Flow Synthesis of Cyanine Dyes for Absorbing Orange Light from the Neon Gas Discharge

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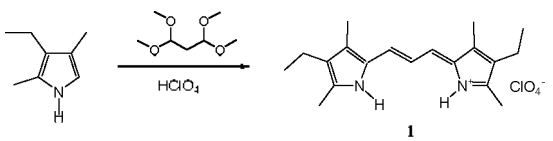
Color compensation technology made it possible to enhance the image quality of plasma panel display (PDP) devices. We examined the chemicals used in color compensation filters for PDP units in this study. Neon excitation during the plasma discharge causes orange light with an emission wavelength of 585 nm to be emitted from PDP devices.[1] This emitted orange light is mainly responsible for the degradation of color purity in PDP devices.[2] We synthesized three types of closed chain trimethine cyanines to attenuate unwanted spectral emissions having a wavelength 585 nm. Their common uses in PDP are near infrared absorbance filter. In this study, cyanines have been applied to neon orange light absorbing filter. By varying the number of carbons in the methine bridge of cyanine compound or by modifying the cyanine ring structure,[3,4] it is possible to synthesize cyanine structure absorbing particular wavelength and solvent solubility.

A simple closed chain trimethine cyanine chromophore was synthesized by the condensation of 3-ethyl-2,4-dimethylpyrrole (kryptopyrrole) and TMOP with perchloric acid as shown in Scheme 1. Cyanine **1** was continuously synthesized using microchannel mixer and an extension tube. Kryptopyrrole was fed into one side of the microchannel mixer and the other reactants were fed into the other side. The reactants were mixed at the microchannel mixer and the reaction was carried out in the extension tube by heating at 60 °C. The microchannel mixer was operated at room temperature to avoid clogging it with precipitated solid particles. The volume of the extension tube was 10 mL, causing the retention time to vary from 0.37 s to 1.6 s depending on the total flow rate used in the experiment. We observed that a retention time of 0.37 s was sufficient to convert all reactants into product. A higher mass flow rate resulted in a shorter reactant retention time, thereby reducing the formation of byproducts. Cyanine **1** was produced with a yield of 95% and was 99.5% pure and dissolved in 2-butanone had a sharp absorption band at 580 nm with a half bandwidth of 36 nm. In comparison, azo or anthraquinone compounds typically had bandwidths of over 100 nm.[5] The width of the absorption band is dependent upon how closely the molecular structure in the first excited state resembles that in the ground state. The long conjugated chain structure of **1** was accompanied by a corresponding decrease in bandwidth.[6] The molar absorptivity of **1** was measured as 136,130 $M^{-1}cm^{-1}$.

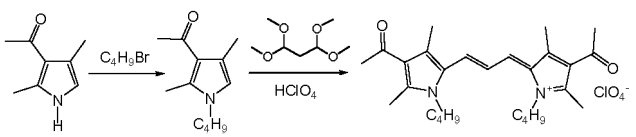
We synthesized a closed chain trimethine cyanine structure using 1-butyl-3-acetyl-2,4-dimethylpyrrole and 1,1,3,3-tetramethoxypropane in the presence of perchloric acid as shown in Scheme 2. For the first step, several basic reagents were tested to generate a pyrrolyl anion for the alkylation of the nucleus in 3-acetyl-2,4-dimethylpyrrole with 1-bromobutane. Alkylation in the presence of potassium hydroxide in dimethyl sulfoxide gave 1-butyl-3-acetyl-2,4-dimethylpyrrole with a 75 % yield. Other strong basic reagents such as potassium hydroxide in a solution of sodium amide or aqueous potassium hydroxide (50%) with tetrabutylammonium bromide in dichloromethane were also tested and delivered yields of 50% and 48%, respectively. Alkylation with sodium hydride in dimethyl sulfoxide increased the yield to 95%. The strong base, sodium hydride, reacts with dimethyl sulfoxide to produce dimsyl ions, which can effectively remove protons from the nucleus in 3-acetyl-2,4-dimethylpyrrole, thereby resulting in a more efficient alkylation with 1-bromobutane. The experimental result showed that **2** was obtained with a 70% yield and 98% purity. Some product loss took place during the washing and solid recovery steps. Cyanine **2** dissolved in 2-butanone had a maximum absorption at 580 nm with a half bandwidth of 39 nm. The molar absorptivity of **2** in 2-butanone was 32,303 $M^{-1}cm^{-1}$.

