

Direct measurement of the photochromism kinetics of salicylideneamines in solid state[†]

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A method for the study of photochromism kinetics of salicylideneamines in the solid state with fluorescence changes as the probe was described. This can be used to quantitatively evaluate the photochromism of some solid photochromic materials.

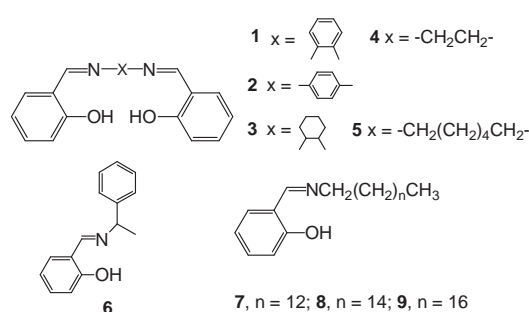
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Devices based on semiconductors have been widely used during the 20th century. However, in order to meet the need of the new photonic era, we have to develop some new electronic or photonic devices of which the operation mechanism is drastically different from that of semiconductor-devices, so that the intrinsic drawbacks of the latter can be overcome. Photochromic material is one of the choices because of its versatile utility in high-frequency switches, supra high-density information storage, *etc.*¹⁻⁴

It is important to evaluate the performance of the solid photochromic material with a quantitative and technically feasible assay because the material in practical devices is usually used in the solid, instead of the solution state. We must realise that the detectable photochromic behaviour of aggregates is drastically different from the result that is obtained with time-resolved spectroscopy (on the femtosecond scale).^{5,6} Thus, it is important to develop a method to evaluate the photochromic property of the material in the aggregated state (in the native solid state or in some rigid matrix, such as in high T_g polymers, for example, polyimide, in which the functional molecules can retain their orientation and the material can withstand high operation temperature), so that we can obtain some preliminary information about the possibility of developing practical devices with these compounds. Here we report a feasible assay to evaluate quantitatively the photochromism in the solid state with fluorescence as the probe.

Salicylideneamines is one kind of important photochromic organic compound (the photochromism is caused by excited intramolecular proton transfer).²⁻⁴ Some salicylideneamines are luminescent photochromic compounds.^{6,7} So, it should be possible to use the sensitive fluorescence spectroscopy method as a convenient probe to study the photochromism of the solid. Our experiment results prove that this is true.

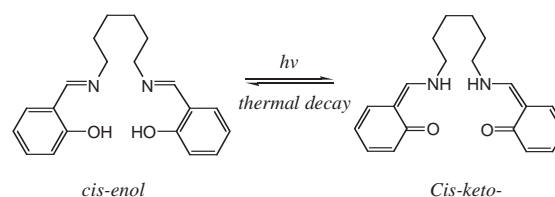
All the compounds used in the study (Scheme 1) are synthesised by routine condensation of salicylaldehyde with relevant amines (the products were characterised by ¹H NMR spectroscopy and elemental analysis),⁸ and used as crystalline solids in the measurements. The fluorescence spectra were recorded with a Shimadzu RF-5301 PC spectrafluorophotometer. All the samples were stored in the dark for more than 72 hours before use to diminish the photochromism caused by room light. The light source of the spectrafluorophotometer was used as the irradiation light source. The rate constants of



Scheme 1 Compounds 1-9 used in the study.

the photochromism were deduced from the time course curves by single-exponential nonlinear regression with the software of SigmaPlot Vers. 2000.

The photochromism of salicylideneamines, Scheme 2, (compounds 1-9) can be characterised by UV-Vis spectroscopy.^{6,7} As an alternative method, the irradiation time dependency of the fluorescence spectra of compound 5 was also investigated (Fig. 1). The inset in Fig. 1 means that the process is reversible. Fig. 1 shows that fluorescence changes can be used to follow the photochromism. The new peak centered at 525 nm is assigned to the photo-generated coloured form: the *keto*-structure of compound 5. Similar results were also found for other compounds, excepting compound 2.



Scheme 2 Photochromism of salicylideneamines—exemplified with compound 5.

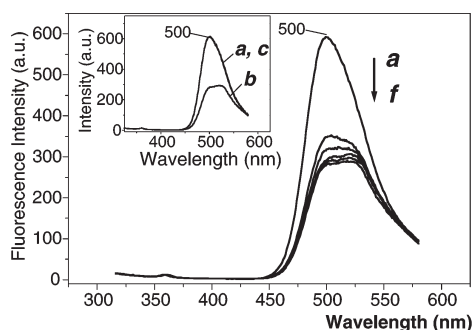
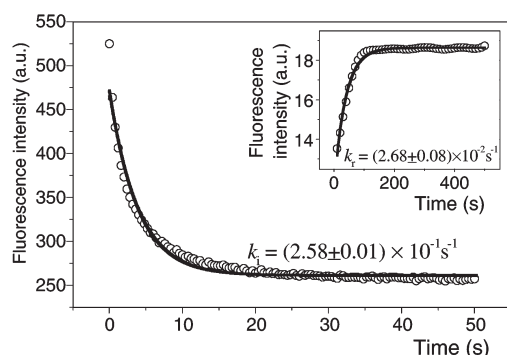
In order to study the photochromism of the solid in a more quantitative manner, we used the time course technique to kinetically follow the real-time changes of the fluorescence intensity during both the irradiation and the relaxation (Fig. 2). Thus, the photochromism rate constants during both the irradiation (k_i) and relaxation (k_r) were obtained. It should be pointed out that the time curves of both the irradiation and the relaxation process do not strictly agree with the nonlinear single-exponential fitting. The reason is that the observed photochromic rate is affected by many possible factors (*vide infra*).

