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Article

이미지 센서 컬러 필터용 유기반도체 화합물 기반의 신규 황색 아로마틱 이민 유도체

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New Yellow Aromatic Imine Derivatives Based on Organic Semiconductor Compounds for Image Sensor Color Filters

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초 록

이미지 센서 컬러 필터에 사용하기 위해 새로운 황색 방향족 이민 유도체가 설계되고 합성되었다. 합성된 화합물은 방향족 이민 그룹을 기반으로 한 화학 구조를 가지고 있다. 새로운 재료는 상업용 장치 제조 공정을 모방한 조건에서 광학적 및 열적 특성을 기반으로 평가되었다. 이들의 관련 성능을 비교한 결과, ((E)-3-methyl-4-((3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene) methyl)-1-phenyl-1H-pyrazol-5(4H)-one (MOPMPO)은 industry에 중점적으로 사용되는 프로필렌 글리콜 모노메틸 에테르 아세테이트 용매에 대한 용해도가 0.5 wt%이고, 290 °C의 높은 분해 온도를 갖는 이미지 센서 컬러 필터 소재로서 우수한 성능을 나타내었다. MOPMPO가 이미지 센서 색재의 황색 염료 첨가제로 사용할 수 있음을 확인하였다.

Abstract

Novel aromatic imine derivatives with yellow were designed and synthesized for their potential application in color filters for image sensors. The synthesized compounds possessed chemical structures using aromatic imine groups. This innovative material was evaluated thoroughly, considering its optical and thermal properties under conditions similar to commercial device manufacturing processes. Following a rigorous performance evaluation, it was found that (E)-3-methyl-4-((3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene)methyl)-1-phenyl-1H-pyrazol-5(4H)-one, abbreviated as MOPMPO, exhibited an impressive solubility of 0.5 wt% in propylene glycol monomethyl ether acetate, predominantly utilized as the solvent in the industry. Furthermore, MOPMPO showed exceptional performance as a color filter material for image sensors, having a high decomposition temperature of 290 °C. These data unequivocally establish MOPMPO as a viable yellow dye additive for coloring materials in image sensor applications.

***Keywords**: Yellow colorant, Aromatic imine group, Image sensor, Color filter, Nano-pigmentation*

1. Introduction

Colorants, encompassing both dyes and pigments, play a pivotal role in a broad spectrum of cutting-edge industries, including displays, energy, biotechnology, and digital printing. In the realm of image sensors, an array of colorant molecules is under scrutiny for their applicability in color filters within liquid crystal display (LCD) panels, profoundly influencing display performance. The technology behind color filters in image sensors necessitates finer pixel sizes and elevated contrast ratios to achieve the production of high quality images[1]. The pigment dispersion method stands as the prevalent approach for red, green, and blue color filters, chiefly due to the remarkable thermal, chemical, and photo stabilities exhibited by pigments. However, this method grapples with the pigment's inherent low solubility, which poses challenges in generating smaller particles and introduces light scattering by aggregated particles[2-3]. In response to these issues, re-

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search efforts have been dedicated to dye-based color filters. The dissolution of dye in the solvent eliminates particle-induced light scattering, considerably enhancing both light absorption and transmittance. Nonetheless, the feasibility of dye-based color filters hinges on the thermal and solvent stability of the dye in industrial solvents such as propylene glycol monomethyl ether acetate (PGMEA)[4-8]. Failure to uphold stability in common industrial solvents such as PGMEA would render the colorant unsuitable for deployment in the color filter, necessitating significant alterations to the manufacturing process. Thus, there exists an imperative need to develop dyes boasting exceptional thermal and solvent stabilities. The present study embarks on the design and synthesis of a novel yellow dye predicated on imidazole and pyrazole derivatives, both belonging to the aromatic imine group category. Furthermore, its suitability for deployment in green filters is explored. Given the intrinsic challenge for green colorants to fully absorb blue light, the incorporation of a yellow additive is imperative in the green colorant mixture to achieve a high-purity green color. The synthesized aromatic imine derivatives undergo thorough scrutiny aimed at optimizing their optical, thermal, and solvent stabilities contingent upon their chemical structures. Their potential to serve as yellow-color filter materials is carefully evaluated.

