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New Copper Complex Derivatives Including Bis-Dipyrrinato Ligand for Color Filter Pigments

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Four red compounds for color filter (CF) pigments in which phenyl, 4-chloro-phenyl, 4-fluoro-phenyl and pentafluorophenyl groups are substituted to 5-position of dipyrrinato group based on bis-dipyrrinato ligand were synthesized, and physical properties from changing the substitution groups of the synthesized materials were systematically examined. The UV-visible spectra of the synthesized materials showed maximum absorption wavelengths of about 460∼477 nm in solution state and 510∼530 nm in film state, indicating red color. It was confirmed that the extinction coefficient values (log ε) of all the synthesized materials are very excellent at 4.7 or above. All HOMO levels measured through cyclic voltammograms showed similar values at 5.4 through 5.5 eV, regardless of the substitution group. They were also shown to possess high potential to be applied as pigment for LCD color filter, since T_m and T_d values of three synthesized materials exhibit thermal stability higher than 250°C. In film surface property, the synthesized compounds showed smooth surface overall.

Keywords Bis(dipyrrinato)copper complex; color filter; molar extinction coefficiency; pigment

Introduction

In the past, dyes and pigments have been mainly used for paints, inks, plastics, fabrics and etc. [1–3]. However, recently with rapid development of display industry in the contemporary society along with the development of information technology industry, these materials are extending their potential of application as the core material of color filter (CF) that implements full color spectrum of liquid crystal display (LCD). Furthermore in these days, the same dye and pigment materials are widely applied in image sensors which are used in charge-coupled device (CCD) camera and web-camera [4]. The way dyes and pigments work in CF is that when white-backlight is injected to CF, red, green and blue pigments, it implements full color spectrum by respectively reflecting or absorbing light of particular wavelength [5–7]. Therefore, since light of desired wavelength should be penetrated massively and light of the remaining wavelengths be filtered to maximum extent, the optical property required of pigments used in CF should have high molar extinction coefficient on the wavelength that requires absorption [4]. Also, another property is that

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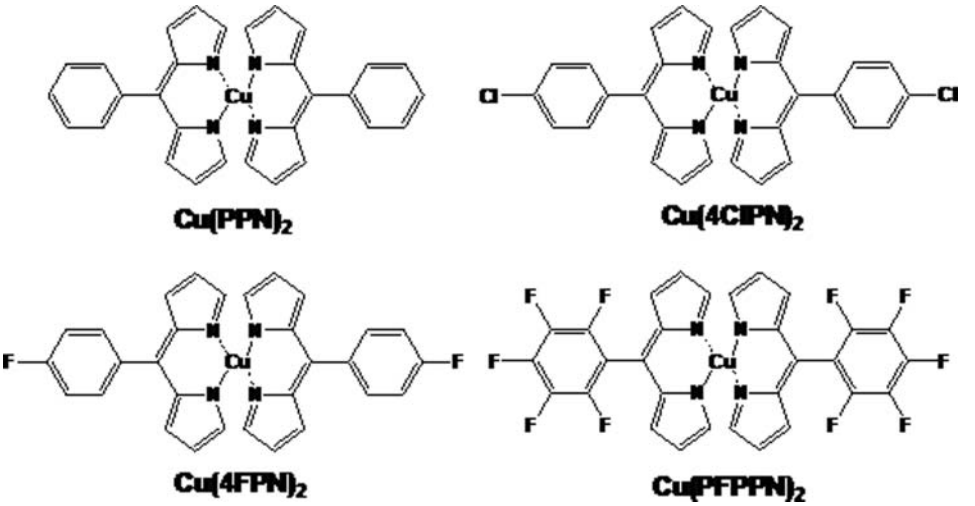
the improvement of thermal stability is required since thermal stability of 250°C or above is necessary during CF manufacturing process. The molecular design for new colorant materials is mainly considered through this concept.

Bis(dipyrrinato)metal complex was first reported by Fischer in 1924 [8]. Thereafter, many research groups synthesized many derivatives of bis(dipyrrinato) metal complex and studied the change of optical property. However, there had not been significant reports on fundamental researches on the potential of bis(dipyrrinato) metal complex derivatives for use as material of color filter through electro-optical property. Therefore, in this study, new red pigments based on bis(dipyrrinato) copper complex were synthesized where various substitution groups like phenyl, 4-chloro-phenyl, 4-fluoro-phenyl and pentafluorophenyl groups were substituted to 5-postion of dipyrrinato group (see Scheme 1). Also through systematic investigation on the change in physical properties such as optical and thermal properties by the structures, their potentials for use as color filter materials in LCD were evaluated.



