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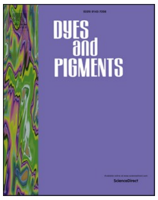

The synthesis of red dyes based on diketo-pyrrolo-pyrrole chromophore to improve heat stability and solubility for colour filter fabrication

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ABSTRACT

To replace the conventional red pigment derived from diketo-pyrrolo-pyrrole by new red dyes prepared in this research, an acetylene linkage was introduced between *N*-alkyl diketo-pyrrolo-pyrrole and naphthalimidyl moiety. TGA analyses and solubility measurement were carried out to compare those of conventional red pigment, C.I. Pigment Red 254, which has been most popular as a red pixel of color filter. Most of the new red dyes were prepared starting from C.I. Pigment Red 254 by the sequent reactions, *N*-alkylation, Sonogashira coupling, hydrolysis and further Sonogashira coupling. Chemical structures of all red dyes were confirmed by ^{1}H NMR and mass spectral analysis. TGA was carried out at 300 °C, and solubility measurement was carried out using by several organic solvents which can be used in the color filter fabrications. TGA indicated that the introduction of an acetylene linkage group into the *N*-alkyl diketo-pyrrolo-pyrrole ring combined by an *N*-butyl-naphthalimidyl system improved its heat stability. The result of weight reduction 1.4% at 300 °C can be identical to that of C.I. Pigment Red 254. The solubility of red dye prepared was observed around 5 g/L, therefore it can be used in the color filter fabrication process to eliminate the conventional photo-etching process.

1. Introduction

The fabrication process of color filters has been crucial for the quality of LCD or QD displays however due to the poor solubility of the trichromatic pigments, such as C.I. Pigment Red 254, C.I. Pigment Green 36, C.I. Pigment Blue 15:6, these colorants have to be prepared by a milling and photoresist solution causing an expensive manufacturing cost. Therefore various attempts to replace the conventional pigments by soluble dyes have tried especially for red color based on diketo-pyrrolo-pyrrole, perylene, naphthalene or coronene system, but most of potential red dyes exhibited insufficient performance in terms of heat stability during a post-baking stage in comparison of pigments [1–10]. In addition, the optical properties, such as a light transmittance and contrast ratio, of pigment-based color pixels reaches to maximum level, therefore most of manufacturing industries require enhanced optical properties. If soluble dye can afford sufficient heat-stability, required optical properties mentioned can be readily improved to substitute conventional pigments.

Judging from the literature, it can be presumed that the presence of one or acetylene groups in the dye molecule readily increases s-character by *sp*-hybridized orbitals resulting in heat stability [11,12]. In case of derivatives of triphenylamine connected with 1,8-naphthalimide via an ethynyl linkage group or up to three groups, 5% weight loss temperature ranged in 421–462 °C [13]. It was also reported that dyes based on 1,8-naphthalimide substituted at 3-position via imine bond with carbazole exhibited 345–368 °C of T_5 value (5% weight loss temperature) and 358–417 °C of T_{10} value (10% weight loss temperature) [14]. However, there is very limited literature reported on the thermal stability for diketo-pyrrolo-pyrrole based dyes containing acetylene linkage group and 1,8-naphthalimide ring.

In this study, the diketo-pyrrolo-pyrrole chromophore was modified by *N*-alkylation and incorporation of an acetylene linkage group substituted by a naphthalimide ring these can contribute the enhanced heat stability of dye molecule. For heat-stability of red dye, the weight reduction % by TGA analysis was tested at both 230 °C and 300 °C, where the results of 230 °C can correspond to the conditions of post-baking stage for color filter manufacturing. To evaluate the optical properties of dyes prepared, a spin-coating method using a pure dye solution was optimized which can be differential approach compared to previous literatures [3,15] those used extra binder system in the dye solution.

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2. Experimental

2.1. Materials and instrumentation

C.I. Pigment Red 254 used in experiment was manufactured by ENF Technology Co., Ltd. 1,8-naphthalic anhydride (99%), bromine (98%), sodium *tert*-butoxide (97%), potassium hydroxide (KOH) 2-methyl-3-butyn-2-ol (99%), ethynyltrimethylsilane (98%), copper iodide (99.5%), and bis(triphenylphosphine)palladium(II) dichloride (98%) were purchased from Sigma-Aldrich. *n*-butylamine (99%), *n*-bromoctane (98%), ethyl 2-bromopropionate (98%), ethyl bromoacetate (98%), were purchased from TCI. Triphenylphosphine (99%), copper(I) chloride (99%), and silver sulfate (98.5%) were purchased from Alfa-Aesar. 1-Methyl-2-pyrrolidone (NMP), trimethylamine (TEA), tetrahydrofuran (THF), *N,N*-dimethylmethanamide (DMF), ethanol, methanol, *n*-hexane, ethyl acetate, methyl chloride, and other solvents were purchased from Duksan Pure Chemical. All chemicals were used without any additional purification.

^{1}H NMR spectra were measured on a Bruker Avance 500 spectrometer at 500 MHz using dimethyl sulfoxide-d6 and chloroform-d as the solvent. Tetramethylsilane (TMS) was used as an internal standard. Elemental analysis was conducted with a ThermoFisher Flash 2000 elemental analyzer. Mass spectrometer was performed by gas chromatography/mass spectrometer (GC-MS; 7890 A-5975C GC/MSD, Agilent, USA).

2.2. Syntheses of dyes

2.2.1. 3,6-bis(4-bromophenyl)-2,5-dibutylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (intermediate 1): N-alkylation

C. I. Pigment Red 254 (4 g, 8.9 mmol) was added to DMF (80 mL) and trimethylamine (4 mL) mixed solvent and stirred at room temperature for 2 h. After stirring, add the potassium *tert*-butoxide (3.0 g, 22.3 mmol) and stir for 1 h. Then, add 1-bromobutane (3 g, 22.3 mmol) and stir for 12 h at room temperature under a nitrogen atmosphere. After reaction, the reaction solution was poured into water (150 mL), allowing precipitation of the crude product. The crude product was filtered and dried. After drying, dissolve the dried crude in 400 mL of ethyl acetate and filter to remove the unreactive C.I. Pigment Red 254 and evaporate the solvent to obtain the product. And pouring the obtained product into the chloroform/n-hexane (1:10) mixture, stir for 30 min to filter the extracted product using the difference in solubility to obtain *N,N′*-dialkylated components. The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 54.1%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 6*H*, CH_3), 1.31 (m, 4*H*, CH_2), 1.52 (m, 4*H*, CH_2), 3.88 (t, $J = 7.7$ Hz, 4*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH); GC-MS 559(M+); Elemental Analysis: Found: C, 55.93; H, 4.69; N, 5.02; calculated for: C, 55.43; H, 4.59; N, 5.12.