2. Experimental

2.1. Materials and instrumentation

In these experiments, all reagents were purchased from reputable suppliers, including Sigma-Aldrich, Tokyo Chemical Industry (TCI), and CK Chem. These reagents boasted a minimum purity level of 98% and were employed without any additional purification steps. For analytical purposes, ^{1}H nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Advance 400 spectrometer. High performance liquid chromatography (HPLC) analyses were conducted employing a Shimadzu Nexera UHPLC system. Furthermore, ultraviolet–visible (UV–Vis) optical absorption spectra were acquired using a Lambda 1050 UV–Vis spectrophotometer manufactured by Perkin Elmer. To explore thermal properties, thermogravimetric analysis (TGA) was executed with a TA Instruments Q5000 IR/SDT Q600 instrument, with the samples subjected to an air atmosphere. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F for detailed microstructural examination.

2.2. Synthesis and characterization of the synthesized quinolinedione derivatives

2.2.1. Synthesis of 9-methoxy-7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (MBIQO)

A solution was prepared by dissolving 3-Methoxybenzene-1,2-diamine (1 g, molar quantity) in 10 ml of distilled water, followed by refluxing until complete dissolution was achieved. Subsequently, 0.1 ml of acetic acid and 0.65 g of 1,8-naphthalic anhydride (molar quantity) were added to the reaction mixture. The resulting mixture was refluxed for 2 h. Upon reaching the endpoint of the reaction, the mixture was allowed to cool to room temperature, followed by filtration and washing with water. The product was then dried under vacuum conditions at 120 °C. A yellow solid was obtained (1.6 g, yield 74%). ^{1}H NMR (400 MHz, THF-d_8) δ 8.72 (d, J = 5.5 Hz, 2H), 8.34 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.06 (s, 1H), 7.84~7.76 (m, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 8.8 Hz, 1H), 3.89 (s, 3H).

2.2.2. Synthesis of (E)-3-methyl-4-((3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene)methyl)-1-phenyl-1H-pyrazol-5(4H)-one (MOPMPO)

4-Hydroxy-2-oxo-2H-chromene-3-carbaldehyde (1 g, 5.3 mmol) was dissolved in ethanol (15 ml), and 3,5-Dimethyl-1-phenylpyrazole (0.9 g, 5.2 mmol) was added. The reaction mixture was refluxed for 10~12 h. The yellow solid obtained upon cooling was filtered, washed with ethanol, and purified by recrystallization with ethanol and benzene (1.16 g, 62% yield). ^{1}H NMR (400 MHz, THF-d_8) δ 7.97 (d, J = 8.8 Hz, 4H), 7.42 (s, 1H), 7.41~7.36 (m, 4H), 7.21 (t, J = 7.4 Hz, 2H), 2.33 (s, 6H).

2.3. Fabrication and measurement of dye-based color filters

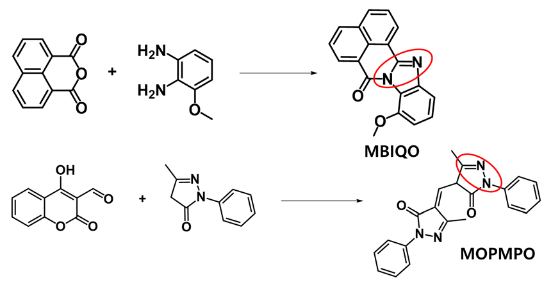
Color resistant solutions were formulated by incorporating the newly synthesized aromatic imine derivatives alongside various additional components. These supplementary elements encompassed an acrylic binder comprising methyl methacrylate groups, carboxylic acid groups, and benzyl methacrylate groups, a leveling agent, and PGMEA serving as the solvent. The resultant solution was uniformly applied to a transparent glass substrate measuring 2.5 × 2.5 cm, employing a MIDAS SPIN-1200D spin-coater at a rotation speed of 850 rpm for 10 s. Subsequently, all colorant films underwent a baking process at 220 °C for 3 min.

3. Results and discussion

To facilitate the molecular design of a novel yellow dye possessing outstanding optical and thermal properties, an aromatic imine group was chosen[9-12]. These newly developed aromatic imine derivatives involved the imidazole and pyrazole segments. It is anticipated that MBIQO, with its imidazole functional group, will exhibit a planar monomeric structure, leading to enhanced thermal stability. On the other hand, MOPMPO, composed of pyrazole functional groups in dimeric form, is expected to show increased absorbance and improved solubility properties. The structural formulas of the synthesized compounds, as well as the corresponding synthetic pathway, are presented in Scheme 1. Each of the compounds underwent a purification process via recrystallization, followed by thorough characterization of NMR spectroscopy (see Figures 1 and 2).