Scheme 1.

Experimental

Synthesis

2.1. Synthesis of Bis[5-(phenyl)-dipyrrinato]copper Complex (Cu(PPN)$_2$). 2,2′-(phenylmethylene)bis(1H-pyrrole) (1 g, 4.5 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.123 g, 4.95 mmol) were stirred in acetonitrile (AN) (20 ml) at room temperature for 4 hours. They were then quenched with triethylamine (TEA) (0.06 ml, 0.45 mmol). Saturated methanol solution of copper acetate (0.413 g, 2.25 mmol) was added to the reaction mixture and stirred for 5 hours. After completion of the reaction, the solvent was evaporated under vacuum and the product was extracted with dichloromethane (CH_2Cl_2). The CH_2Cl_2 solution was washed with water and dried with magnesium sulfate anhydrous ($MgSO_4$). The solvent was evaporated to give $Cu(PPN)_2$ as green solid, which was recrystallized from dichloromethane (CH_2Cl_2) and methanol. (Yield 22%), $C_{30}H_{22}CuN_4$, found C,71.79; H,4.41; N,11.11 calculated C,71.77; H,4.42; N,11.16, FAB-Mass: 501 m/z

2.2. Bis[5-(4-fluorophenyl)-dipyrrinato]copper Complex (Cu(4-FPN)$_2$). The synthetic procedure is similar to that of Cu(PPN)$_2$. (Yield 48%), $C_{30}H_{20}CuF_2N_4$, found C,66.89; H,3.79; N,10.40, calculated C,66.97; H,3.75; N,10.41, FAB-Mass: 537 m/z

2.3. Bis[5-(pentafluorophenyl)-dipyrrinato]copper Complex (Cu(PFPPN)$_2$). The synthetic procedure is similar to that of Cu(PPN)$_2$. (Yield 48%), $C_{30}H_{12}CuF_{10}N_4$, found C,53.24; H,1.75; N,8.24, calculated C,52.84; H,1.77; N,8.22, FAB-Mass: 681 m/z

2.4. Bis[5-(4-chlorophenyl)-dipyrrinato]copper Complex (Cu(4-ClPN)$_2$). The synthetic procedure is similar to that of Cu(PPN)$_2$. (Yield 18%), $C_{30}H_{20}C_{l2}CuN_4$, found C,63.17; H,3.57; N,9.75, calculated C, 63.11; H, 3.53; N, 9.81, FAB-Mass: 569 m/z

Measurements

1H-NMR spectra were recorded on Bruker, Advance 300 and 500, and fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained using HP 8453 UV-VIS-NIR spectrometer. The melting temperatures (T_m) and degradation temperatures (T_d) of the compounds were measured by carrying out differential scanning calorimetry (DSC) under nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). The redox potentials of the compounds were determined with cyclic voltammetry (CV) using AUTOLAB/PG-STAT128N model system with a scanning rate of 100 mV/s. We used synthesized material coated ITO as working electrode, a saturated $Ag/AgNO_3$ as a reference electrode and Acetonitrile (AN) with 0.1M tetrabutylammonium tetrafluoroborate (TBAT) as electrolyte. Ferrocene was used for potential calibration and reversibility criteria.

