



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 22 Sep 2010

To cite this article: Yong-Jae Hwang & Dong-Myung Shin (2007): Highly Efficient Color Filter Using Fluorescent Materials, (Z)-3-(4'-(dimethylamino)biphenyl-4-yl)-2-phenylacrylonitrile, *Molecular Crystals and Liquid Crystals*, 472:1, 25/[415]-32/[422]

To link to this article: <http://dx.doi.org/10.1080/15421400701544786>

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Highly Efficient Color Filter Using Fluorescent Materials, (Z)-3-(4'-(dimethylamino)biphenyl-4-yl)-2-phenylacrylonitrile

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The transmittance and color characteristics of color filters are directly related to the energy efficiency and image quality of LCD panels. We tried to investigate the effect of fluorescent dyes, (Z)-3-(4'-(dimethylamino)biphenyl-4-yl)-2-phenylacrylonitrile, on the transmittance and the color gamut of LCD panel. The fluorescent dye was synthesized and dispersed in polymer matrix and implemented at the lamp side before the color filters. Energy transfer from blue to green using fluorescent dye 1 can be applied to increase energy efficiency of green color resist. The fluorescent films using dye 1 can improve the transmittance about 4–5% and the color gamut and color purity that can be inferred from the color coordinate change from (X = 0.309, Y = 0.467) to (X = 0.325, Y = 0.521).

Keywords: color filter; energy transfer; fluorescent dye; transmittance

INTRODUCTION

The transmittance and color characteristics of color filters have been improved recently. The physical characteristics are critical to improve image quality. Color filters are composed of glass substrate, black matrix, RGB color resist, overcoat layer, ITO layer. The structure of color filters varies with the LCD types and liquid crystal mode [1–3]. The manufacturing techniques are very diverse which include dyeing method, printing method, electro-deposition method, and pigment-dispersed method. Recently, large panel size requires many physical characteristics which

This work was supported by Seoul Research and Business Development Program (2005) and 2004 Hong-Ik University Research Fund.

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are printability, transmittance, clarity, and manufacturing feasibility. The pigment-dispersed method, which has been applied to the manufacturing a-Si TFT-LCD, uses the color resist that consists of pigments dispersed photo-responsive resin. The color patterns are made using photo-lithography process [4–6].

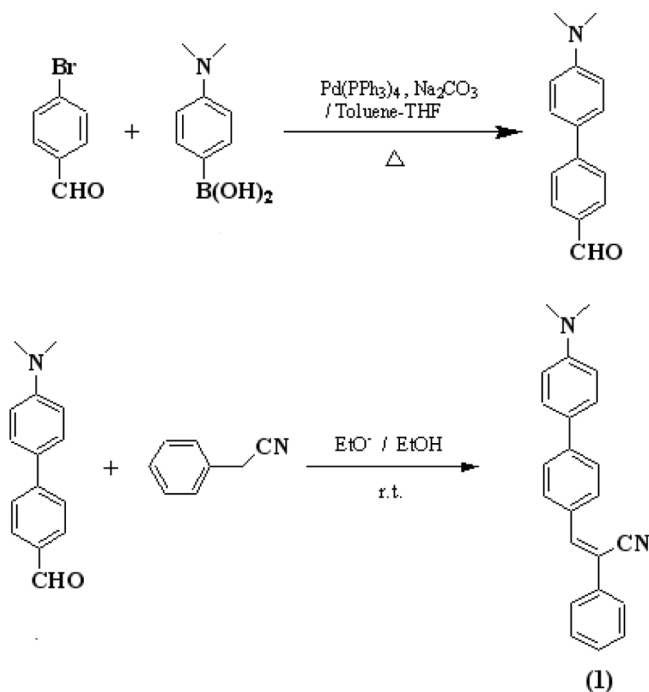
When dye contents are high, the color characteristic can be improved. However the transparency of the films can be drastically deteriorated. Transparency of the films directly affects the energy efficiency of the LCD devices. Low dye contents can improve transparency and many film characteristic and manufacturing feasibility losing color characteristics such as brightness, hue and colorfulness [7–9].

We tried to investigate the effect of fluorescent dyes on the color gamut of LCD panel. Improvement of color gamut without losing other optical characteristics of color filters is of current interest. LCD industries do not tend to use fluorescent dyes for the color filters, because many fluorescent dyes are apt to fade color. To improve the transmittance of color filter, we tried to use energy transfer from the light which has to be removed to generate color to the region fitted to the color we want. Using adequate fluorescent dyes, we can improve the hue and the transmittance of color filter by cutting the unnecessary light and dumping that light energy to the color filter region.