2.2.2. 3,6-bis(4-bromophenyl)-2-butylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (intermediate 2): N-alkylation

Intermediate **2** was synthesized following the same procedure for intermediate **1** using 1-bromobutane (1.8 g, 13.4 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 64.2%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 3*H*, CH_3), 1.31 (m, 2*H*, CH_2), 1.52 (m, 2*H*, CH_2), 3.88 (t, $J = 7.7$ Hz, 2*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 8.0 (s, 1*H*, NH); GC-MS 535(M+); Elemental Analysis: Found: C, 52.62; H, 3.61; N, 5.58; calculated for: C, 52.42; H, 3.51; N, 5.60.

2.2.3. 3,6-bis(4-bromophenyl)-2-octylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (intermediate 3): N-alkylation

Intermediate **3** was synthesized following the same procedure for intermediate **1** using 1-bromooctane (2.6 g, 13.4 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane(1:5). Yield: 53.2%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.88 (t, $J = 6.5$ Hz, 3*H*, CH_3), 1.29 (m, 10*H*, CH_2), 1.63 (m, 2*H*, CH_2), 3.88 (t, $J = 7.7$ Hz, 2*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 8.0 (s, 1*H*, NH); GC-MS 591(M+); Elemental Analysis: Found: C, 55.93; H, 4.69; N, 5.02; calculated for: C, 55.99; H, 4.72; N, 5.01.

2.2.4. ethyl 2-(3,6-bis(4-bromophenyl)-1,4-dioxo-4,5-dihydropyrrolo[3,4-c]pyrrol-2(1H)-yl)acetate (intermediate 4): N-acylation

Intermediate **4** was synthesized following the same procedure for intermediate **1** using ethyl bromoacetate (2.6 g, 13.4 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 51.1%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.29 (t, $J = 7.1$ Hz, 3*H*, CH_3), 4.13 (m, 2*H*, CH_2), 4.28 (s, 2*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 8.0 (s, 1*H*, NH); GC-MS 533(M+); Elemental Analysis: Found: C, 49.65; H, 3.03; N, 5.26; calculated for: C, 49.58; H, 3.01; N, 5.20.

2.2.5. ethyl 2-(3,6-bis(4-bromophenyl)-1,4-dioxo-4,5-dihydropyrrolo[3,4-c]pyrrol-2(1H)-yl)propanoate (intermediate 5): N-acylation

Intermediate **5** was synthesized following the same procedure for intermediate **1** using 2-bromopropionate (2.4 g, 13.4 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 57.2%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.29 (t, $J = 7.1$ Hz, 3*H*, CH_3),1.61 (s, 3*H*, CH_3) 4.21 (m, 2*H*, CH_2), 5.88 (s, 1*H*, CH), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 8.0 (s, 1*H*, NH); GC-MS 547(M+); Elemental Analysis: Found: C, 50.58; H, 3.32; N, 5.13; calculated for: C, 50.52; H, 3.29; N, 5.10.

2.2.6. 3-(4-bromophenyl)-2,5-dibutyl-6-(4-((trimethylsilyl)ethynyl)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-di one (intermediate 6)

A mixture of intermediate **1** (1.1 g, 2.0 mmol), ethynyltrimethylsilane (0.2 g, 2.0 mmol), cuprous iodide (0.008 g, 0.04 mmol), triphenylphosphine (0.026 g, 0.1 mmol), and bis(triphenylphosphine) Palladium(II)dichloride (0.04 g, 0.06 mmol) was carefully degassed and charged with nitrogen. Tetrahydrofuran (15 mL) and triethylamine (10 mL) were then added. The reaction mixture was refluxed for 24 h under a nitrogen atmosphere. The reaction was terminated with ammonia water (10 mL), then extracted with ethyl acetate (10 mL), washed with water (10 mL), dried over anhydrous magnesium sulfate, and evaporated to obtain the crude product. The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 50.1%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.08 (s, 9*H*, CH_3), 0.9 (t, $J = 6.5$ Hz, 6*H*, CH_3), 1.31 (m, 4*H*, CH_2), 1.52 (m, 4*H*, CH_2), 3.88 (t, $J = 7.7$ Hz, 4*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH); GC-MS 576(M+); Elemental Analysis: Found: C, 64.68; H, 6.13; N, 4.87; calculated for: C, 64.60; H, 6.11; N, 4.88.

2.2.7. 2-Butyl-5-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (Intermediate 7): hydrolysis

2-Butyl-5-(3-hydroxy-3-methylbut-1-ynyl)-1H-benzo[*de*] isoquinoline-1,3(2*H*)-dione (0.34 g, 1 mmol) and potassium hydroxide (0.16 g, 3 mmol) were added to anhydrous toluene (3 mL). The mixture was refluxed for 6 h under a nitrogen atmosphere and then filtered. The filtrate was evaporated to obtain the crude product, which was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/hexane). Yield: 72.3%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 3*H*, CH_3), 1.31 (m, 2*H*, CH_2), 1.56 (m, 2*H*, CH_2), 3.14 (t, $J = 7.7$ Hz, 2*H*, CH_2), 4.05 (s, 1*H*, CH), 7.79 (m, 1*H*, ArH), 8.10 (s, 2*H*, ArH), 8.41 (d, $J = 1.8$ Hz, 2*H*, ArH); GC-MS 278(M+); Elemental Analysis: Found: C, 77.96; H, 5.45; N, 5.05; calculated for: C, 77.90; H, 5.43; N, 5.10.