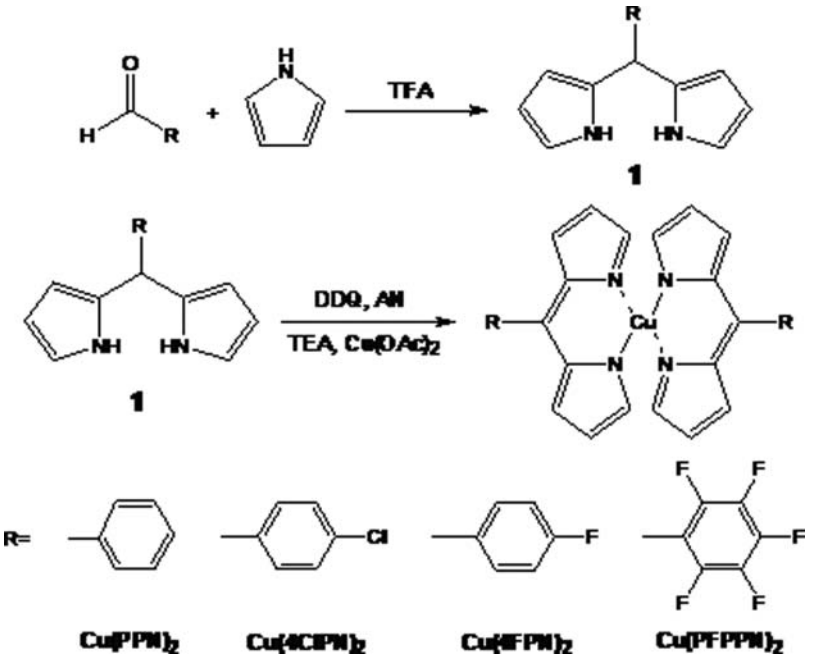
Results and Discussion

The synthesized materials, substitution groups existing in 5-position of dipyrrinato moiety in bis(dipyrrinato)copper complex core, are the new red pigments that connect phenyl, 4-chloro-phenyl, 4-fluoro-phenyl and pentafluorophenyl groups, and their molecular structures are depicted in Scheme 1.

Some metal complexes can be paramagnetic. This can lead the very large shifts and unobservable data in the NMR resonances [9–11].

As for the specific synthesis method, as shown in Scheme 2, the substituted aromatic aldehyde and pyrrole were reacted at room temperature under presence of trifluoroacetic acid (TFA), synthesizing the two substituted dipyrromethane 1. After oxidizing the synthesized 1 compound with DDQ and reacting it with copper acetate, final Cu complexes were synthesized through combination with Cu metal and ligands.

Optical properties of the synthesized materials were evaluated by UV-visible absorption (UV-Vis.) spectra and were summarized in Fig. 1 and Table 1. Cu(PPN)$_2$, Cu(4ClPN)$_2$, and Cu(4FPN)$_2$ to which phenyl, 4-chloro-phenyl and 4-fluoro-phenyl groups were substituted showed maximum absorption wavelengths between 463 and 467 nm and shoulder peaks of about 500 nm. On the other hand, Cu(PFPPN)$_2$ to which pentafluorophenyl group was substituted showed maximum absorption wavelength of 477 nm and shoulder peak of 513 nm, indicating that both maximum peak and shoulder peak were red-shifted by about 10 nm or more, respectively. This may be due to strong electron withdrawing effect of five fluoride atoms attached to phenyl ring. In addition, the results of the UV-vis spectra



Scheme 2.

were measured from the films which were prepared by through chloroform (1 w/wt%) solution and spin-coating method. The maximum absorption wavelengths of $Cu(PPN)_2$, $Cu(4ClPN)_2$ and $Cu(4FPN)_2$ were about 513 $\pm$ 1 nm, and in the case of $Cu(PFPPN)_2$, maximum absorbing wavelength appeared at 530 nm, which is about 18 nm red-shifted

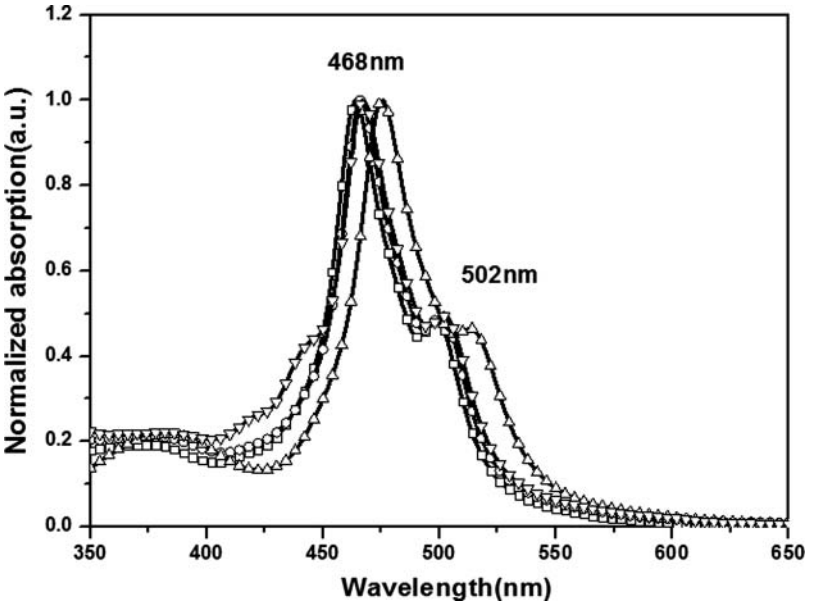


Figure 1. UV-Visible absorption spectra of $Cu(PPN)_2$(□), $Cu(4\text{-}ClPN)_2$(▽), $Cu(4\text{-}FPN)_2$ (○) and $Cu(PFPPN)_2$ (△) in THF solution.