Another closed chain trimethine cyanine chromophore was synthesized using 1-dodecyl-2-methylindole as shown in Scheme 3. The alkylation of 2-methylindole was carried out using a strong base such as sodium hydride in dimethyl sulfoxide as discussed above. However, alkylation resulted in a low yield. To improve the alkylation reactivity, we employed a Finkelstein reaction, which resulted in the in situ conversion of 1-dodecyl bromide to 1-dodecyl iodide. The yield of 1-dodecyl-2-methylindole in this case increased to 95.5% as



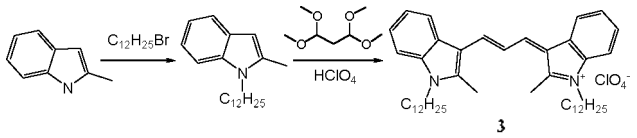
1

Scheme 1



2

Scheme 2



3

Scheme 3

shown at Table 1. Cyanine **3** was produced using 1-dodecyl-2-methylindole at a 64% yield and a purity of 99.9%. When dissolved in 2-butanone, **3** had a maximum absorption band at 570 nm with a half bandwidth of 39 nm and a molar absorptivity of 29,178 $M^{-1}cm^{-1}$.

A trimethine chain was used to join the two nitrogens, which were each independent parts of a heteroaromatic moiety such as pyrrole or indole. The pyrrole derivates for **1** were produced easily using flow chemistry with a 95% yield and a purity of 99.5% without byproducts. The alkylation of the pyrrole derivatives was carried out using a C_4 linear hydrocarbon and a strong base such as sodium hydride or dimethyl sulfoxide. The alkylation yield of **2** exceeded 95%. For the long chain alkylation of the indole derivatives in **3**, we employed sodium iodide with sodium hydride and dimethyl sulfoxide. The alkylation yield in this case was 95.5%.

All the cyanines could absorb orange light from a neon gas discharge. Among them, however, cyanine **1** had a greater molar absorptivity. Cyanine **1** was capable of absorbing the same amount of light as the other cyanine dyes, but with a molar concentration that was five times less. High temperature tests were conducted for cyanine **1** coated films at 80 °C for 500 h. Cyanine **1** offered an absorbance deterioration of less than 1% at these conditions when it was coated on a PET film. Table 2 shows that the coordinates in the Commission Internationale de l'Eclairage (CIE) chromaticity diagram of the PDP device spectrum. The color reproducibility was increased by 7.9% overall and the red color purity was greatly enhanced with the cyanine dye coated color compensation filter. The center of color coordinates, the white light emission, moved from (x = 0.292, y = 0.299) to (x = 0.282, y = 0.292) and corresponded to an increase in color temperature from 7800 K to 10,300 K when the color compensation filter was applied.

Experimental Section

All of the reagents and solvents were obtained from Sigma Aldrich Co. and were used without further purification. Absorption spectra were obtained using a UV-Vis spectrophotometer (Shimadzu UV-2450). Our HPLC findings are described as area % (AP).

(Z)-4-Ethyl-2-((E)-3-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl) allylidene)-3,5-dimethyl-2*H*-pyrrolium perchlorate (1). The two feeds were pumped such that they mixed in the micromixer (HPIMM with hastelloy high pressure mixer inlays, channel width 45 μm, 250 μm channel depth, Institut für Mikrotechnik Mainz GmbH, Germany) followed by the extension tube. Cyanine **1** was collected in the jacketed filter reactor after cooling with an anti-solvent. Upon drying, cyanine **1** was assessed by NMR spectroscopy. Kryptopyrrole (0.405 mol) was fed into one side of the micromixer at a flow rate of 2.224 mL/min. The other feed contained TMOP (0.177 mol), perchloric acid (0.555 mol), ethanol (0.834 mol) and chloroform (1.214 mol) and was pumped at a flow rate of 8.490 mL/min. After mixing in the micromixer, the temperature of the resulting solution was maintained at 60 °C. The suspension of **1** was collected in 2 L in a jacketed filter reactor by washing with octane and water and drying for 12 h. After drying, **1** was assessed by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.70 (s, 2H), 7.31 (dd, J = 9.5, 7.5 Hz, 1H), 7.24 (d, J = 9.5 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 2.40 (s, 6H), 2.37 (q, J = 6.5 Hz, 4H), 2.17 (s, 6H), 1.04 (t, J = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 149.67, 138.64, 137.97, 131.51, 130.65, 114.28, 17.33, 14.48, 12.62, 9.66. FTIR (KBr, cm^{-1}, peak intensity): 3305 (m), 2961 (m), 2928 (m), 1504 (s), 1539 (s), 1427 (s), 1163 (s), 1101 (s), 942 (s), 631 (s), 566 (m). Anal calcd. for $C_{20}H_{31}ClN_2O_4$: C, 60.22; H, 7.83; N, 7.02. found: C, 60.10; H, 7.61; N, 6.87.