2.2.8. 2-Butyl-5-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (Dye 1): hydrolysis

Intermediate **6** (0.6 g, 1 mmol) and potassium hydroxide (0.16 g, 3 mmol) were added to anhydrous toluene (3 mL). The mixture was refluxed for 1 h under a nitrogen atmosphere and then filtered. The filtrate was evaporated to obtain the crude product, which was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/hexane). Yield: 48.3%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 9*H*, CH_3), 1.31 (m, 6*H*, CH_2), 1.56 (m, 6*H*, CH_2), 3.14 (t, $J = 7.7$ Hz, 6*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 7.79 (m, 1*H*, ArH), 8.14 (s, 2*H*, ArH), 8.41 (s, 2*H*, ArH); GC-MS 754 (M+); Elemental Analysis: Found: C, 66.75; H, 5.43; N, 5.50; calculated for: C, 66.80; H, 5.41; N, 5.56.

2.2.9. 5-((4-(4-(4-bromophenyl)-2,5-dibutyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethyn yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (Dye 2)

A mixture of intermediate **1** (1.1 g, 2.0 mmol), intermediate **7** (0.6 g, 2.0 mmol), cuprous iodide (0.008 g, 0.04 mmol), triphenylphosphine (0.026 g, 0.1 mmol), and bis(triphenylphosphine)Palladium(II)dichloride (0.04 g, 0.06 mmol) was carefully degassed and charged with nitrogen. Tetrahydrofuran (15 mL) and triethylamine (10 mL) were then added. The reaction mixture was refluxed for 24 h under a nitrogen atmosphere. The reaction was terminated with ammonia water (10 mL), then extracted with ethyl acetate (10 mL), washed with water (10 mL), dried over anhydrous magnesium sulfate, and evaporated to obtain the crude product. The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 48.6%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 9*H*, CH_3), 1.31 (m, 6*H*, CH_2), 1.56 (m, 6*H*, CH_2), 3.14 (t, $J = 7.7$ Hz, 6*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 7.79 (m, 1*H*, ArH), 8.14 (s, 2*H*, ArH), 8.41 (s, 2*H*, ArH); GC-MS 754(M+); Elemental Analysis: Found: C, 69.98; H, 5.30; N, 5.57; calculated for: C, 70.02; H, 5.34; N, 5.57.

2.2.10. 5-((4-(4-(4-bromophenyl)-5-butyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethynyl) -2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (Dye 3)

Dye **3** was synthesized following the same procedure for dye **2** using intermediate **2** (1 g, 2.0 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 47.6%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 6*H*, CH_3), 1.31 (m, 4*H*, CH_2), 1.56 (m, 4*H*, CH_2), 3.14 (t, $J = 7.7$ Hz, 4*H*, CH_2), 7.34 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 7.79 (m, 1*H*, ArH), 8.0 (s, 1*H*, ArH), 8.14 (s, 2*H*, ArH), 8.41 (d, $J = 1.8$ Hz, 2*H*, ArH); GC-MS 699(M+); Elemental Analysis: Found: C, 68.77; H, 4.62; N, 6.01; calculated for: C, 68.80; H, 4.60; N, 6.03.

2.2.11. 5-((4-(4-(4-bromophenyl)-5-octyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethyny l)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (Dye 4)

Dye **4** was synthesized following the same procedure for dye **2** using intermediate **3** (1 g, 1.8 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 43.2%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 6*H*, CH_3), 1.29 (m, 12*H*, CH_2), 1.63 (m, 4*H*, CH_2), 3.14 (t, $J = 7.7$ Hz, 2*H*, CH_2), 3.88 (t, $J = 7.7$ Hz, 2*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 5.5$ Hz, 4*H*, ArH), 7.79 (m, 1*H*, ArH), 8.0 (s, 1*H*, ArH), 8.19 (s, 2*H*, ArH), 8.41 (d, $J = 1.8$ Hz, 2*H*, ArH); GC-MS 755(M+); Elemental Analysis: Found: C, 70.12; H, 5.34; N, 5.47; calculated for: C, 70.03; H, 5.32; N, 5.58.

2.2.12. Ethyl 2-(3-(4-bromophenyl)-6-(4-((2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-5-yl)ethyn yl)phenyl)-1,4-dioxo-4,5-dihydropyrrolo[3,4-c]pyrrol-2(1H)-yl)acetate (Dye 5)

Dye **5** was synthesized following the same procedure for dye **2** using intermediate **4** (1 g, 1.9 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 45.2%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 3*H*, CH_3), 1.31 (m, 5*H*, CH_2), 1.56 (m, 2*H*, CH_2), 3.14 (t, $J = 7.7$ Hz, 2*H*, CH_2), 4.13 (m, 2*H*, CH_2), 4.28 (s, 2*H*, CH_2), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.79 (m, 1*H*, ArH), 8.0 (s, 1*H*, NH), 8.19 (s, 2*H*, ArH), 8.41 (d, $J = 1.8$ Hz, 2*H*, ArH); GC-MS 729(M+); Elemental Analysis: Found: C, 65.94; H, 4.15; N, 5.77; calculated for: C, 65.89; H, 4.10; N, 5.80.

2.2.13. Ethyl 2-(3-(4-bromophenyl)-6-(4-((2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-5-yl)ethynyl) phenyl)-1,4-dioxo-4,5-dihydropyrrolo[3,4-c]pyrrol-2(1H)-yl)propanoate (Dye 6)

Dye **6** was synthesized following the same procedure for dye **2** using intermediate **5** (1 g, 1.9 mmol). The crude product was purified by column chromatography (adsorbent: silica gel, eluent: ethyl acetate/n-hexane). Yield: 48.9%, ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.9 (t, $J = 6.5$ Hz, 3*H*, CH_3), 1.31 (m, 5*H*, CH_2), 1.62 (m, 5*H*, CH_3), 3.14 (t, $J = 7.7$ Hz, 2*H*, CH_2), 4.21 (m, 2*H*, CH_2), 5.58 (m, 1*H*, CH), 7.27 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.55 (d, $J = 8.1$ Hz, 4*H*, ArH), 7.79 (m, 1*H*, ArH), 8.0 (s, 1*H*, NH), 8.19 (s, 2*H*, ArH), 8.41 (d, $J = 1.8$ Hz, 2*H*, ArH); GC-MS 743(M+); Elemental Analysis: Found: C, 66.31; H, 4.34; N, 5.66; calculated for: C, 66.29; H, 4.31; N, 5.71.