Table 1. Optical properties of synthesized materials

Compounds	Solution[a] UV_{max} (nm)	Film UV_{max} (nm)	Log ε (L/mol·cm)	HO MO (eV)	LU MO (eV)	Band Gap (eV)
$Cu(PPN)_2$	463	512	4.89	5.48	3.25	2.23
$Cu(4ClPN)_2$	467	513	4.89	5.51	3.28	2.23
$Cu(4FPN)_2$	466	514	4.81	5.46	3.24	2.22
$Cu(PFPPN)_2$	477	530	4.78	5.51	3.35	2.16

a: THF solution (1×10^{-5} M).

compared with $Cu(PPN)_2$ (see Fig. 2). However, all the synthesized pigments showed red color in appearance [1].

As a result of measuring the extinction coefficient (ε) of the synthesized materials in THF solution, all pigments showed very high values of log scale 4.78 or higher (see Table 1), which are very excellent values beyond average (log ε: 4.24) of the derivatives of diketopyrrolopyrrole (DPP), major red pigment widely known as a commercial material [12]. It means that such high molar extinction coefficient can be applied as a pigment for color filter of LCD.

Using the band gap calculated through cyclic voltammogram (CV) and UV-vis. spectra of the synthesized materials, HOMO and LUMO levels were calculated (see Table 1). In the case of HOMO levels of the synthesized materials, all compounds showed similar values of 5.4∼5.5 eV. However, LUMO levels of $Cu(PPN)_2$, $Cu(4ClPN)_2$ and $Cu(4FPN)_2$ had similar values of about 3.2eV, but $Cu(PFPPN)_2$ substituted by pentafluorophenyl group with large electron-accepting ability showed LUMO level of 3.35 eV, indicating a decrease of about 0.15 eV.

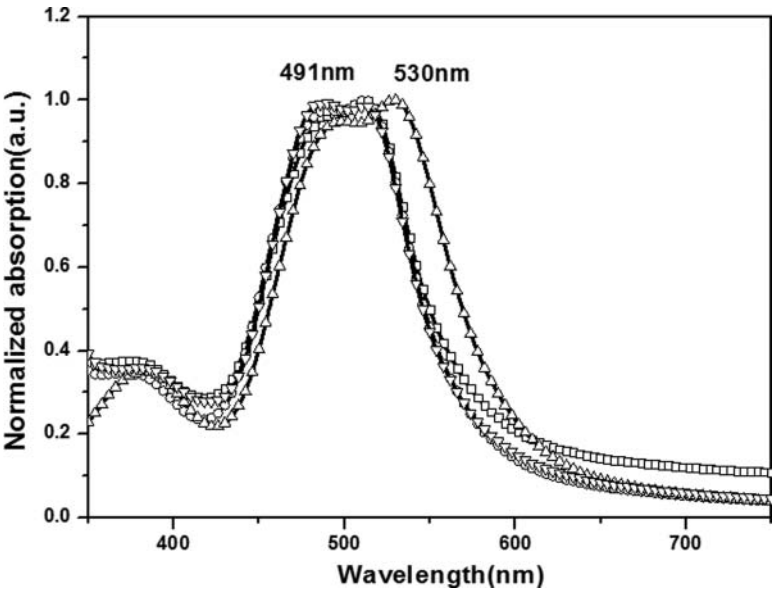


Figure 2. UV-Visible absorption spectra of $Cu(PPN)_2$(□), $Cu(4\text{-}ClPN)_2$(▽), $Cu(4\text{-}FPN)_2$(○), and $Cu(PFPPN)_2$(△) in spin-coated (1 w/w% $CHCl_3$ solution) films on glass substrate.

Table 2. Thermal properties of synthesized materials

Compounds	T_m/°C	T_d/°C
$Cu(PPN)_2$	276	270
$Cu(4ClPN)_2$	262	262
$Cu(4FPN)_2$	—	234
$Cu(PFPPN)_2$	—	277

T_m: melting-point temperature, T_d: decomposition temperature (5% weight loss).