The optical data for the newly synthesized yellow aromatic imine colorant are summarized in Figure 3 and Table 1. Transmittance spectrum measurements were performed using a 1 × 10^{-4} M solution of propylene glycol monomethyl ether acetate (PGMEA), a condition in line with industry standards. To assess the optical absorption characteristics of the newly synthesized materials, the molecular extinction coefficients using the following Beer-Lambert Law formula was calculated:

$$A = \varepsilon cl \quad (1)$$



Scheme 1. Synthetic routes and chemical structures of the aromatic imine derivatives: (a) MBIQO and (b) MOPMPO.

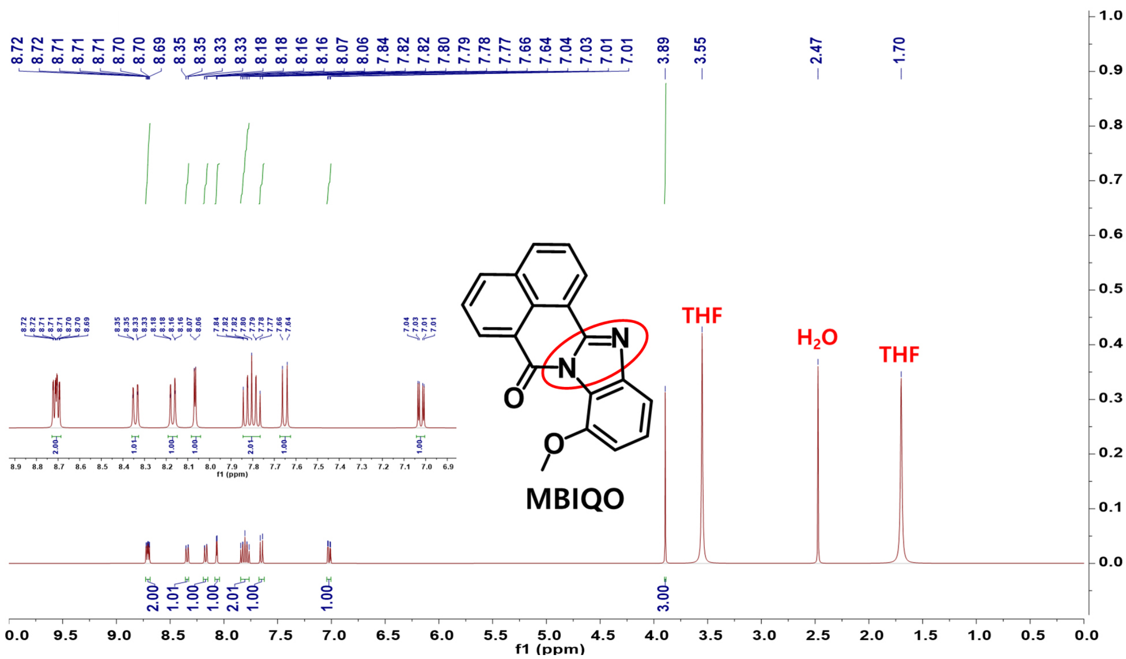


Figure 1. ^{1}H NMR spectrum of MBIQO.

