Dyes and Pigments 101 (2014) 186–195

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The influence of aggregation behavior of novel quinophthalone dyes on optical and thermal properties of LCD color filters

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ARTICLE INFO

Article history:
Received 8 August 2013
Received in revised form
12 September 2013
Accepted 13 September 2013
Available online 22 September 2013

Keywords:
Dyes
Quinophthalone
Aggregation
Liquid crystal display
Color filter
Contrast ratio

ABSTRACT

Four novel yellow quinophthalone dyes were designed and synthesized in order to examine the influence of aggregation behavior on the optical and thermal properties of liquid crystal display color filters. These synthesized dyes showed different absorption spectra and thermogravimetric behavior according to their characteristic structures. When the synthesized dyes were dissolved in industrial solvent-binder composites and spin-coated onto a glass substrate, re-aggregation or migration of the dye molecules were shown in the field emission scanning electron microscopy images after the baking processes. The degree of aggregation depended on the structures of the dyes and affected various properties of the color filters. The transmittances of the color filters decreased as the aggregation of the dye molecules increased. The contrast ratios of the color filters also reduced with aggregation after the baking process. The color difference values of the color filters increased remarkably with more aggregation as the baking process was repeated.

1. Introduction

Nowadays, dyes are employed in a wide range of high technology industries, such as displays [1–5], energy [6–8], bio [9–11] and digital printing [12–14]. Currently, various dye molecules are investigated for application to the color filters of a liquid crystal display (LCD) panel, whose quality influences the performance of an LCD display. The color filter, a key component which converts the white backlight into various colored lights, consists of RGB (red, green, and blue) pixels with pigments, a black matrix for prevention of light leakage, an overcoat for improving the flatness of pigments, and a column spacer for control of the gap between cells [15,16].

The pigments, being used as the main colorants of the RGB pixels, show superior thermal and photo-chemical stability, but low optical and chromatic properties due to their aggregation behavior [17,18]. Dyes can be attractive alternatives to overcome this limitation because they dissolve in media and exist in molecular form, and this property can reduce light scattering. However, such advantages of the dyes can be effective only when they are compatible with the color resist, which consists of an industrial solvent, macromolecular binder, and various additives. If the structures of the dye molecules are not suitable for preventing intermolecular aggregation, the particle sizes of the dye can become bigger than those of the pigments. Also, if the structures are not sufficiently compatible with the binder and additives of the color resist, the dye molecules can re-aggregate after the baking process even though their structures are sufficiently soluble in the industrial solvents. Such problems have been pointed out as the major factors that deteriorate the optical property and thermal stability of dye-based LCD color filters [19]. Nevertheless, relatively little research has been carried out on these kinds of problems.

In this study, four novel yellow quinophthalone dyes were designed and synthesized to examine the relation between their molecular structures and aggregation behavior. In addition, the influence of the aggregation behavior on the properties of LCD color filters with the synthesized dyes was discussed thoroughly. The change of the dye aggregate size was observed by field emission scanning electron microscopy (FE-SEM), and the spectral and thermal property of the dye molecules were examined. In addition, the transmittance, contrast ratio, and color difference

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http://dx.doi.org/10.1016/j.dyepig.2013.09.024

values of spin-coated films with the synthesized dyes were investigated.

2. Experimental

2.1. Synthesis

2.1.1. 2-Methyl-8-quinolinylamine (*1*)

8-Nitroquinaldine (1.88 g, 0.01 mol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in ethanol (20 mL). An amount of $SnCl_2$ (11.27 g, 0.05 mol) was added and the resulting solution heated to 70 °C and stirred for 0.5 h. After reaction, the mixture was cooled to room temperature, and then poured into distilled water/ice (300 mL). Sodium bicarbonate was carefully added to adjust the pH to between 7–8. The crude product was extracted by treating with ethyl acetate (700 mL) in a separatory funnel and washed several times with brine. To remove the remaining moisture, the ethyl acetate solution of the crude product was dried with $MgSO_4$. After vacuum distillation, **1** was obtained as yellow oil, frozen to solid to be reacted for next step (1.30 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.70 (s, 3H), 4.95 (s, 2H), 6.89 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 7.24 (m, 2H), 7.94 (d, J = 8.5 Hz, 1H).

2.1.2. Trimellitic anhydride ethyl ester (*2*)

Trimellitic acid anhydride (1.92 g, 0.01 mol) was boiled with thionyl chloride (7.14 g, 0.06 mol) in THF (30 mL) for l h. The anhydride acid chloride was isolated by vacuum distillation of the solvent. The intermediate was then recrystallized from heptane giving rise to fine colorless needles.

Trimellitic anhydride acid chloride (6.32 g, 0.03 mol) and absolute ethanol (1.44 g, 0.045 mol) were dissolved in dry CH_2CI_2 (30 mL) and cooled to −60 °C (CO_2/acetone) under a dry N_2-atmosphere. Distilled pyridine (2.4 mL, 0.03 mol) was then added dropwise to the stirred mixture. After the addition was over, the solution was kept at −60 °C for 1 h, and then heated to room temperature, where it was stirred for a further 4 h. The reaction mixture was washed with water and dried over Na_2SO_4. After distillation of the solvent the residue was recrystallized from n-heptane to give **2** as a white solid (5.75 g, 87%) [20]. Mp > 95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (t, J = 20.5 Hz, 3H), 4.41 (q, J = 17.5 Hz, 2H), 7.78 (d, J = 13.0 Hz, 1H), 8.21 (s, 1H), 8.42 (d, J = 8.5 Hz, 1H).