As for thermal stability of the synthesized materials, T_d values of $Cu(PPN)_2$, $Cu(4ClPN)_2$, $Cu(4FPN_{)2}$ and $Cu(PFPPN)_2$ were respectively 270, 262, 234, and 277°C. For T_m, $Cu(4FPN)_2$ and $Cu(PFPPN)_2$ did not show clear values of T_m and $Cu(PPN)_2$ and $Cu(4ClPN)_2$ respectively had 276 and 262°C. In conclusion, $Cu(PPN)_2$, $Cu(4ClPN)_2$ and $Cu(PFPPN)_2$, excluding $Cu(4FPN)_2$, possess relatively high thermal stability (see Table 2). This is equivalent to the level of thermal stability higher than 250°C, which is the highest temperature applied during LCD manufacturing process. This material has high potential for application as a pigment for LCD.

In order to evaluate thin film property of the synthesized compounds, scanning electron microscopy (SEM) was examined after spin-coating the compounds onto a glass (see Fig. 3). Commercial product called Red 254 exhibited a rough surface shown in Fig. 3(a), but the synthesized compounds generally showed smooth surfaces.

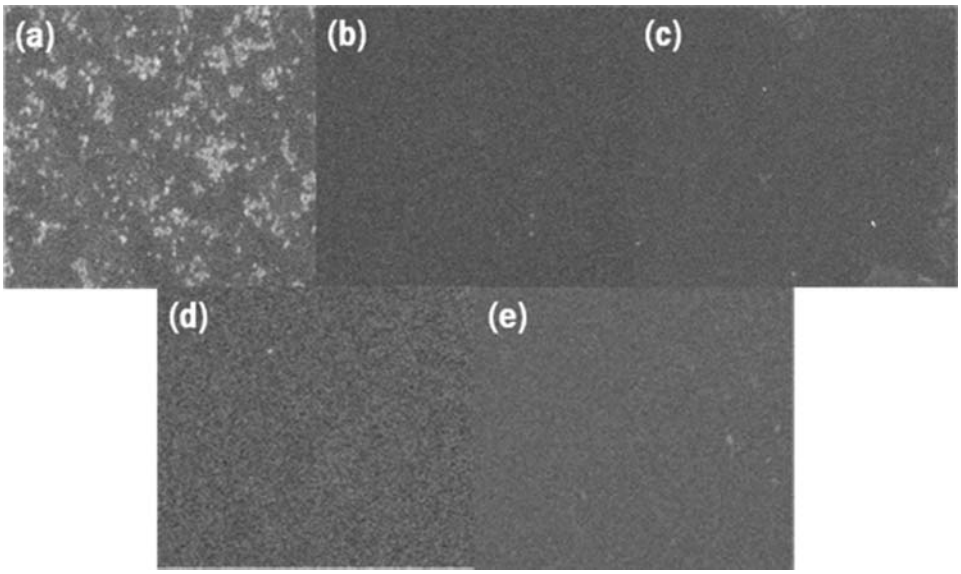


Figure 3. SEM images (×8000) of bis(dipyrrinato)copper complex derivatives and Red 254: spin-coating (0.1 wt%, THF solution) films on glass substrate, (a) Red 254, (b) $Cu(PPN)_2$, (c) $Cu(4ClPN)_2$, (d) $Cu(4FPN)_2$, (e) $Cu(PFPPN)_2$.

Conclusions

Four red compounds for CF pigment substituted with phenyl, 4-chloro-phenyl, 4-fluoro-phenyl and pentafluorophenyl groups to 5-position of dipyrrinato group based on bis(dipyrrinato)copper complex were synthesized. UV-visible absorption spectra of the synthesized materials showed maximum absorbing wavelengths of about 460∼477 nm in solution state and 510∼530 nm in film state, indicating red color. Extinction coefficient values (log ε) of all the synthesized materials were confirmed to be very excellent at 4.7 or above. In addition, all HOMO levels measured through CV showed similar values between 5.4 and 5.5 eV regardless of substitution group. In addition, since T_m and T_d values of three synthesized materials showed thermal stability higher than 250°C, they possess high potential for application as pigments for LCD color filter. In thin film surface property, the synthesized compounds generally showed smooth surface.

Acknowledgment

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