2.3. PPP- MO (pariser–parr–pople molecular orbital) calculations

PPP MO calculations were carried out by using a PISYSYEM Version 6.2.

2.4. Discrete fourier transform (DFT) calculations

DFT calculations were carried out using the Gaussian 09 programs using the B3LYP, 6-31G as the standard for the geometry optimization of dyes. The band gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and electron density were calculated by FMO calculations.

2.5. Spectroscopic properties

UV–Visible spectroscopic analysis, the dyes were dissolved in *N,N*-dimethylformamide, and absorbance spectra were collected using a Thermo Scientific Evolution 300 UV–Visible spectrophotometer. Visible light transmission was measured using the UV–Vis spectrophotometer (Varian, Cary 4000). The incident beam and test piece surface are adjusted to 90°. The test piece was measured five times in the 200–800 nm area and then averaged out three transmittances except the highest and lowest values.

2.6. Solubility test

The solubility measurements were carried out according to KS M ISO 7579.

2.7. Thermal stability test

To investigate the thermal stability of dyes **1–6**. Thermogravimetric analyses (TGA) were performed. All samples were heated at a rate 10°C/min, under flowing nitrogen up to 400 °C.

2.8. Fabrication of color filters using synthesized dyes

A coating solution was prepared by mixing the dye **5** or **6**, PGMEA (1-Methoxy-2-propyl acetate) in the weight-ratio of 1–30 to 10. The resultant mixtures were coated on clean glass substrate sized of 5X5 cm. The initial speed of spin coating was 200 rpm for 10 s. Then, it was increased to 500 rpm for further 20 s. The solution coated glass was pre-baked at 80 °C for 20 min and finally post-baked at 230 °C for 1 h.

2.9. *Transmittance test*

Transmittance of red lights was measured using the Olympus Colorimeter OSP-200. The incident beam and test piece surface are adjusted to 90°. The test piece was measured five times in the 200–800 nm area and then averaged out three transmittances except the highest and lowest values.

2.10. *Contrast ratio*

Contrast ratio of color filter prepared was measured by BM-5A of Topcon SpectroRaidoMeter. The measurement standard was based on the contrast 1/30,000 (bare scale) of the glass substrate.

3. Results and discussion

3.1. *Dye structure design of target molecules*

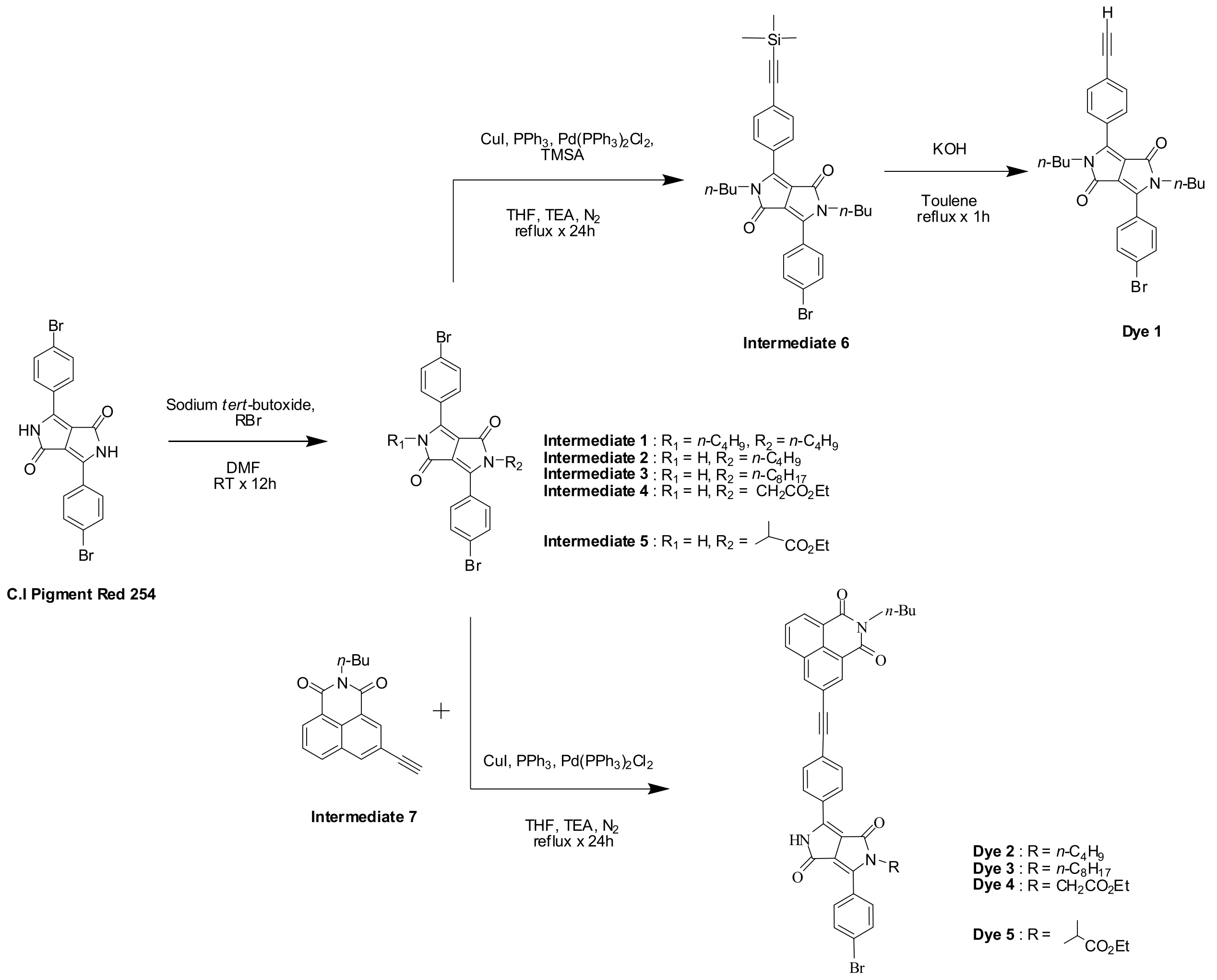
In the previous studies, 1,8-naphthalimidyl based dyes containing an ethynyl linkage group exhibited improved thermal-stability compared to that of corresponding dye which can due to the higher optical band gap calculated by TD-DFT method (B3LYP/6-31G) [11,16]. In case of dyes based on triphenylamine core group connected with 1 or 2–3 multiple 1,8-naphthalimidyl ethynyl linkage, the resultant thermal properties ($T_{5\%}$) found to be 421–462 °C [13]. Therefore, to improve the thermal-stability of the final dyes, an ethynyl group was substituted at 3-carbon position of naphthalene ring, then it was coupled to a phenyl ring of the diketo-pyrrolo-pyrrole, as shown in Scheme 1. As *N*-alkyl-1, 8-naphthalimidyl moiety can afford good stability to heat, the combination of an ethynyl group and 1,8-naphthalimidyl system was attempted to prepare final dyes.

