



New Yellow Azo Pyridone Derivatives with Enhanced Thermal Stability for Color Filters in Image Sensors

Sunwoo Park¹, Sangwook Park¹, Saeyoung Oh¹, Hyukmin Kwon¹, Hayoon Lee¹, Kiho Lee¹, Chun Yoon^{2,*} and Jongwook Park^{1,*}

- ¹ Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin-si 17104, Republic of Korea; mdrafix@khu.ac.kr (S.P.); pswook@khu.ac.kr (S.P.); tpdud5821@khu.ac.kr (S.O.); hm531@khu.ac.kr (H.K.); kssarang1@khu.ac.kr (H.L.); kiholee@khu.ac.kr (K.L.)
- ² Department of Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 05006, Republic of Korea
- * Correspondence: chuny@sejong.ac.kr (C.Y.); jongpark@khu.ac.kr (J.P.)

Abstract: Two new yellow azo pyridone derivatives, (E)-6-hydroxy-1-(3-methoxypropyl)-4-methyl-2oxo-5-(p-tolyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (APY-M) and 5,5'-((1E,1'E)-(methylenebis (4,1-phenylene))bis(diazene-2,1-diyl))bis(6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile) (APY-D), were designed and synthesized as yellow colorants for image sensors. The properties of these new compounds were evaluated in both solution and color filter film forms, focusing on their optical and thermal characteristics. The molar extinction coefficient values of APY-M and APY-D in solution were found to be 2.7×10^5 and 3.0×10^5 L/mol·cm, respectively. The transmittance of the newly synthesized compounds met commercial requirements, showing values below 0.21% at 435 nm and above 97.1% at 530 nm. APY-D exhibited a molar extinction coefficient value in solution that was 1.15 times higher than that of the commercially used yellow colorant Disperse Yellow 241. Both newly synthesized compounds satisfied the decomposition temperature requirement of over 230 °C, which is essential for the color filter manufacturing process in image sensors. In particular, APY-D, with its dimeric structure and increased molecular weight, demonstrated enhanced thermal stability, with a 50 °C increase in decomposition temperature compared to Disperse Yellow 241. Color filter films for image sensors were fabricated using the new compounds, and their thermal resistance was evaluated. APY-D maintained its transmittance due to the enhanced thermal stability provided by its dimer structure and increased molecular weight. Consequently, APY-D is anticipated to be a promising candidate for use as a yellow colorant in image sensors, owing to its excellent optical and thermal properties.

Keywords: azo pyridone derivative; yellow colorant; color filter; image sensor

1. Introduction

Organic colorants are being utilized as essential materials in core visual informationbased semiconductor technologies such as 3D printing, artificial intelligence, big data, cloud computing, and the Internet of Things (IoT). As a result, the demand for and development of related technologies are continuously increasing. Additionally, research on organic semiconductors utilizing organic colorant materials has also been reported. These organic electronic materials are being recognized for their application as core components in organic transistors, offering excellent thermal stability and suitability for flexible devices [1]. Along with the growing demand for the utilization of visual information, there is a corresponding need for improved performance in cameras and display devices. This has highlighted the importance of advancing color filter technology for image sensors, which directly impacts image quality. Color filters in image sensors play a crucial role by selectively transmitting specific colors from the full spectrum of incident light, enabling the conversion of optical images into electrical signals [2–5]. With the rising demand for high-resolution, high-clarity,



Citation: Park, S.; Park, S.; Oh, S.; Kwon, H.; Lee, H.; Lee, K.; Yoon, C.; Park, J. New Yellow Azo Pyridone Derivatives with Enhanced Thermal Stability for Color Filters in Image Sensors. *Photonics* **2024**, *11*, 989. https://doi.org/10.3390/ photonics11100989

Received: 17 September 2024 Revised: 17 October 2024 Accepted: 19 October 2024 Published: 21 October 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and high-sensitivity capabilities in smartphones and digital cameras, the pixel size of image sensor units has been progressively miniaturized [6,7]. As pixel size decreases, finer colorants suitable for this miniaturization are required, and the amount of colorant applied to each pixel has also been reduced [8,9]. Therefore, in miniaturized pixel structures, it is essential to optimize the absorption and transmission characteristics of the color filter to achieve high-quality images. To achieve this, it is essential to develop materials that provide high absorption efficiency at specific wavelengths while minimizing optical interference. Developing new dye materials with high molar extinction coefficient values has emerged as a critical challenge in addressing this issue [10,11]. Furthermore, research into colorant materials with high thermal stability is necessary to ensure stable and high-performance components in small pixel structures [12–16]. These requirements apply to all primary colors-red, green, and blue-but are particularly critical for green colorants. Conventional green colorants are unable to fully absorb blue light, necessitating the incorporation of yellow colorants to achieve higher color purity [17]. Consequently, yellow colorants are crucial additives in green color filters to enhance their optical properties [18]. Yellow colorants should exhibit fundamental optical characteristics, such as low transmittance below 5% at 435 nm and high transmittance above 90% at 530 nm in film state [19].