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Table 1 Photochromism kinetics of solid compounds **1–9**, probed by the variation of the fluorescence intensity during irradiation (k_i , s⁻¹) and relaxation (k_r , s⁻¹)

Compd.	1	2	3	4	5	6	7	8	9
k_i	$(7.19 \pm 0.01) \times 10^{-3}$	- ^a	$(9.28 \pm 0.00) \times 10^{-2}$	$(1.71 \pm 0.01) \times 10^{-2}$	$(2.58 \pm 0.01) \times 10^{-1}$	$(2.14 \pm 0.00) \times 10^{-1}$	$(1.19 \pm 0.01) \times 10^{-2}$	$(1.54 \pm 0.01) \times 10^{-1}$	$(9.58 \pm 0.04) \times 10^{-2}$
k_r	$(2.05 \pm 0.00) \times 10^{-3}$	- ^a	$(2.33 \pm 0.01) \times 10^{-3}$	$(2.15 \pm 0.10) \times 10^{-4}$	$(2.68 \pm 0.08) \times 10^{-2}$	$(1.59 \pm 0.00) \times 10^{-2}$	$(3.17 \pm 0.20) \times 10^{-2}$	$(1.45 \pm 0.18) \times 10^{-1}$	$(4.30 \pm 0.19) \times 10^{-2}$

^a No changes.**Fig. 1** Fluorescence spectral changes for solid compound **5** with irradiation ($\lambda_{\text{ex}} = 283$ nm, irradiation time: a: 0 s; b: 5 s; c: 10 s; d: 20 s; e: 30 s; f: 60 s. Inset: fluorescence spectra of unirradiated solid (a); irradiated for 60 seconds (b) and relaxed for 100 s in dark after the finish of the irradiation (c).**Fig. 2** Direct measurement of the photochromism rate constants of solid compound **5** (k_i) — probed with fluorescence intensity variations during irradiation. $\lambda_{\text{ex}} = 296$ nm. Monitored at 500 nm (open circle lines: experimental data; solid lines: fitted with single-exponential nonlinear regression. Inset: relaxation kinetics of the irradiated solid **5** (k_r). Irradiation time is 60 seconds, $\lambda_{\text{ex}} = 315$ nm, monitored at 500 nm).

In order to confirm this method, we studied compound **2** with similar measurements. The result shows that its fluorescence intensity did not change at all. This result shows the credibility of our fluorescence-probe measurement because solid compound **2** is thermochromic, not a photochromic compound⁹—with irradiation, it will not undergo the isomerisation, and as a result, no fluorescence changes should be detected.

The photochromic kinetics of compounds **1–9** were studied with the method depicted in Figs 1 and 2. The photochromic rate constants are summarised in Table 1. The kinetics of the irradiation process (k_i) are relative values because the k_i is correlated to the intensity of the incident light. In order to compare the photochromic performance, the intensity was the same in all the experiments. We learn from Table 1 that the photochromic kinetics of compounds **1–9** are different from each other (in some cases, the difference is significant), although their photochromism is based on the same mechanism. The kinetics of compound **1** and compound **4** are relatively slow. Other compounds usually have a more rapid kinetics, such as compound **3**, **5**, **6** and **8**. Compounds **5**, **6** and **8** are special in that their photochromic processes are fast. Theoretical analysis show that the excited state proton transfer for novel photochromic compound **6**¹⁰ is nearly barrierless.¹¹

Fabrication of an LB film, in which the molecules can be asymmetrically aligned together, is a method to study novel optical properties.¹² Compounds **7**, **8** and **9** are amphiphilic compounds. The study of these compounds shows some promising results, especially compound **8** (Table 1). No fatigue phenomenon was found for these compounds.

There are a few possible factors that contribute to the variation of the photochromism kinetics in the solid state for the analogues **1–9**, such as the intrinsic molecular structure (the dimension of the π -conjugated system, the steric constraints of the molecular structure, etc) and the packing mode of the molecules in the crystal. In this case, we noted that compounds **1** and **2** were reluctant to undergo the photochromism, perhaps due to their extended π -conjugated system and the tight packing of their molecules in the crystalline state (due to the molecular shape and the favorable strong π - π interaction). For the compounds with similar π -conjugated systems, such as compounds **3–9**, the rigidity of the molecular backbone may play an important rule in their photochromic performance. It should be pointed out that the fluorescence intensity depends not only on the photochromism, but also on several other possible factors, such as the powder size of the sample, the change of the refractive index of the solid upon photochromism, irradiation wavelength and the re-absorption of the photo-generated *keto*-isomers. Thus, there is no guarantee of linearity between the detected fluorescence intensity and the concentration of fluorescent isomers, and it is difficult to determine the quantum yield under such a condition. Further studies are needed in order to explain the experimental results in detail. However, the most important thing is whether we can observe a fluorescence variation that occurs with rapid kinetics and sufficient amplitude, because these factors have to be checked before a compound is to be considered for device development. Fortunately, the fluorescence method described here is the exact candidate to reach this goal.

In summary, the direct measurement of the photochromism kinetics of salicylideneamines in the solid state with fluorescence as probe has been described. This method can be used to evaluate quantitatively the photochromic property of solid fluorescent photochromic materials. Further study about the structure-property relationship of these solid compounds is continuing.

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