To provide the red color, in this study, C.I. Pigment Red 254 which is based on diketo-pyrrolo-pyrrole chromophore was utilized as a starting material for the preparation of final red dyes **1**–**6**, however the displacement of the bromine atom by an ethynyl group should affect the absorption maximum of analogue dye comparing to that of C.I. Pigment Red 254, an *N*-substituent of the diketo-pyrrolo-pyrrole ring was carefully optimized to achieve absorption maximum to be in the range of red.

It was also reported that the *N*-alkylation of diketo-pyrrolo-pyrrole ring to be attributable to reduce strong intermolecular interactions caused by inherent stacking between red pigment molecules resulting in considerably increased solubility of 6.5–14.4 g/L in PGMEA (1-methoxy-2-propyl acetate) [1]. However, the requirement of the solubility for color filter fabrications to be compromised with the chemical stability of dyes, which should give rise to an opposite effect to solubility, thus the target of solubility was set to be around 5 g/L.

3.2. *Dye synthesis*

As described in Scheme 1, six red dyes **1**–**6** were prepared starting from C.I. Pigment Red 254, which contained two bromo substituents at



Scheme 1. Synthetic routes of the red dyes 1–6.

the phenyl ring, by the sequent reactions, *N*-monoalkylation or dialkylation, Sonogashira coupling, hydrolysis and Sonogashira coupling. In the alkylation process, a mixture of mono-alkylated intermediate and di-alkylated analogue was inevitably formed, therefore two products were simply separated by adding the reaction mixture into chloroform and n-hexane (1:10) solvent system resulting in a precipitation of mono-alkylated product, which was less soluble, leaving di-alkylated analogue in the solution. The reaction yields for intermediates **1**–**5** varied between 50–64% depending on an alkyl group that was due to the formation of a mixture, as mentioned above. For the preparation of final dyes **2**–**6**, a direct substitution reaction using Sonogashira coupling conditions starting from *N*-alkylated intermediates **1**–**5** with intermediate **7**, respectively, provided a reasonable reactivity where the resultant yields were obtained in the range of 43–48% after purification. The structure of six red dyes prepared shown in Fig. 1.