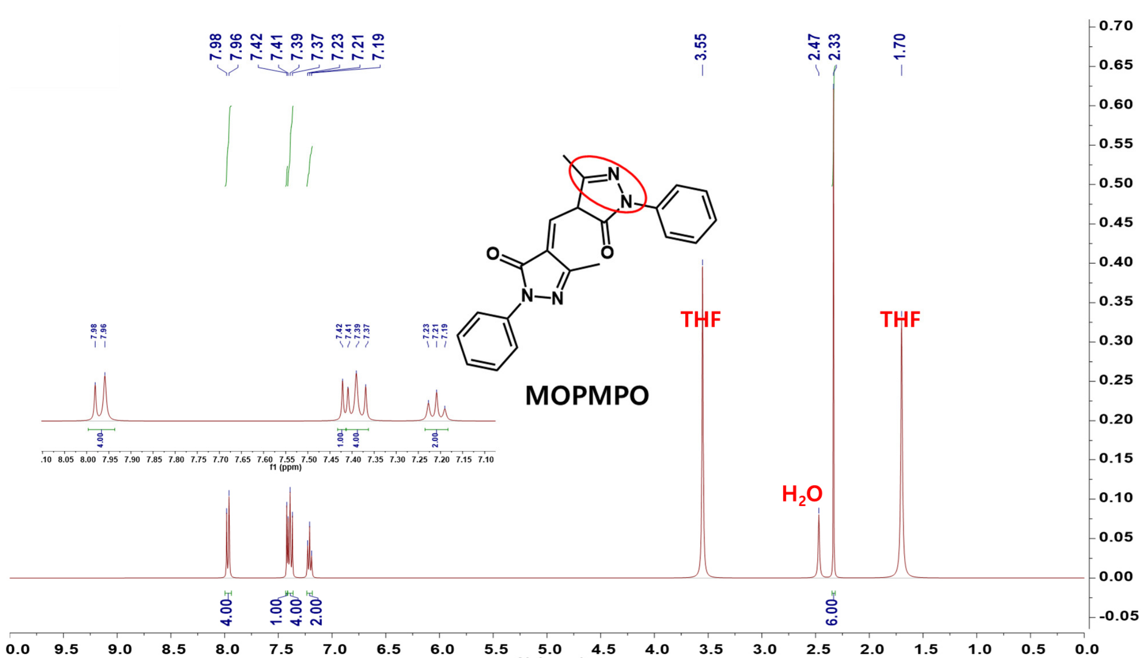


Figure 2. ^{1}H NMR spectrum of MOPMPO.

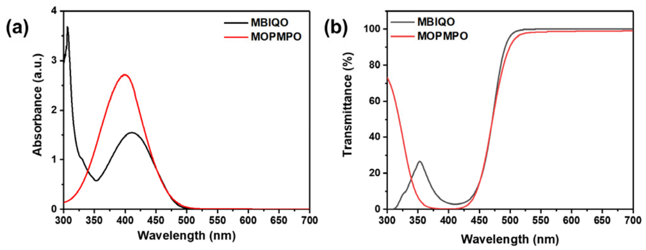


Figure 3. UV-Vis spectra: (a) absorbance spectra and (b) transmittance spectra of the synthesized materials in 1 × 10^{-4} M PGMEA solution.

Table 1. Transmittance and Molar Extinction Coefficient Values of the Synthesized Yellow Materials in 1 × 10^{-4} M PGMEA Solution

Transmittance	MBIQO	MOPMPO
435 nm	4.30%	3.77%
530 nm	99.80%	97.9%
Molar extinction coefficient[a] [L $mol^{-1}cm^{-1}$]	1.23 × 10^4	2.72 × 10^4 (221%)[b]

[a] at maximum absorption wavelength
[b] the percentage relative to the molar extinction coefficient value of MBIQO

A: absorbance, ε: molecular extinction coefficient, c: molar concentration, l: optical path length

The specifications for the yellow colorant millbase mandated a molecular extinction coefficient exceeding 1.0 × 10^4 L $mol^{-1}cm^{-1}$, along with a transmittance requirement of less than 5% at 435 nm and more than 90% at 530 nm. The molecular extinction coefficients at the maximum absorption wavelength for the two newly synthesized compounds, MBIQO and MOPMPO, were found to be 1.23 × 10^4 and 2.72 × 10^4 L $mol^{-1}cm^{-1}$, respectively. MOPMPO exhibited a remarkable 2.21 times improvement in its molecular extinction coefficient compared to MBIQO. Both of these newly synthesized materials met the requirements for the yellow transmittance spectrum, firmly positioning them within the purview of industrial commercialization standards. These yellow colorants were designed with the objectives of minimizing color interference and ensuring high color purity within the confines of small-sized image sensor pixels. To achieve yellow color purity through blue wavelength absorption, this yellow material can be seamlessly integrated into the green millbase colorant. The slope of the graph depicting the relationship between the absorption maximum and band edge is indicative of the compound's color purity. In the context of high resolution image sensor pixels, the absorption band edge values for the two synthetic compounds, MBIQO and MOPMPO, were determined to be 497 nm and 493 nm, respectively. Additionally, their maximum absorption wavelengths were 410 nm and 399 nm, with transmittance levels satisfying the criteria of less than 5% at 435 nm and more than 90% at 530 nm. Consequently, these compounds can be effectively incorporated into commercial image sensor green materials. The transmittance data of the newly synthesized materials in film state was measured and summarized in Figure 4 and Table 2. The transmittance of MBIQO and MOPMPO was 36.6% and 6.03% at 435 nm, and 95.7% and 88.3% at 530 nm, respectively.

