

## Solvent-controlled Aggregation of a Photoconductive Dye

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UV–VIS spectroscopy is used to show that the photoconductive squaraine **1** can exist in the form of two novel aggregates which form preferentially in different DMSO–water compositions and that a dynamic conversion between aggregate types occurs in specific DMSO–water solvent mixtures.

Research aimed at developing a molecular level understanding of photoconduction in organic solids has shown that this phenomenon is dependent on both the intrinsic molecular properties of the potential photoconductive material and the intermolecular interactions that occur in the solid state.<sup>1</sup> The former can be evaluated using conventional spectroscopic techniques<sup>2</sup> while single-crystal systems are ideal for studying the latter.<sup>3</sup> Unfortunately, isolation of suitable single crystals of most organic photoconductive dyes and pigments has proved to be problematic so that progress by this route has been limited.

Alternatively, the preparation and characterization of *solution aggregates* of organic photoconductive dyes and pigments could provide insights into the effects of intermolecular interactions on the properties of these molecules. Although this task is generally complicated by the poor solubility of these materials, we sought to develop methods for preparing aggregates of one class of organic photoconductors, the squaraine dyes,<sup>4</sup> in different solvent media. In this communication we report that aggregates of the squaraine **1** can be produced in dimethyl sulfoxide (DMSO)–water mixtures and that this aggregation process is strongly directed by the composition of the binary solvent system. As a result variations in the composition of the DMSO–water mixtures can be used to determine which of two novel squaraine aggregates is produced and to effect a transformation from one aggregate to the other.

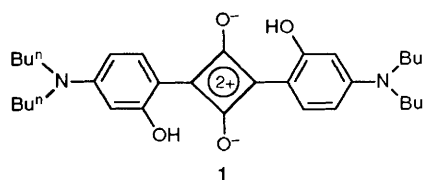
Dye aggregation is generally promoted in water and retarded in solvents such as DMSO. Solutions of non-

associated squaraines are characterized by an intense visible absorption and since spectroscopic analysis of a DMSO solution of **1**<sup>5</sup> showed a strong absorption at 660 nm,  $\epsilon_{660} \approx 300\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ , it was concluded that the dye was not aggregated in this solvent.

Based on this and our previous observations of the unusual effects of DMSO–water media on chemical phenomena,<sup>6</sup> we have sought to determine if aggregation could be induced upon addition of this photoconductive dye to DMSO–water mixtures.

Our studies involved using a consistent experimental protocol, to add an aliquot of **1** in a 2,2,2-trifluoroethanol stock solution to a series of DMSO–water mixtures followed by sonication for 60 s. The resulting solutions contained a maximum of 1% of the alcoholic cosolvent and were monitored by UV–VIS absorption spectroscopy.

When squaraine **1** was added to DMSO–water mixtures with greater than 70 v/v% DMSO spectroscopic characterization of the solutions showed a single intense absorption indicative of the non-associated squaraine,  $\lambda_{\text{max}} = 664\text{ nm}$ ,  $\epsilon_{664} \approx 300\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ .



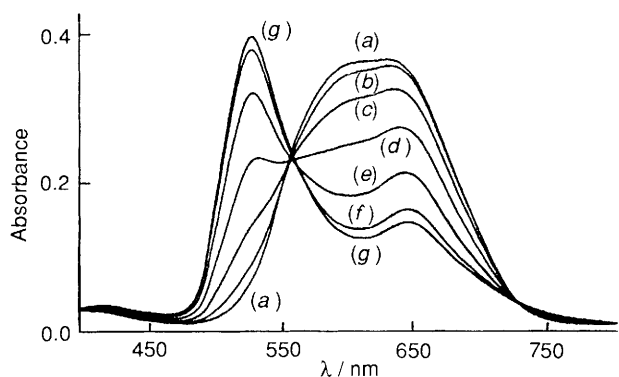


Fig. 1 UV-VIS spectra of **1** in 30% DMSO monitored at 12 min intervals after sample preparation, showing the dynamic conversion of aggregate B [spectrum (a)] to aggregate A [spectrum (g)]

When squaraine **1** was added to solutions in the range 50–70 v/v% DMSO–water dull purple solutions were obtained,  $\lambda_{\text{max}} = 530 \text{ nm}$ ,  $\epsilon_{530} \approx 80\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (sh ca. 650 nm). Based on the reduction in the extinction coefficient and the broadness of these absorbances, it is believed that in these DMSO–water media squaraine aggregation had occurred. The resulting species which had an absorption spectrum identical to Fig. 1(g), was found to be stable for several days, and will henceforth be denoted as aggregate A.