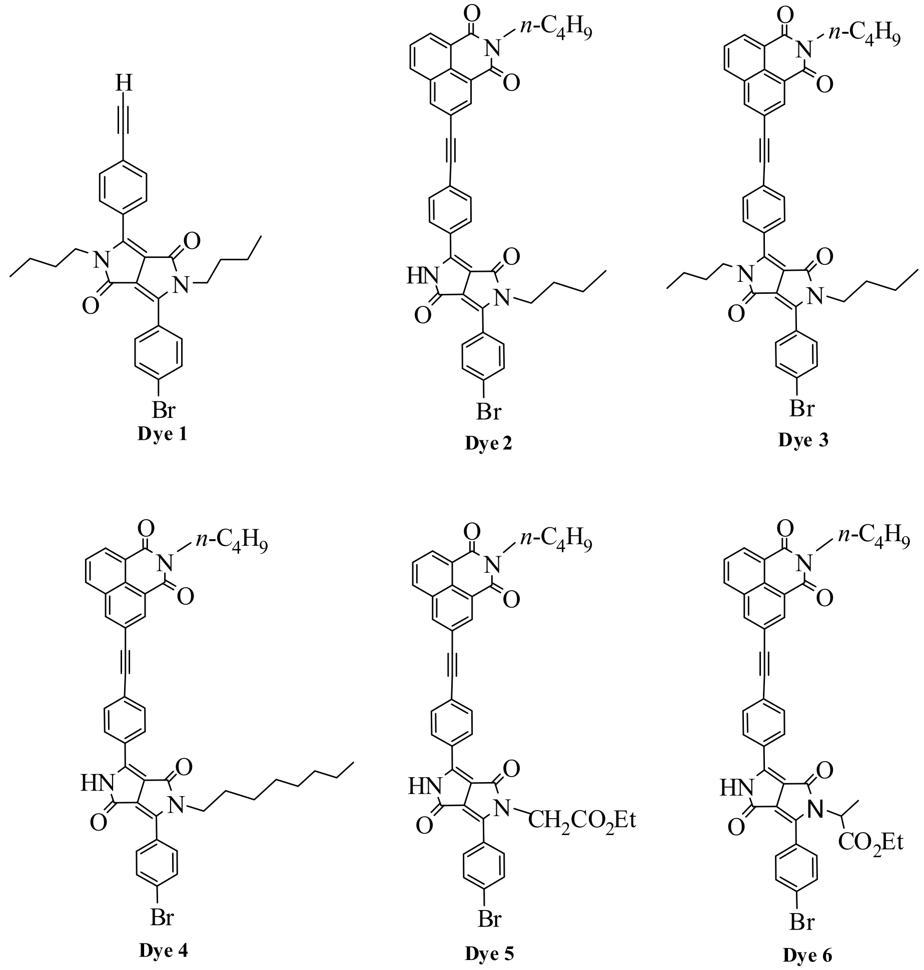
3.3. Spectroscopic properties

All six dyes blue-shifted in absorption maximum measured in DMF comparing to that of C.I. Pigment Red 254, as summarized in Table 1. The smallest deviation in hypsochromic shift was observed with dye **6** relative to absorption maximum of C.I. Pigment Red 254, whereas dye **3** containing an *N*-*n*-octyl substituent provided most blue shifted absorption maximum. Overall, the introduction of an electron donating group (R) into the nitrogen of diketo-pyrrolo-pyrrole ring gave rise to a hypsochromic shift, where the most red shifted dye was observed by *N*-isopropyl substituent comparing to that by normal alkyl analogues. By comparing the effects of *N*-substituent, dye **6** absorbed at a maximum of 508 nm whereas *n*-butyl substituted analogue (dye **3**) showed 498 nm of absorption maximum which can be explained that an ethyl ester group of propionate exerted smaller hypsochromic shift due to its electron-withdrawing inductive effect. In a direct comparison between *n*-butyl substituted dye **3** and *n*-octyl analogue **4**, it was observed that a longer carbon chain gave rise to a small bathochromic shift of 6 nm, thus dye **4** absorbed maximally at 504 nm whereas dye **3** was 498 nm in λ_{max}. In the case of di-*n*-butyl substituted dye **2** the difference of absorption maximum was found to be only 3 nm in comparison with that of mono-*n*-butyl substituted analogue **3**, therefore it can be assumed that introduction of a second alkyl substituent into the nitrogen of diketo-pyrrolo-pyrrole system exerted very small effect to the energy gap between ground state (HOMO) and excited state (LUMO).

In terms of molar extinction coefficient values, both dyes **5** and **6** provided relatively stronger color strength, 41,770 and 43,200 of ε_{max}, respectively, thus it can be explained by the contribution of comparatively weaker electron-donating groups, *n*-propionate and iso-

Table 1
Absorption maxima and molar extinction coefficient of dye **1–6** in DMF solution.

Dye	Absorption maximum (nm)	ε_{max} (L mol^{-5} cm^{-1})
C.I. Pigment Red 254	516 [1]	–
Dye **1**	494	31,600
Dye **2**	501	39,800
Dye **3**	498	38,400
Dye **4**	504	40,900
Dye **5**	502	41,700
Dye **6**	508	43,200



Dye 1 **Dye 2** **Dye 3**

Dye 4 **Dye 5** **Dye 6**

Fig. 1. Chemical structure of red dyes **1**–**6** based on diketo-pyrrolo-pyrrole.

propionate, relative to *n*-butyl or *n*-octyl analogues. The significant increases in molar extinction coefficient value were observed with the introduction of a naphthalimidyl system to the diketo-pyrrolo-pyrrole ring. All dyes **2**–**6** containing a naphthalimidyl ring showed ε_{max} higher than 38,400 up to 43,200, whereas dye **1** only gave 31,600 of ε_{max} value. Therefore it can also conclude that the extended conjugation of π orbitals exerted by naphthalimidyl ring readily contributed increased molar extinction coefficient value.

3.4. PPP-MO calculations

The PPP-MO method aims at a reliable theory to predict absorption maxima and intensities for coloured molecules by virtue of the successful combination of theoretical Roothaan equations with a semi-empirical theory. In this study, two analogue dyes **2** & **3** were calculated to compare the effects of mono-*N*-butyl substituent and *N,N′*-dibutyl substituents, as well as the calculations for dye **1** that only contains an acetylene group. Judging from the calculated band gaps between HOMO-LUMO for dyes **1–3**, the absorption maximum to be bathochromic shifted by the order of dye **1** → dye **3** → dye **2**. Similarly, the HOMO-LUMO band gap was predicted that dye **1** had the largest band gap (2.31 eV) compared with that of the dyes **2–3** (2.26–2.28 eV), therefore it was accordant with the observed absorption maximum, as shown Table 1 for dye **1**. However, the values of absorption maximum for all three dyes **1**–**3** seem to be not accurate by a PPP-MO method since the difference in absorption maximum between calculated and observed values was found with 42 nm, 46 nm, and 44 nm, respectively. Nevertheless, PPP-MO calculation can be useful to predict the tendency of absorption maxima for the analogue dyes.

The HOMO/LUMO band gap of the dyes **1**–**3** calculated with a PPP-MO method and observed absorption maximum data are shown in Table 2.

3.5. Discrete fourier transform (DFT) calculations

To compare the expected geometries of the highest occupied molecular (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by density functional theory (DFT) at B3LYP/6-31G(d) for two dyes **3** and **5**. As shown in Fig. 2, the calculated HOMO levels of dye **3** and **5** were obtained by −5.43, −5.42 eV, respectively. The HOMO energy levels of the synthesized dyes were similar. In the HOMO, the electron density distributions were delocalised due to the electron being localised in the DPP moiety and acetylene linkage, which act as electron-donating groups. The calculated LUMO levels of dyes **3** and **5** were also obtained by −2.61, −2.88 eV, respectively. In the case of dye **3**, the electron density distributions in the LUMO were localised due to the distortion of phenyl ring of DPP and naphthalimidyl group around the ethylene linkage. As a result, LUMO level of dye **3** was calculated to be higher than that of dye **5**. In contrast, dye **5** the LUMO energy value was lowered because benzene ring of DPP and naphthalimidyl were delocalised on the same side with respect to acetylene linkage. Also, it was confirmed that dye **5** exerted a small bathochromic shift in absorption maximum compared to that of dye **3** because the acyl group, which provided electron-withdrawing effect, was delocalised at the LUMO energy level.

Table 2
The HOMO-LUMO band gap, absorption maxima and color strength of the synthesized dyes **1–3** calculated by PPP-MO calculations.