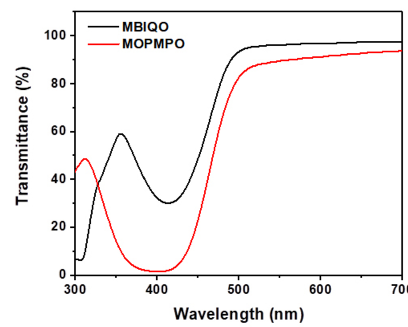


Figure 4. Transmittance spectra of the synthesized materials in film state.

Table 2. The Transmittance Values of the Synthesized Yellow Materials in Film State

	MBIQO	MOPMPO
435 nm	36.6	6.03
530 nm	95.7	88.3

Table 3. Solubility of the Synthesized Materials in the PGMEA Solvent

	MBIQO	MOPMPO
Solubility	0.15	0.5 (333%)[a]

[a] the percentage relative to the solubility value of MBIQO

To serve as a color filter material for a camera image sensor, a colorant must be capable of dissolving in PGMEA solvent, a commonly used solvent in both the display and camera industries. Remarkably, both MBIQO and MOPMPO exhibit solubility in PGMEA solvent, with solubilities of 0.15 wt% and 0.5 wt%, respectively, as summarized in Table 3. The solubility of MOPMPO surpasses that of MBIQO by a substantial factor of 3.33. This improvement in solubility for MOPMPO can be attributed to its molecular structure, which incorporates relatively more polar components capable of interacting effectively with the solvent. Furthermore, the introduction of a methyl group serves to enhance its solubility, contributing to the impressive solubility characteristics of MOPMPO compared to the structure of MBIQO.

To examine the thermal characteristics of the commercialized material, the degradation temperature (T_d) at a 5% weight loss was determined through thermogravimetric analysis (TGA) of the synthesized material. The results are summarized in Figure 5 and Table 4, revealing that both MBIQO and MOPMPO exhibited T_d values of 290 °C and 288 °C, respectively. The synthesized aromatic imine derivatives showed nearly identical thermal properties. It is noteworthy that MOPMPO exhibited a slight increase in decomposition temperature compared to MBIQO, and this enhancement in thermal stability can be attributed to the higher molecular weight of MOPMPO. Importantly, these T_d values surpassed the process temperature of 200 °C typically utilized in color filter manufacturing processes. Thus, the thermal properties of the synthesized MBIQO and MOPMPO render them emi-

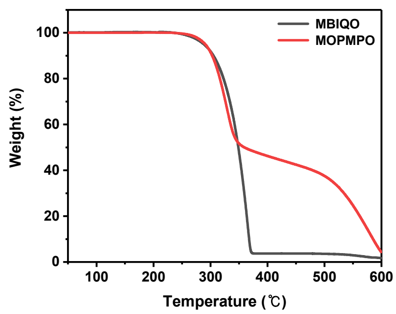


Figure 5. Thermogravimetric analysis (TGA) curves of the synthesized aromatic imine derivatives.

Table 4. Degradation Temperatures and Molecular Weights of the Newly Synthesized Compounds

	MBIQO	MOPMPO
$T_{d=95\%}$	288 °C	290 °C
M.W (g/mol)	300.32	358.40

nently suitable for deployment in industrial processes.

To prepare a color-resistant (CR) mixture, it is essential to follow the nano-pigmentation process subsequent to the synthesis of the colorant. This process involves the incorporation of dispersion additives to create a millbase mixture. Afterward, by blending the millbase material with a monomer, photoinitiator, and solvent, a finalized CR mixture can be obtained. When the conventional nano-pigmentation processes used in general display and semiconductor applications were applied to the synthesized MBIQO and MOPMPO, the average particle sizes achieved were 225 nm and 150 nm, respectively, as illustrated in Figure 6. Before the nano-pigmentation process, MOPMPO had formed spherical shapes with diameters ranging from 200 to 400 nm. After the nano-pigmentation process, the particle size decreased to 150 nm, while maintaining its spherical morphology. It is noteworthy that, following the nano-pigmentation process, the particle size of MOPMPO decreased to 150 nm, representing a remarkable 33% reduction when compared to MBIQO. This reduction in particle size is an important factor contributing to the superior color purity and high extinction coefficient attained during the manufacture of CR films. The ability to generate such diminutive particles is an inherent characteristic stemming from the molecular structure and is deemed a critical attribute in the production of high-performance CR particles.