EXPERIMENTAL

Commercial color resists were obtained from the company which supply color resist to LCD manufacturing company. The color resists were coated on 2 cm × 2 cm glass substrate using spin and split coating method. The transmittance and absorbance of the films were measured by using UV-visible spectrophotometer (HP model 8453). The film was coated by two steps, 800 rpm followed by 1500, 2000 or 2500 rpm by using spin coater (home made). The solvent for color resist was PGMEA (Propylene glycol monomethyl ether acetate), which was dried after spin coating. A fluorescent color film was fabricated as the same method. The fluorescence spectrum was obtained from spectrofluorometer (Perkin Elmer LS50). The fluorescent biphenyl derivative was obtained from 4-bromobenzaldehyde and 4-dimethyl aminoboronic acid which generated 4'-(Dimethylamino)biphenyl-4-carbaldehyde. The carbaldehyde was reacted with benzyl cyanide under basic condition using sodium ethoxide in ethanol. The (Z)-3-(4'-(dimethylamino)biphenyl-4-yl)-2-phenylacrylonitrile **1** (Scheme 1) was yellow color and very fluorescent at solid state.

The fluorescent dye **1** dissolved in chloroform and PGMEA was blended with the commercial color resist solution. The ratio of the



SCHEME 1 Synthesis of (Z)-3-(4'-(dimethylamino)biphenyl-4-yl)-2-phenylacrylonitrile.

solution was varied and the resultant mixture solution was spin-coated to form a single layer of color resist. We tried to maintain dye concentration for all photoresist solutions. The spin-coated film was thermal-cured at 150°C for 10 min. Two layers, fluorescent layer on top of color resist layer, of the fluorescent films were spin-coated with polymethylmethacrylate (PMMA) chloroform solution containing **1**. The film characteristics were investigated as a function of fluorescent dye concentration and coating conditions, such as spin speed and curing temperature. Also, The color coordinate was obtained with MINOLTA Chroma meter CS-100A. The back light was fluorescence light covered with white copy paper, which passed through a polarizer.

RESULTS AND DISCUSSION

The maximum absorption wavelength of **1** was 402 nm and maximum emission wavelength was 515 nm which is exactly on the center of

green region. Figure 1 illustrates that the fluorescence band of **1** resides under transmission band of green color resist, and absorption band removes transmission band of color resist at 300–420 nm. The quantum efficiency of **1** was low in polar solvent and very high at solid state and rigid matrixes include polymer film.

The transmittance at 540 nm increases slightly, from 92% to 95% with addition of 10% dye solution (3×10^{-2} M), Figure 2. As the concentration of **1** increases, the light absorption of **1** clearly block the light transmittance at around 400 nm.

However, for concentrated solution the whole transmittance was lower, due to light scattering of the film and the front face self absorption of **1** reduced the energy transfer from blue light to green. The similar trend was observed from 5:9 (v/v) mixture films with various concentration of **1**. Dye **1** (10^{-1} M, 0.2 ml) was dissolved in PMMA solution (2 g of PMMA and 10 mL of chloroform) and was coated on glass substrate. A lower dye concentration films were obtained by dilution from the concentrated dye solution. Color resist was coated on top of dye-PMMA films by spin-coating method in order to utilized energy transfer by green emission. Figure 3 shows that the transmittance is lowered over the whole spectral range when the concentration of **1** in PMMA is 10^{-1} M. At the lower concentration range, the green

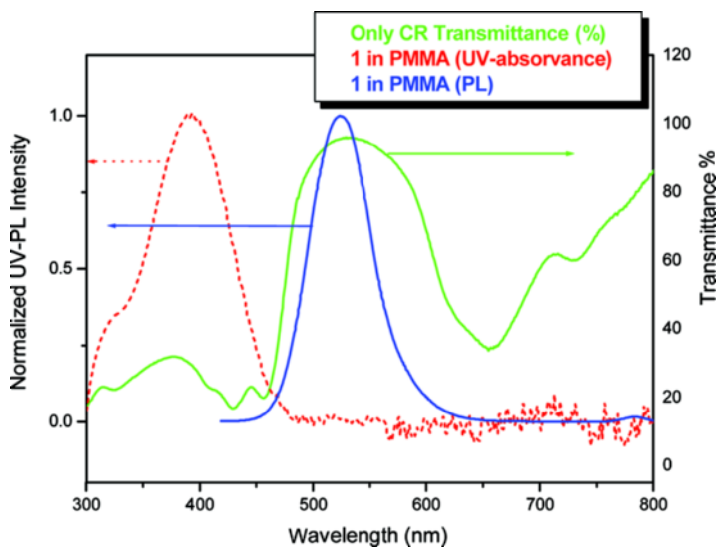


FIGURE 1 The absorption and emission properties of **1** solubilized in PMMA and transmission bands of color resist (CR).