Dye	Band gap (eV)	Absorption maxima (nm)	
		Calculated	Observed
Dye **1**	2.31	536	494
Dye **2**	2.26	547	501
Dye **3**	2.28	542	498

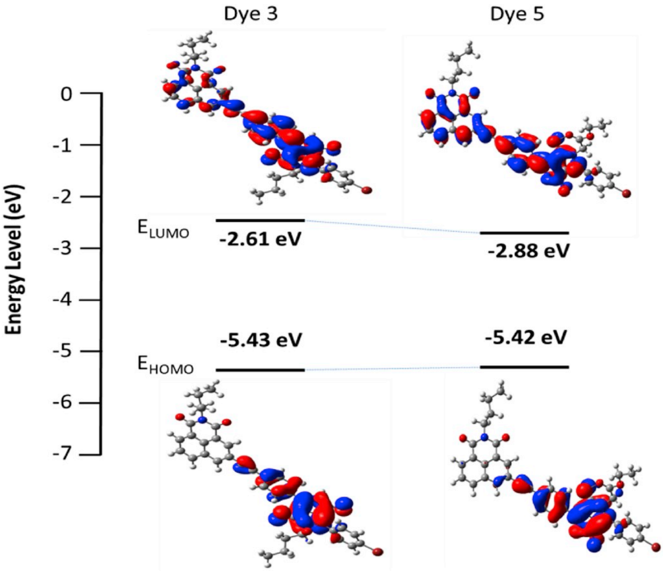


Fig. 2. The frontier orbitals of synthesized dyes **3** & **5**.

3.6. Thermal-stability properties

Thermal-stability was evaluated by the weight reduction (%), as mentioned in the experimental part. As summarized in Table 3, weight reduction (%) was checked at 230 °C and 270 °C, where 230 °C was corresponding to the post-baking temperature in the color filter fabrication process, and weight loss results at 270 °C was intended to discriminate relative thermal-stability of dyes **1**–**6** at a more severe temperature. Two dyes **1** & **2** substituted by *N*-di-alkyl groups in the diketo-pyrrolo-pyrrole ring showed comparatively inferior thermal-stability compared to that of other dyes **3**–**6** containing an *N*-mono-alkyl substituent. In case of dye **1**, the weight reduction was observed by 15.8% and 26.2% at 230 °C, 270 °C, respectively, and dye **2** also exhibited 14.7% and 21.0% at 230 °C, 270 °C, respectively. It can be explained that di-alkyl groups of nitrogen atoms readily diminished strong intermolecular interactions existing between dye molecules as usually formed pigment molecules, resulting in significantly decreased stability to heat. In contrast, four other dyes **3**–**6** provided much higher stability which ranged 0.6–4.4% at 230 °C and 0.9–5.6% at 270 °C, particularly two dyes **5** & **6** performed similar properties to that of C.I. Pigment Red 254. As it was clearly illustrated, the introduction of a naphthalimidyl ring via an ethynyl linkage group apparently contributed the enhancement of thermal-stability which can be attributable to the increased π orbital (*sp*) conjugation throughout dye molecule. Although the gaps in weight reduction (%) were not too large, however it can be also revealed that *N*-alkyl substituents containing ethyl ester moiety in dye **5** & **6** contributed improved stability further in comparison with *N*-*n*-butyl or *N*-*n*-octyl groups. The results observed by dye **5**, weight reduction of 0.6% and 0.94% at 230 and 270 °C, respectively, to be extremely stable to heating conditions for simulating to color filter

Table 3
The weight loss (%) of dye **1–6** by TGA analysis measured at 230 °C and 270 °C.

Dye	Weight loss (%)	
	230 °C	270 °C
C.I. Pigment Red 254	0.37	0.43
Dye **1**	15.8	26.2
Dye **2**	14.7	21.0
Dye **3**	2.1	4.9
Dye **4**	4.4	5.6
Dye **5**	0.6	0.94
Dye **6**	1.8	1.4

fabrication. It was interesting that dye **4** exerted comparatively less weight reduction over 300 °C which may be associated with a long carbon chain, *n*-octyl group, presented in the nitrogen atom of diketo-pyrrolo-pyrrole ring, as shown in Fig. 3.

Judging from these results mentioned, two dyes **5** & **6** exerted comparatively similar thermal-stability to that of C.I. Pigment Red 254, therefore these were selected as potential red dye for the fabrication process of color filter.

3.7. *Solubility properties*

It was reported that *N*-substitution by an alkyl group in the DPP (diketo-pyrrolo-pyrrole) based pigment molecule afforded solubility in common organic solvents, such as PGMEA [1]. Two dyes **1** & **2** exhibited inferior thermal-stability, as discussed previously, were excluded for the solubility test, thus Table 3 shows the results of solubility measured in methylene chloride for dyes **3**–**6**. All four dyes provided similar solubility irrespective to their structure in the range of 4.4% for dye **5** up to 5.6% for dye **4**. From the industrial point of view, the required solubility for a spin-coating process using a dye solution eliminating any dispersing agent or binder to be around 4–5 g/L, therefore the results illustrated in Table 4 can sufficient for the industrial requirement. Nevertheless, only two dyes **5** & **6**, featured as more stable dye to heat, were carried out to examine their transmittance property and contrast ratio after a spin-coating & backing treatments.

Table 4
Solubility of dye **3–6** in methylene chloride.

Dye	Solubility (g/L)
C.I. Pigment Red 254	insoluble
Dye **3**	5.3
Dye **4**	5.6
Dye **5**	4.4
Dye **6**	5.0

3.8. *Transmittance and contrast ratio properties*

Transmittance of red lights after post-baking process of red dye on a glass substrate directly relate to the efficiency of back-light of LED displays, therefore it will be beneficial that this value close to 100%. However irrespective of dye or pigment, some parts of red lights have to be absorbed and reflected when lights pass through the glass substrate, thus it is generally acceptable that transmittance value is over 90% in the industrial aspects. In this study, two dyes **5** & **6** those exerted comparatively higher thermal-stability were examined by their transmittance, as shown in Fig. 4 and Table 5. In the range of 550–580 nm, it was observed that two dyes **5** & **6** absorbed some lights compared to C.I. Pigment Red 254 which may be associated with their shorter λ_{max} than pigment analogue. Although the difference seems to be small, dye **6** exhibited higher transmittance than dye **5**, where 94.5% of transmittance for dye **6** was equivalent to that of C.I. Pigment Red 254. Therefore, dye **6** was chosen for the contrast ratio test.

The contrast ratio, that is the ratio of the luminance of the brightest color (white) to that of the darkest color (black), becomes a crucial property to provide improved quality of LED displays, particularly as the panel size increased the contrast ratio to be paid attentions. As higher the contrast ratio value, the black and white colours can be highly distinguished leading to improved quality of displays. Thus color filter and final panel manufacturers have been in pursuit of improving contrast ratio particularly for red color to meet the requirements in the market. Among trichromat pigments, the contrast ratio of red color has been lowest, around 10000 for C.I. Pigment Red 254, whereas 20000 for blue and green pigments. As Table 6 illustrates, the contrast ratio of dye **6** was significantly improved by 14300 that was 43% higher than C.I. Pigment Red 254. Therefore, the improved contrast ratio reported in this study, can contribute the overall enhancement of the quality for display panels.

