# Synthesis, application of thermally stable red dyes for LCD colorfilter ; Influence of dye structures on the aggregation property in the film state

*Chun Sakong, Young Do Kim and Jae Pil Kim*

**Department of Material Science Engineering, Seoul National University, Gwanak-gu, Seoul 151-744, Korea**

*TEL:82-2-880-7238, e-mail: chuni79@snu.ac.kr.*

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## Abstract

Three thermally stable red dyes of azo, quinacridone and perylene derivatives were synthesized and dye-based color filters were manufactured for liquid crystal display. Aggregation behavior of the dyes and their spectral property in film state were investigated by concentration dependent spectroscopy and field emission scanning electron microscopy (FE-SEM). These dyes have remarkable difference on their aggregation behavior in film state. Such difference of aggregation behavior affects the spectral property of the film, and it can cause decreasing the transmittance of dye-based color filters.

## 1. Introduction

Color filter is a fundamental component of the thin-film transistor liquid crystal display (TFT-LCD) with three-primary colors of red, green and blue. Conventional fabrication process of the color filter is pigment dispersion method using pigments as colorants. Although this process is currently used in the flat panel display industry, it has some disadvantages such as the complicated process, the waste of photoresist and low chromaticity of the manufactured color filter.

Recently, ink-jet printing method has been studied to simplify the complicated process and reduce manufacturing cost of LCD color filter. In pigment-based ink-jet printing method, ink-jet nozzle is easily blocked by large pigment particles and ink-jetted color filters with pigments have a limitation of chromatic property due to aggregation of pigment particles. In order to overcome these problems, ink-jet printing method using dyes with a high solubility and excellent color saturation can be an alternative. However, the dyes are difficult to be used for LCD color filter because of their restriction of thermal resistance.

In the previous report, ink-jetted color filters with thermally stable dyes were prepared and their characteristics were examined. The dyes had sufficient thermal stability for LCD color filter and the dye-based color filters had superior chromatic properties compared to those of pigment-based color filters.

However, dyes mostly have different aggregation behavior according to their classes, and these aggregation effects may change the spectral properties of dyes, for example, transmittance and broadness of color filter. Such aggregation behavior of dyes is greatly influenced by their intermolecular interaction as well as their geometry. Therefore, a study on relationship between dye structure and aggregation behavior can be suggested to enhance the chromatic property of dye-based color filter, especially transmittance.

In this study, we synthesized three thermally stable red dyes of azo, quinacridone and perylene derivatives and the influence of dye structure both on their aggregation behavior and spectral property in prepared color filter was studied. The size change of dye aggregates were investigated through the field emission scanning electron microscopy (FE-SEM). The transmittance of dye-based color filters was measured to analyze the influence of aggregation behavior on the spectral property.

## 2. Experimental

The three dyes of azo, quinacridone and perylene derivatives were prepared by synthetic routs illustrated in Fig. 1. Trisulfonated monoazo dye (TAD) was synthesized by diazotization of 5-amino-1-naphthalenesulfonic acid followed by coupling with 1-Naphthol-3,6-disulfonic acid sodium salt. And disulfonated quinacridone dye (DSQ) and disulfonated perylene dye (DSP) were prepared by direct sulfonation with 98% sulfuric acid and 20% oleum.

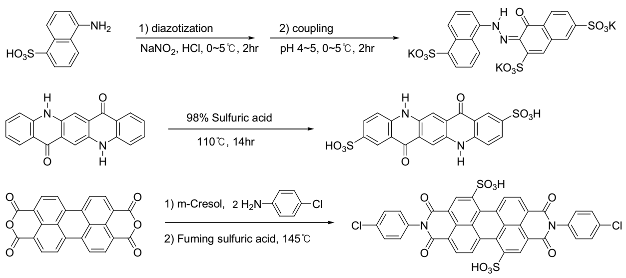



**Fig. 1. Synthesis of thermally stable red dyes.**

Three aqueous inks were prepared with dye, distilled water and LGM 3050 as a binder based on acrylate. Prepared dye-based inks were coated on transparent glass substrates using spin-coating method. The coating speed was kept for 5 seconds at the rate of 300rpm, and then raised at 1000rpm and kept for 10 more seconds. Wet dye-coated color filters were prebaked at 180℃ for 30 minutes, and baked for 1 hours at 220℃.

CAChe 6.1.8 software package was used in order to optimize the geometry of dye structures by using molecular mechanics MM3, conducting the iteractive energy minimizing routines with the conjugate gradient minimizer algorithm. CONFLEX conformational search procedure was used for finding low-energy conformations of dye molecules. The semi-empirical method, PM5, was also examined with respect to geometry optimization, but was found to be no more satisfactory than the molecular mechanical method.

The size of dye aggregate was investigated with a JEOL JSM 6700F field emission scanning electron microscopy at an acceleration voltage of 15Kv.

The transmittance spectra of each color filter of the three kinds of concentration were measured and the spectrum change was observed.