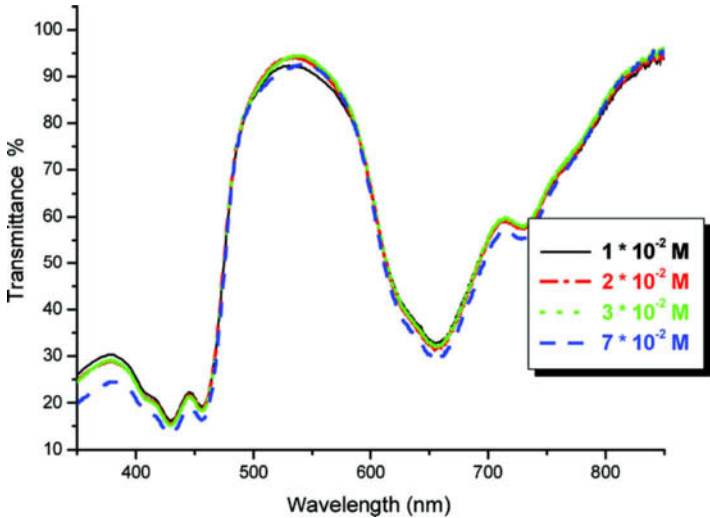


FIGURE 2 Transmittance spectra of dye solution of **1** and green color resist (1:91 v/v). The concentrations of **1** were 1, 2, 3 and $7 \times 10^{-2} \text{ M}$.

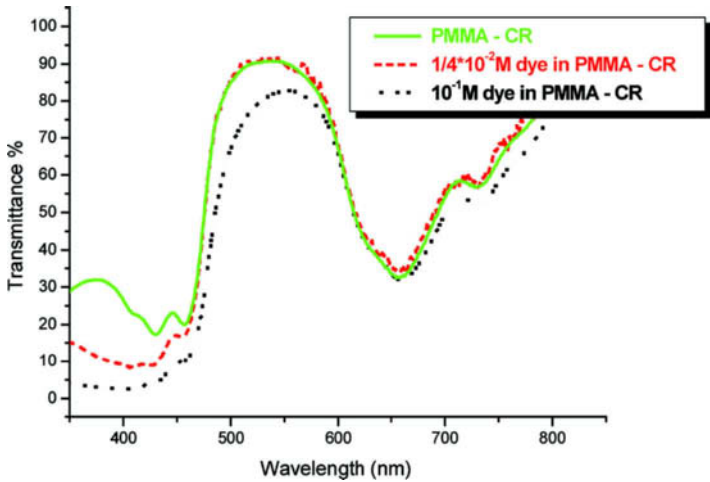


FIGURE 3 Transmission spectra of green color resist spin coated on top of PMMA containing **1** compared with that with containing **1** (straight line).

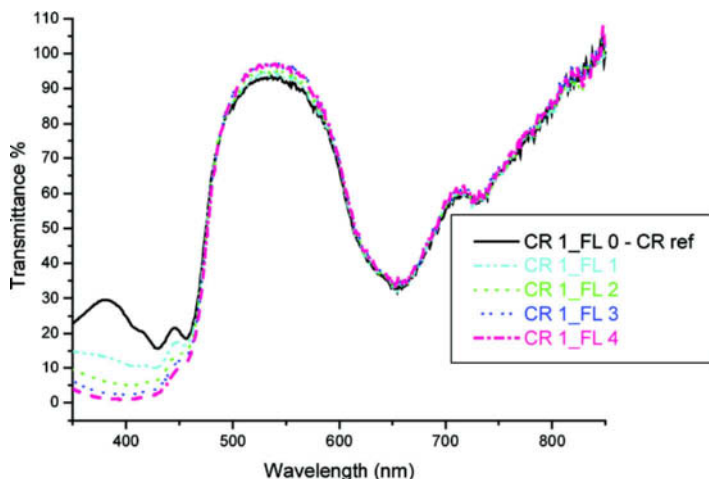


FIGURE 4 Transmittance spectra of color resist film and that with stack (1–4 layers) fluorescent films containing **1**.

transmittance unchanged with significant loss in transmittance at blue region, which affects hue generated from LCD panel.