1-Butyl-3-acetyl-2,4-dimethylpyrrole. Sodium hydride (7 g,

Table 1. Alkylation of 2-methylindole

2-methylindole (equivalent)	NaH (equivalent)	NaI (equivalent)	1-bromododecane (equivalent)	1-dodecyl-2-methylindole (area %)
1	3.0	-	1.3	41.2
1	1.3	0.2	1.3	90.8
1	2.5	0.2	1.7	94.5
1	2.1	0.2	1.7	95.5

Table 2. Color coordinates of the CIE chromaticity of the PDP devices and NTSC (National Television Standard Committee) standard

	NTSC	PDP module	PDP module with optical filter
Red (x,y)	(0.670, 0.330)	(0.642, 0.353)	(0.666, 0.325)
Green (x,y)	(0.210, 0.710)	(0.282, 0.656)	(0.247, 0.673)
Blue (x,y)	(0.140, 0.080)	(0.148, 0.060)	(0.146, 0.057)
White (x,y)	(0.333, 0.333)	(0.292, 0.299)	(0.282, 0.292)
Color reproducibility	100%	80.3%	92.8%

60% dispersion in mineral oil, 0.175 mol), washed with hexane under nitrogen, was suspended in dimethyl sulfoxide (291.6 mL) at 60 °C. 3-Acetyl-2,4-dimethylpyrrole (20 g, 0.15 mol) was slowly added to the sodium hydride solution over 10 min. 1-Bromobutane (28 g, 0.2 mol) was then slowly added and the temperature raised to 70 °C. The resulting solution was stirred for an hour at 60 °C and then cooled to room temperature. After 1 h at room temperature, water (583 mL) was added and extracted with ethyl acetate (145 mL). After evaporating the solvents, 1-butyl-3-acetyl-2,4-dimethylpyrrole (28.2 g) was obtained with 95% purity. A HP 1100 LC/MSD (Agilent) was used to identify 1-butyl-3-acetyl-2,4-dimethylpyrrole. The analyses were performed on a reversed phase column (Capcellpak C18, 3 μm, 50 × 4.6 mm column) with UV detection at 254 nm and with a 30% to 100% acetonitrile elution over 15 min at a flow rate of 1 mL/min. 1-Butyl-3-acetyl-2,4-dimethylpyrrole (RT 5 min) displayed a protonated molecular ion $[M+H]^+$ at m/z 194.

(Z)-4-Acetyl-2-((E)-3-(4-acetyl-1-butyl-3,5-dimethyl-1*H*-pyrrol-2-yl)allylidene)-1-butyl-3,5-dimethyl-2*H*-pyrrolium perchlorate (2). The production setup was the same as previous experiments. Two HPLC pumps were used to feed the two reactants into the micromixer. One feed was 1-butyl-3-acetyl-2,4-dimethylpyrrole (0.22 mol, 42.5 g). The other feed contained TMOP (16.4 g), perchloric acid (32.16 g), ethanol (49.26 g) and chloroform (16.4 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (t, 1 H, J = 13.25 Hz), 8.54 (d, 1 H, J = 13.31 Hz), 4.34 (t, 4 H, J = 7.29 Hz), 2.7 (s, 6 H), 2.6 (s, 6 H), 2.5 (s, 6 H), 1.75 (m, 4 H, J = 8.31 Hz, J = 7.61 Hz), 1.47 (m, 4 H, J = 7.96 Hz, J = 7.27 Hz), 0.97 (t, 6 H, J = 7.33 Hz). ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 151.47, 138.91, 125.65, 125.33, 125.21 (2C), 121.70, 119.60, 118.22, 111.51, 45.10, 31.90, 29.59, 29.54, 29.43, 39.32, 29.26 (2C), 26.94, 22.68, 14.11, 11.65. FTIR (KBr, cm^{-1}, peak intensity): 2922 (s), 2852 (m), 1587 (m), 1568 (s), 1439 (s), 1189 (s), 1140 (s), 1088 (s), 753 (w). Anal calcd. for $C_{28}H_{43}ClN_2O_6$: C, 62.38; H, 8.04; N, 5.20. found: C, 62.56; H, 7.88; N, 4.96.