The optical properties of the thin film post-CR (color filter) fabrication are summarized in Figure 7 and Table 5. These optical properties were achieved by combining the pure yellow colorant with other additives, ensuring that the transmittance remained below 5% at 435 nm and exceeded 90% at 530 nm. For MOPMPO, the wavelength value corresponding to the high transmission portion near the band edge closely resembled that of MBIQO. However, a detailed analysis of transmittance ranging from 350 to 450 nm revealed significantly superior characteristics in favor of MOPMPO. In the critical 400~450 nm range encompassing visible light, MOPMPO exhibited a transmittance of 0%, indicating no interference with other colors. Conversely,

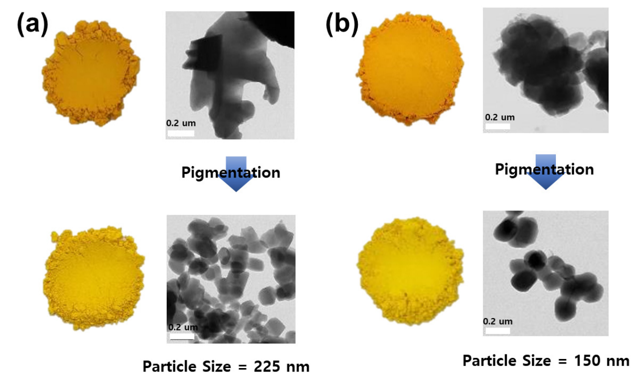


Figure 6. TEM images of (a) MBIQO and (b) MOPMPO.

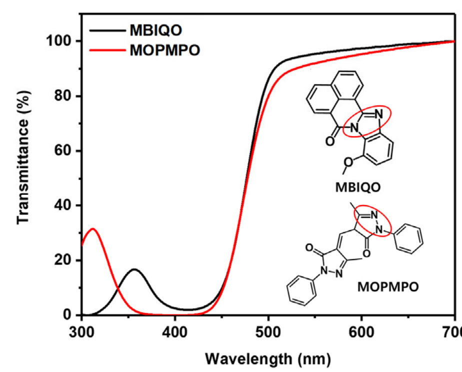


Figure 7. Transmittance spectra of the materials synthesized on CR films.

Table 5. Transmittance Values of the Synthesized Yellow Materials at 435 and 530 nm on the CR Film

	MBIQO	MOPMPO
435 nm	3.63%	1.51%
530 nm	94.1%	90.1%

MBIQO demonstrated a 3.5% transmittance in this region, leading to crosstalk with other colors. The lower transmittance of MOPMPO in the visible light region can be attributed to its high extinction coefficient, a characteristic of pyrazole derivatives. This high coefficient amplifies absorbance at wavelengths within that range, consequently reducing transmittance. The newly synthesized materials were effectively transformed into nanoparticles through a nano-pigmentation process. The transmittance of the color filter film was significantly enhanced compared to that of the solution state. In the solution state, aggregation of the synthesized materials led to decreased permeability. However, with the incorporation of CR, the additives effectively mitigated colorant agglomeration, resulting in improved absorption characteristics as the quantity of micronized colorant increased. The newly synthesized yellow colorant successfully met the stringent requirements for yellow color in commercial image sensors. In particular, MOPMPO met all the prerequisites for commercial image sensor applications, including solubility, transmittance characteristics, and thermal stability.

4. Conclusion

New yellow aromatic imine dye compounds have been successfully synthesized for use as colorants in image sensors. Two distinct materials were developed and subjected to a comprehensive evaluation based on their optical and thermal characteristics. Among the two compounds scrutinized, MOPMPO exhibited notable solubility, with a solubility of 0.5 wt%, surpassing that of MBIQO in PGMEA by a factor of 3.33. Moreover, both MOPMPO and MBIQO demonstrated optical properties akin to commercially available yellow colorants, particularly in terms of transmittance. The particle size analysis of MOPMPO, which was fabricated using the pigmentation process with the synthesized material, revealed a size of 150 nm. This represents a significant 33% reduction when compared to MBIQO. Importantly, MOPMPO exhibited outstanding light absorption and transmission characteristics when employed in the creation of a CR (color filter) film. Upon conducting a comprehensive assessment of the CR film-related performance of the two compounds, MOPMPO emerged as the superior choice. It had optimized optical and thermal properties, including less than 1% transmittance at 435 nm, more than 90% transmittance at 530 nm, and a thermal decomposition temperature (T_d) of 290 °C. In summation, this study confirms the suitability of MOPMPO as a color material for applications in image sensors, owing to its exceptional optical and thermal attributes.

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