## 3. Results and discussion

Fig. 2 shows UV-Visible absorption spectra of TSA, DSQ and DSP in water. DSQ and DSP exhibited double absorption maxima ($\lambda_{max}$) at 506 / 542nm and 506 / 544nm, while TSA exhibited single absorption maxima at 518nm. Fig. 2 also shows the thermal stability of dyes through the thermogravimetric analysis graph (TGA). These dyes were stable up to 250℃ - the highest temperature in LCD manufacturing process, and they met the requirements in LCD color filter.

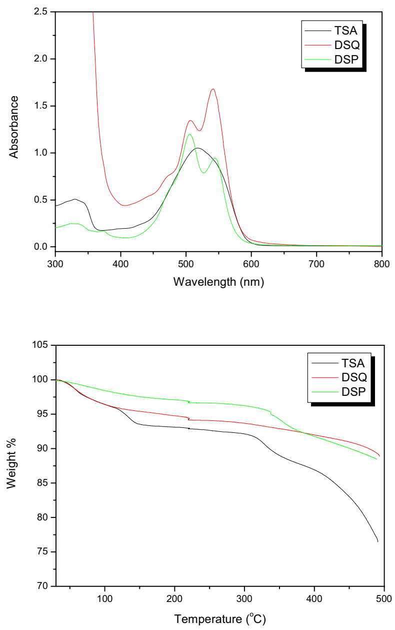



**Fig. 2. Absorption spectra (left) and TGA graph (right) of prepared dyes.**

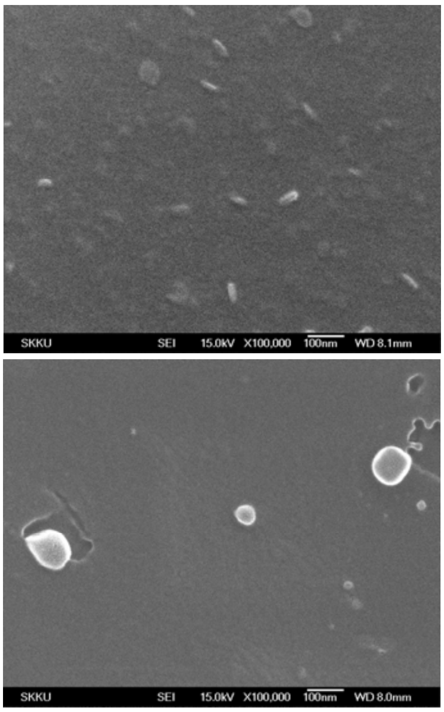
The related factors to the intermolecular interactions that affect the aggregation of the dyes can be divided into three including (1) π-π stacked interaction by the aromatic ring (2) flatness of the molecular structure and (3) intermolecular hydrogen bond. There is close correlation between the factor (1) and (2), and the flatter the molecule the stronger the π-π stacked interaction.

Intermolecular π-π stacked interaction is related to the number and type of the aromatic rings included in the molecule. The three dyes used have different numbers of aromatic rings, 4 for TSA, 5 for DSQ and 9 for DSP. Therefore, if only the intermolecular π-π stacked interaction is considered, the degree of the intermolecular interaction will be in the order of DSP>DSQ>TSA.

However, from the geometrical point of view, DSP has twisted structure toward the x-, y- and z-plane, while TSA and DSQ have excellent flatness. Such twisted geometry of DSP is caused by the introduction of bulky N-aryl and sulfonic acid group to the precursor with excellent flatness. The twisted structure of DSP seems to introduce strong steric hindrance between the molecules, which results in extremely decrease the degree of the π-π stacked interaction.

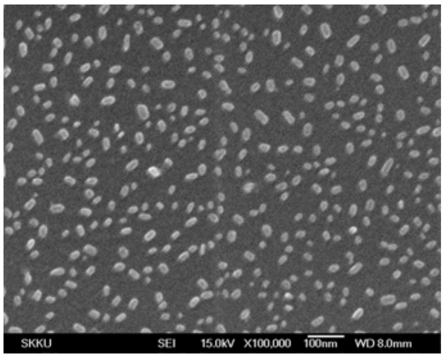
On the contrary, π-π stacked interaction of TSA and DSQ with less aromatic rings is smaller than that of DSP, but they are too flat to decrease the intermolecular interaction caused by π-π stacked interaction. Moreover, DSQ with excellent molecular flatness forms strong intermolecular hydrogen bond at the 4 locations with the 2 nearby molecules, and it become additional factor increasing the intermolecular interaction.