1-Dodecyl-2-methylindole. Sodium hydride (22.9 g, 60% dispersion in mineral oil, 0.57 mol), washed with hexane under nitrogen, was suspended in dimethyl sulfoxide (457.4 mL) at 60 °C. Sodium iodide (6.86 g, 0.046 mol) and 2-methylindole (30 g, 0.23 mol) was slowly added to the sodium hydride solution over 10 min. When mixed, the sodium hydride and sodium iodide solution was white in color. When 1-bromododecane (74 g, 0.30 mol) was slowly added, the solution turned purple. The resulting solution was stirred for an hour at 60 °C and was then cooled to room temperature. The final mixture was orange in color. After 1 h at room temperature, water (457 mL) was added and extracted with ethyl acetate (205 mL). After evaporating the solvents, 1-dodecyl-2-methylindole (68.4 g) was obtained with 95% purity. A HP 1100 LC/MSD (Agilent) was used to identify 1-dodecyl-2-methylindole. The analyses were performed on a reversed phase column (Capcellpak C18, 3 μm, 50 × 4.6 mm column) with UV detection at 280 nm and with an acetonitrile elution from 50% to 100% over 10 min at a flow rate of 1 mL/min. The elution was held for 10 min. 1-dodecyl-2-methylindole (RT 11.7 min) displayed a protonated molecular ion $[M+H]^+$ at m/z.

(Z)-1-Dodecyl-3-((E)-3-(1-dodecyl-2-methyl-1*H*-indol-3-yl)allylidene)-2-methyl-3*H*-indolium perchlorate (3). As described above, two HPLC pumps were used to feed the two reactants. One feed was 1-dodecyl-2-methylindole (0.080 mol) in ethanol (0.218 mol) and was pumped at a flow rate of 2.595 mL/min. The other feed contained TMOP (0.037 mol), perchloric acid (0.050 mol), ethanol (0.098 mol) and chloroform (0.098 mol) and was pumped at a flow rate of 3.577 mL/min. The two feeds mixed in the micromixer followed by the extension tube. Cyanine **3** was collected in the jacketed filter reactor after cooling with an anti-solvent. Upon drying, **3** was assessed by NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, 1 H, J = 7.1 Hz), 8.04 (d, 1 H, J = 7.1 Hz), 7.51 (m, 1 H), 7.44-7.41 (m, 2 H), 4.19 (m, 2 H), 2.93 (m, 3 H), 1.83 (m, 2 H), 1.40-1.21 (m, 18 H), 0.84 (t, 3 H, J = 6.4 Hz). ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 195.67, 151.52, 149.00, 132.79, 129.95, 44.64, 33.05, 31.98, 19.78, 15.42, 13.85, 13.82. FTIR (KBr, cm^{-1}, peak intensity): 2960 (w), 2933 (w), 1668 (m), 1574 (s), 1395 (s), 1356 (s), 1170 (s), 1137 (s), 1093 (s), 1035 (m), 955 (m), 623 (w), 574 (w). Anal calcd. for $C_{45}H_{67}ClN_2O_4$: C, 73.49; H, 9.18; N, 3.81. found: C, 73.24; H, 8.95; N, 3.98.

References

1. Ralchenko, Y. Y.; Kramida, A. E.; Reader, J. and NIST ASD Team, *NIST Atomic Spectra Database*, available: http://physics.nist.gov/PhysRefData/ASD/.
2. Boeuf, J. P. *J. Phys. D:Appl. Phys.* **2003**, *36*, R53.
3. Zhang, X. H.; Wang, L. Y.; Zhai, G. H.; Wen, Z. Y.; Zhang, Z. X. *Bull. Korean Chem. Soc.* **2007**, *28*, 2382.
4. Treibs, A.; Grimm, D. *Justus Liebigs Annalen der Chemie* **1978**, *12*, 2028.
5. Gordon, P. F.; Gregory, P. *Organic Chemistry in Colour*, Springer-Verlag: 1987.
6. Klessinger, M. *Theoret. Chim. Acta* **1966**, *5*, 251.