The interface form between PMMA and color resist film was very unstable and the optical quality was not reproducible due to the polarity difference of PMMA and the PGMEA containing color dye stuff. At the higher dye content in PMMA, the interfacial mismatch pronouncedly deteriorates optical quality of color resist. The interfacial scattering was significantly reduced after using separate fluorescent PMMA film containing **1**, Figure 4. The transmittance at 540 nm increases gradually with the number of fluorescent films. Accordingly, the absorbance gradually decrease around 400 nm region.

The color coordinate obtained from the color resist film and the mixed stack of color filter and fluorescent film. The color coordinate can be influenced by the light illuminated from backside. The color coordinate also gradually shift to pure color region, Figure 5. The color coordinate ($X = 0.309$, $Y = 0.467$) was obtained from the color resist only, and with one fluorescence layer of **1** in PMMA, it shifted to ($X = 0.315$, $Y = 0.490$). For two layers, it became ($X = 0.319$, $Y = 0.502$) and ($X = 0.322$, $Y = 0.513$) and ($X = 0.325$, $Y = 0.521$) for 3 and 4 layers, respectively [10–13].

The color coordinates represent quite same color in X coordinate, but the increase in Y coordinate clearly shows that the color becomes more pure and removes yellowish taint.

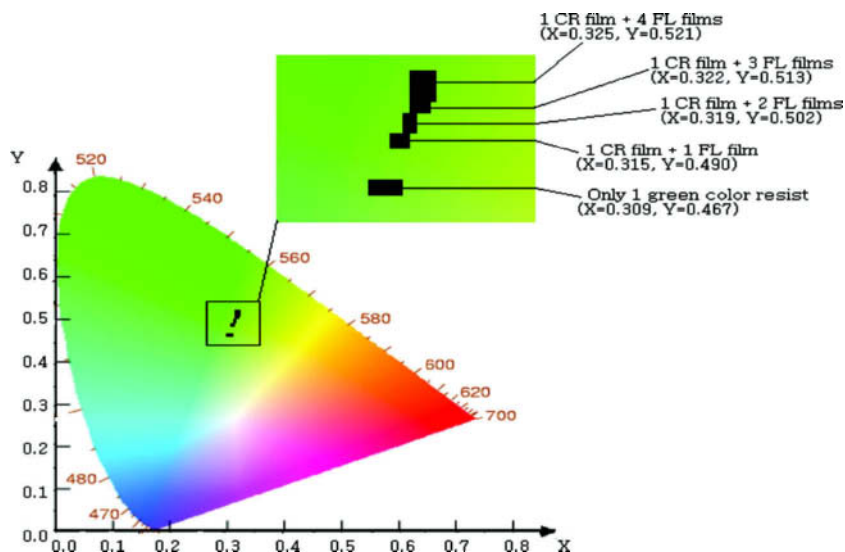


FIGURE 5 The CIE (x, y) chromaticity diagram and color coordinate obtained from the color resist only, and with 1 to 4 fluorescence layers of 1 in PMMA.

It was very difficult to increase transmittance of color resist which already has more than 90% transmittance. Energy transfer from blue to green using fluorescent dye **1** can be applied to increase energy efficiency of green color resist. Accordingly, it can be applied to the color efficiency of red color filter, too. The fluorescent films using dye **1** can improve 4–5% transmittance and the color gamut and color purity that can be inferred from the color coordinate change from (X = 0.309, Y = 0.467) to (X = 0.325, Y = 0.521).

CONCLUSIONS

The fluorescent dye, (Z)-3-(4'-(dimethylamino)biphenyl-4-yl)-2-phenylacrylonitrile, was synthesized and showed high fluorescence efficiency. The dye **1** was dispersed in polymer matrix and implemented at the lamp side before the color filters. Energy transfer from blue to green using fluorescent dye **1** occurred by absorption of light at the blue region (350–450 nm) and emission at the green region (480–620 nm). The fluorescent films using dye **1** can improve the transmittance about 4–5% and the color gamut and color purity that can be inferred from the color coordinate change from (X = 0.309,

$Y = 0.467$) to ($X = 0.325$, $Y = 0.521$). We think that these results go with the capacity of fluorescent filter and the compatibility with commercial color resist. Therefore, this study is meaningful at the side that the light transmittance of color resist was increased with maintaining the color purity of the existing color resist.

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