2.1.3. N-[2-(2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-8-quinolyl] phthalimide (*QP1*)

1 (1.58 g, 0.01 mol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in trichlorobenzene (40 mL). Phthalic anhydride (1.48 g, 0.01 mol) was added and the resulting solution heated to 220 °C and stirred for 4 h. The mixture was then added with phthalic anhydride (1.48 g, 0.01 mol) again with $ZnCl_2$ (0.45 g, 0.003 mol) and heated under reflux further for 5 h. After reaction, the mixture was cooled to room temperature, and then poured into n-hexane (1000 mL) to be precipitated. The resulting suspension was filtered, washed with 1% aqueous NaOH several times and dried in vacuum oven for 24 h. The crude product was dissolved in $CHCl_3$, filtered again and the filtrate was evaporated to remove the solvent. The solid was purified on a silica gel column using 1.25/1 ethyl acetate/hexane as the eluent. The bright orange band was collected and concentrated producing **QP1** as a bright orange solid (2.18 g, 52%). Mp > 320 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, J = 7.0 Hz, 1H), 7.50 (t, J = 9.0 Hz, 1H), 7.52 (d, J = 5.5 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 7.68 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.93 (t, J = 8.5 Hz, 2H), 8.09 (d, J = 5.0 Hz, 1H), 8.11 (t, J = 11.5 Hz, 2H), 8.64 (d, J = 10.0 Hz, 1H); MALDI-TOF MS: m/z 418.99 (100%, [M + H$^+$]); Found: C, 74.41; H, 3.42; N, 6.73. Calc. for $C_{26}H_{14}N_2O_4$: C, 74.64; H, 3.37; N, 6.70.

2.1.4. N-[2-(2,3-dihydro-1,3-dioxo-1H-phenalen-2-yl)-8-quinolyl] 1,8-naphthalimide (*QP2*)

QP2 was synthesized in the same manner with **QP1** using **1** (1.58 g, 0.01 mol) and 1,8-naphthalic anhydride (1.98 g, 0.01 mol) twice and obtained as a yellow solid (2.07 g, 40%). Mp > 250 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 5.0 Hz, 2H), 7.82 (t, J = 7.5 Hz, 2H), 7.90 (t, J = 9.5 Hz, 2H), 8.01 (t, J = 10.5 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.0 Hz, 2H), 8.43 (d, J = 8.0 Hz, 1H), 8.66 (d, J = 7.5 Hz, 2H), 8.74 (d, J = 7.0 Hz, 1H), 9.68 (d, J = 9.5 Hz, 1H); MALDI-TOF MS: m/z 519.32 (100%, [M + H$^+$]); Found: C, 78.71; H, 3.42; N, 5.53. Calc. for $C_{34}H_{18}N_2O_4$: C, 78.76; H, 3.50; N, 5.40.

2.1.5. 4-tert-Butyl-N-[2-(5-tert-butyl-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-8-quinolyl]phthalimide (*QP3*)

QP3 was synthesized in the same manner with **QP1** using **1** (1.58g, 0.01 mol) and 4-*tert*-butylphthalic anhydride (2.04 g, 0.01 mol) twice and obtained as a bright orange solid (2.92 g, 55%). Mp > 320 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 1.48 (s, 9H), 7.49 (d, J = 7.5 Hz, 1H), 7.52 (s, 1H), 7.57 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.94 (t, J = 7.5 Hz, 1H), 8.03 (d, J = 7.0 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 7.0 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 14.20 (d, J = 8.5 Hz, 1H); MALDI-TOF MS: m/z 531.11 (100%, [M + H$^+$]); Found: C, 76.43; H, 5.72; N, 5.18. Calc. for $C_{34}H_{30}N_2O_4$: C, 76.96; H, 5.70; N, 5.28.

2.1.6. N-[2-(2,3-dihydro-1,3-dioxo-1H-inden-2-yl ethyl ester)-8-quinolyl]phthalimide ethyl ester (*QP4*)

QP4 was synthesized in the same manner with **QP1** using **1** (1.58 g, 0.01 mol) and **2** (2.20 g, 0.01 mol) twice and obtained as a bright orange solid (2.87 g, 51%). Mp > 320 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (t, J = 8.0 Hz, 3H), 1.48 (t, J = 8.0 Hz, 3H), 4.38 (q, J = 7.5 Hz, 2H), 4.52 (q, J = 7.0 Hz, 2H), 7.56 (d, J = 6.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H), 8.15 (s, 1H), 8.20 (t, J = 7.5 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 8.63 (d, J = 9.5 Hz, 1H), 8.67 (d, J = 10.0 Hz, 1H), 8.76 (d, J = 4.5 Hz, 1H), 14.47 (s, 1H); MALDI-TOF MS: m/z 563.03 (100%, [M + H$^+$]); Found: C, 68.14; H, 3.99; N, 5.01. Calc. for $C_{32}H_{22}N_2O_8$: C, 68.32; H, 3.94; N, 4.98.

2.2. Materials and instrumentation

8-Nitroquinaldine, trimellitic acid anhydride, $ZnCl_2$ purchased from TCI, and phthalic anhydride, 1,8-naphthalic anhydride, 4-tert-butylphthalic anhydride, $SOCl_2$, $SnCl_2$ purchased from Sigma–Aldrich were used as received. All the other reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Transparent glass substrates were provided by Paul Marienfeld GmbH & Co. KG. Commercial pigment-based color filter and acrylic binder were supplied by LG chem ltd.

^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz using chloroform-d and TMS, as the solvent and internal standard, respectively. Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI-TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix. Absorption and transmittance spectra were measured using an HP 8452A spectrophotometer. Elemental analysis was carried out with a Flash EA 1112 CNH analyzer. Chromatic characteristics of the spin-coated