Addition of squaraine **1** to DMSO–water mixtures containing 20–50% DMSO yielded solutions that were initially characterized by a broad absorbance from 550 to 700 nm. Continued monitoring of these solutions revealed a dynamic effect in which the broad absorption decreased in intensity while an absorption at 530 nm developed, see Fig. 1.

When equilibrium was reached the sample exhibited a spectrum [Fig. 1(g)] corresponding to aggregate A. Investigations with a series of binary solvent mixtures in the 20–50% DMSO range showed that the rate of this dynamic process increased with increasing DMSO content. The first spectrum [Fig. 1(a)] is believed to characterize the second squaraine aggregate identified in this study, henceforth denoted as aggregate B.

Addition of squaraine **1** to mixtures of less than 20% DMSO yielded blue solutions. Spectroscopic examination showed that only aggregate B formed in these media and was stable for at least one day.†

Based on these observations, it is clear that the composition of the binary solvent system can be used to control the outcome of the aggregation process. Squaraine aggregate A was stabilized in DMSO-rich solutions containing 50–70% DMSO, squaraine aggregate B was stabilized in water-rich solutions containing less than 20% DMSO, while with solutions from 20–50% DMSO it was possible to observe a dynamic conversion from aggregate B to A. The low intensity, broad absorptions are characteristic of the intermolecular interactions occurring within the squaraine aggregates. The dissimilarity in the spectra of the two aggregates indicated that these interactions were considerably different in the two species.

Law and Chen studied by the Langmuir–Blodgett (LB) film technique surfactant squaraines and reported the isolation of two stable films.<sup>7</sup> Characterization of these films by absorption spectroscopy showed that in both cases aggregation between dye molecules had occurred. One of the films

contained aggregates of squaraines that were reported to be stabilized by intermolecular C–O dipole–dipole interactions. This assignment of aggregate structure was made on the basis of similarities between the spectroscopic properties of this film and a crystalline squaraine dye. Aggregate A in our studies features an absorption spectrum identical to this C–O dipole–dipole stabilized LB film and as a result, it is believed that the alignment of dye molecules in the solution aggregate allows for similar intermolecular interactions to occur. The second film isolated in the LB film study involved aggregates which were concluded, on the basis of studies with solid-state squaraines, to be stabilized by intermolecular charge-transfer interactions between the donor (aniline) and acceptor (four-membered ring) squaraine moieties on adjacent molecules. The absorption spectrum of this film was similar to that of aggregate B in our DMSO–water studies, although the former featured a more distinct absorbance maximum at 650 nm. This would indicate that the orientation of molecules in the solution aggregate would allow for a similar interaction to occur.

Within the framework of exciton theory,<sup>8</sup> the splitting observed in the absorbance spectrum of aggregate A would indicate that the molecular transition dipoles are not oriented in a random manner, but rather they show a degree of ordering. However, the studies so far do not provide information as to the type of aggregates; dimers, trimers, etc. or of a colloidal nature.<sup>9</sup>

In summary, in this communication we have reported the observation of two novel aggregates of squaraine **1** in DMSO–water mixtures where the solvent composition has been found to control the outcome of the aggregation process. Similarities between the properties of aggregates produced in DMSO–water and those reported for squaraine LB films<sup>7</sup> have been noted. Further work is in progress to fully characterize these aggregates and their potential colloidal properties, and to isolate both as solids. Incorporation of these materials into xerographic devices would permit an evaluation of the effects of known intermolecular interactions on the photoconduction of squaraine **1**. This information is considered to be germane in efforts to develop an understanding of the molecular basis of photoconduction.

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† In some cases a species with an absorption maximum at 600 nm and a less intense absorbance at 715 nm was observed in media containing less than 20% DMSO. At this point the factors controlling the formation of this aggregate are not clear.