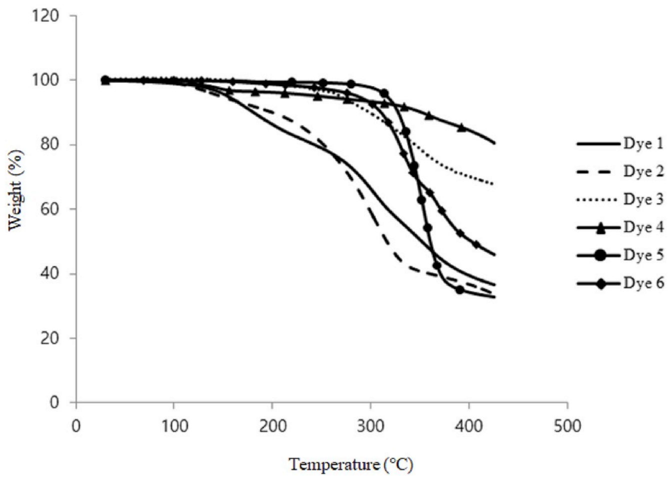


Fig. 3. The weight reduction curves of dyes **1–6** determined by TGA at the heating rate of 10 °C min^{-1}.

4. Conclusion

Six red dyes were prepared starting from C.I. Pigment Red 254, which contained two bromo substituents at the phenyl ring, by the sequent reactions, *N*-monoalkylation or dialkylation, Sonogashira coupling, hydrolysis and Sonogashira coupling. By comparing the effects of *N*-substituent, dye **6** absorbed with a maximum at 508 nm whereas *n*-butyl substituted analogue (dye **3**) showed 498 nm of absorption maximum which can be explained that an ethyl ester group of propionate exerted smaller hypsochromic shift due to its electron-withdrawing inductive effect. In terms of molar extinction coefficient, all dyes **2**–**6** containing a naphthalimidyl ring showed ε_{max} higher than 38,400 up to 43,200, whereas dye **1** only gave 31,600 of ε_{max} value. For dyes **1–3**, the absorption maximum to be bathochromic shifted in the order of dye **1** → dye **3** → dye **2** which was exactly accordant to the calculated order by a PPP-MO method. In terms of weight reduction (%) by TGA analyses, two dyes **5** & **6** performed similarly to that of C.I. Pigment Red 254 that indicated that the introduction of a naphthalimidyl ring via an ethynyl linkage group apparently contributed the enhancement of thermal-stability which can be attributable to the increased π orbital (*sp*) conjugation throughout dye molecule. Four dyes **3**–**6** provided similar solubility in CH_2Cl_2 irrespective to their structure in the range of 4.4% for dye **5** up to 5.6% for dye **4**, these values can be sufficient for the preparation of a dye solution using PGMEA to evaluate their contrast ratio and transmittance properties. When dye solution was spin-coated on a glass substrate then post-baking treated, dye **6** exhibited higher transmittance than dye **5** which was equivalent to that of C.I. Pigment Red 254. The contrast ratio of dye **6** was significantly improved by 14300 which was 43% higher than C.I. Pigment Red 254.

It should be emphasized that the enhancement of contrast ratio after post-baking by new red dye containing an ethynyl linkage group connecting diketo-pyrrolo-pyrrole chromophore with a naphthalimidyl group can enable red dye to be prepared as a dye solution without any binder or dispersing agent, then to be stable to post-baking temperature of the color filter fabrications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

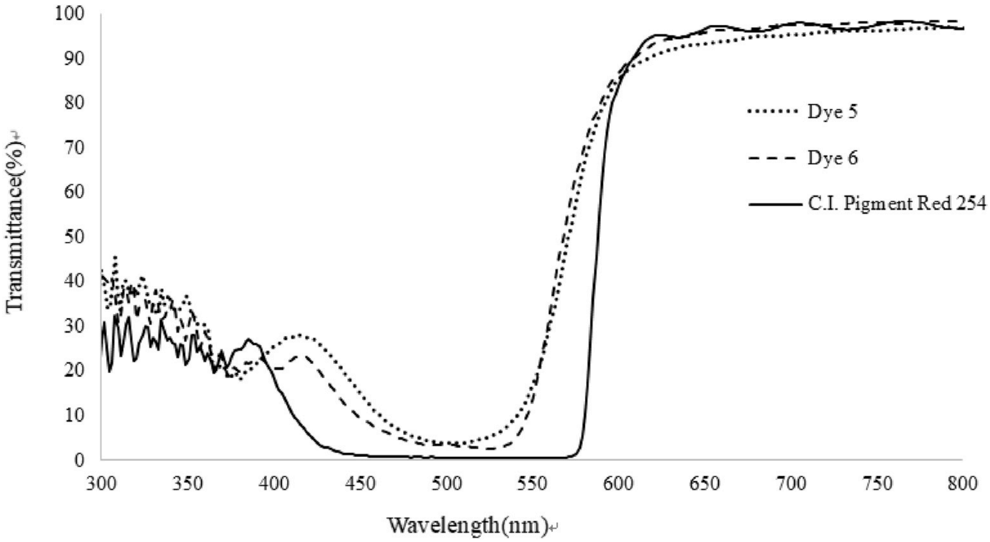


Fig. 4. Transmittance of synthesized dyes **5** and **6** compared to C.I. Pigment Red 254 after post-baking at 230 °C.

Table 5
Transmittance of synthesized dyes **5** and **6** at 630 nm compared to C.I. Pigment Red 254 after post-baking at 230 °C.

Dye	Maximum transmittance (%)
C.I. Pigment Red 254	94.9
Dye **5**	92.1
Dye **6**	94.5

Table 6
Contrast ratio of synthesized dye **6** compared to that of C.I. Pigment Red 254.

Dye	Contrast ratio
C.I. Pigment Red 254	10000
Dye **6**	14300

Acknowledgements

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