Fig. 3 is the FE-SEM images of dye-based color filters with 0.00025mol concentration at the 100,000 magnification each. In Fig. 3, the size of the dye aggregation is 20~45nm for TSA, 46~100nm for DSQ, and 15~35nm for DSP. In other words, the aggregation size of DSP that has 9 aromatic rings is smaller than that of TSA and DSQ that has 4 and 5 aromatic rings each. This result corresponds with the intermolecular interaction analyzed in the optimization of the molecular structure. Although, DSP has more aromatic rings compared to other two kinds of dyes, the steric hindrance due to the twisted structure decreases π-π stacked interaction among the molecules introduced by the aromatic ring intensively resulting in the relatively less formation of the aggregate. On the other hand, DSQ with excellent flatness forms 4 intermolecular hydrogen bonds with its 2 nearby molecules and forms huge aggregate that reaches almost 100nm due to the increase in the intermolecular interaction.




(a)

(b)




(c)

**Fig. 3. FE-SEM images of 0.00025mol dye-based color filters ; (a) TSA, (b) DSQ and (c) DSP.**

The transmittance spectrum of each color filter of the 3 kinds of concentration manufactured above was measured and the spectrum change was observed. Moreover, based on the transmittance spectrum of the color filters and the aggregate size of the dyes, the effect of aggregation behaviors in the film state to the spectral property was analyzed.

Fig. 4 shows the transmittance spectra of the color filters. TSA and DSP show very small change of the transmittance spectrum for each concentration within the long wavelength range. Also, the spectrum becomes broader as concentration increase on the whole wavelength, TSA shows bigger change of broadness compared to DSP. In case of DSQ, on the contrary, formation of a new absorption band was observed within the long wavelength range near about 700m as concentration increases. This is due to the formation of huge dye aggregate of DSQ as shown in the FE-SEM result. Dye aggregation influences on the ground state of the dyes, and the formed dye aggregate creates another electronic transition level between the HOMO-LUMO levels of monomolecules that has the smaller energy gap. As a result, new absorption band within the long wavelength range with low energy appears. In case of TSA and DSP, new absorption band within the long wavelength is very small compared to that of DSQ, it seems to be due to the degree of aggregation. The formation of a new absorption band by dye aggregate induces absorption within the transmittance range and could become the cause to decrease the transmittance of the color filter.

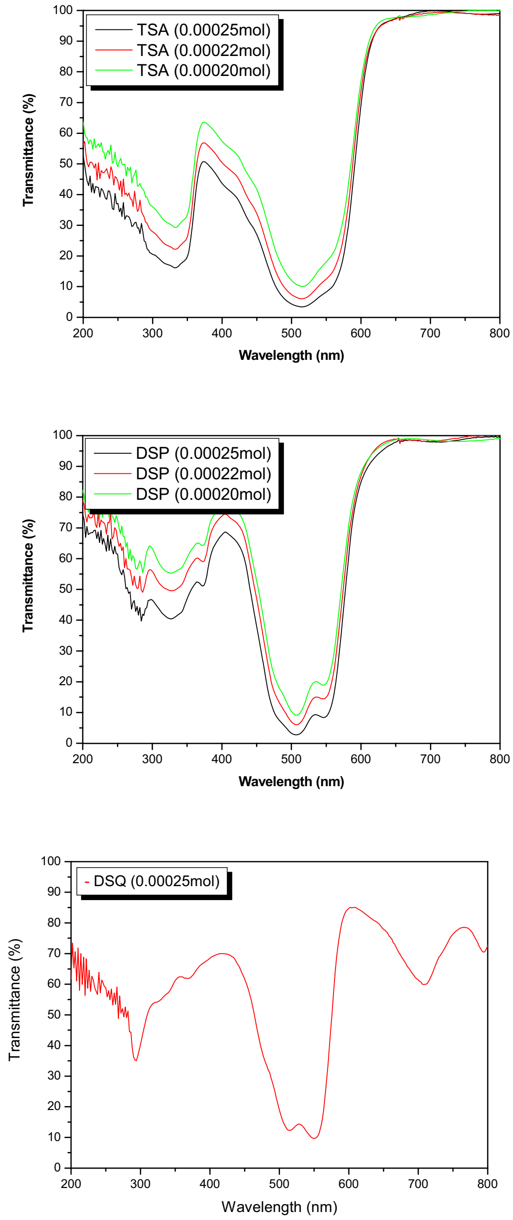



**Fig. 4. Concentration dependent transmittance of dye-based color filters.**

## 4. Summary

Three thermally stable red dyes were synthesized and dye-based color filters were manufactured for liquid crystal display. Also, the aggregation behavior of dyes and spectral property in the film state were investigated. The structural difference of the dyes influences the intermolecular interaction creating the difference of aggregation behaviors at the film state, and this, in some cases, affects the transmittance of the film enormously. It is true that it has been designed to enhance π-π stacked interaction between the molecules to increase the thermal resistance of the dyes so far. As it is shown above, although aggregation is the way to increase the thermal resistance, it could also rather act as a factor to reduce transmittance. Therefore, when designing the dyes with high thermal resistance for optical use it is very important to adjust the aggregation degree to satisfy both thermal resistance and transmittance, and, as a result of this study, about 45nm dye aggregate seems to satisfy both factors.

## 5. References

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