log ε 4.63); **1d** λ_{max} 624 nm (log ε 4.58); **2b** λ_{max} 573 nm (log ε 4.30) in EtOH)]. The products were reprecipitated with ethanol–diethyl ether and identified from their ^{1}H NMR spectra. We have succeeded in coating glass surfaces with these reactive dyes by the following sol–gel coloured coating method. A transparent blue or violet coating layer on a glass slide was formed by the dipping–withdrawing method (rate of drawing: 2 mm s^{-1}) using a coloured coating solution which consisted of Si(OEt)$_4$–EtOH–H$_2$O–HCl–dye (**1c**, **1d** or **2b**) (1 : 1.5 : 0.84 : 0.01 : 0.008 mass ratio). Heating this coating layer for 15 min at 100 °C formed a hard, coloured silica gel layer by further gelation.

The absorption spectrum of the glass slide coloured by **1c** is shown in Fig. 1. The absorption band is broad in the silica thin layer (0.2 μm thickness of the coating on each side of the slide glass) and shifted to shorter wavelength compared with a similar concentration of the dye in water. A similar broadening of the absorption bands of dyes **1d** and **2b** was observed in a silica film coating.

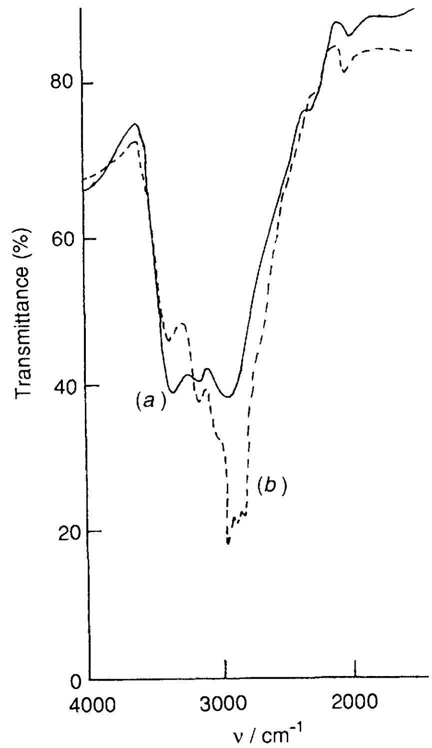


Fig. 2 IR spectra of dye **1c** in KBr (*a*) after and (*b*) before hydrolysis

Hydrolysis of dyes **1c** and **2b** was performed under the silica sol processing conditions to examine the reactivity of the terminal triethoxysilyl group. The hydrolysis product resembled a gel powder, and was insoluble in organic solvents. The IR spectra of the hydrolysed and unhydrolysed dyes **1c** differ noticeably. In the hydrolysis product of **1c**, the peak intensity at 2990 cm^{-1} assigned to CH$_3$ and CH$_2$ stretching mode decreased, and the peak intensity around 3500 cm^{-1} for the OH group increased, as shown in Fig. 2. Also, the peaks at 950 and 1070 cm^{-1} assigned to Si–OEt bond stretching and deformation disappeared. An endothermic peak at 120 °C, which is assigned to the polycondensation of the Si–OH group, was observed in the DTA–TGA (differential thermal analysis –thermal gravimetric analysis) of the hydrolysis product of **1c**. Such an endothermic peak is generally observed in silica gels produced by the sol–gel process. The IR spectra and thermal analyses of the hydrolysis products of **1d** and **2b** were similar.

Thus, the reactive dyes **1c**, **1d** and **2b** with a terminal triethoxysilyl group are easily hydrolysed and directly polycondensed with the hydroxysilane generated during the gelation of the alkylsilane. These reactive dyes can be directly connected with an Si–O network in the silica-coating layer, and are easily coated on the glass by this new method.

This method could be applied to the coloration of soda glass and other types of glasses, and to the preparation of advanced composite materials which consist of organic dyes and inorganic materials.

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