In this study, two new yellow colorants based on azo pyridone derivatives, (E)-6hydroxy-1-(3-methoxypropyl)-4-methyl-2-oxo-5-(p-tolyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (APY-M) and 5,5'-((1E,1'E)-(methylenebis(4,1-phenylene))bis(diazene-2,1diyl))bis(6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile) (APY-D), were designed and synthesized. These compounds were investigated for their optical and thermal properties as yellow colorant additives for green color filters. The synthesized azo pyridone derivatives were analyzed for their optical properties based on their chemical structures, and their enhanced thermal stability was measured and confirmed. This evaluation aimed to assess the potential of the new yellow colorants as additives for green color filter materials.

2. Materials and Methods

2.1. Materials and Instrumentation

6-hydroxy-1-(3-methoxypropyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile, 4,4'-methylenedianiline and 6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile were purchased from CK Chem with a minimum purity of 98%. Other reagents used in these experiments were purchased from Sigma-Aldrich (St. Louis, MO, USA) or Tokyo Chemical Industry (TCI); their purity was 98% or higher, and they were used without further purification. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECZ400S/L1 (Jeol, Tokyo, Japan). High-resolution mass spectrometry (HRMS) was performed using fast atom bombardment (FAB) using a JMS-700, 6890 Series mass spectrometer (JEOL, Tokyo, Japan). Optical UV-Visible absorption spectra were obtained using a UV-1900i UV/Vis/NIR spectrometer (Shimadzu, Kyoto, Japan). Degradation temperatures (T_d) of the compounds were measured by thermogravimetry analysis (TGA) using a SDT Q600 (TA Instruments, Lukens Dr, New Castle, DE, USA). Samples were heated to 700 °C in a nitrogen atmosphere at a rate of 10 °C/min. The ORCA program package (V 5.0.4) was utilized to perform density functional theory (DFT) calculations to carry out geometry optimization and electronic structure calculations for the molecule [20]. The applied exchange-correlation functional was the B3LYP-D3 hybrid functional, and the basis set chosen was def2-TZVPP. Cyclic voltammetry measurements were performed using a WizEQCM-1000 instrument (Wizmac, Daejeon, Republic of Korea). The voltammograms were recorded over a potential range of 0 to 3.0 V, with 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte solution at scan rate 100 mV/s. A platinum wire served as the counter electrode, a glassy carbon electrode as the working electrode, and an Ag/AgCl electrode as the reference electrode. The film data were obtained using a high-efficiency multiple co-evaporator (DAEKI HI-TECH CO., LTD, Daejeon, Republic of Korea) at the Core Facility Center for Analysis of Optoelectronic Materials and Devices, Korea Basic Science Institute (KBSI). The thicknesses of the thin films were measured by Dektak 150 surface profiler (Veeco, Plainview, NY, USA).

2.2. Synthesis

2.2.1. Synthesis of (E)-6-hydroxy-1-(3-methoxypropyl)-4-methyl-2-oxo-5-(p-tolyldiazenyl)-1,2-dihydropyridine-3-carbonitrile, APY-M

A mixture of 100 g of ice, 100 mL of deionized (DI) water, and 20 mL of 35% concentrated hydrochloric acid was prepared, and p-toluidine (5.36 g, 0.05 mol) was added. The resulting solution was cooled to 0 $^{\circ}$ C. Sodium nitrite (3.62 g, 0.053 mol) was dissolved in 50 mL of DI water and slowly added to the mixture over 30 min. After the addition, the reaction temperature was maintained at 4–6 °C and stirring was continued for an additional hour. 6-Hydroxy-1-(3-methoxypropyl)-4-methyl-2-oxo-1,2-dihydropyridine-3carbonitrile (11.11 g, 0.05 mol) was dissolved in 100 mL of DI water and 12.3 g (0.15 mol) of sodium acetate. This solution was then slowly added to the previous reaction mixture over one hour. The reaction was stirred for an additional 16 h. The resulting solid was collected by filtration under reduced pressure, washed with DI water, and recrystallized from acetone to yield APY-M as a solid (15.13 g, 89% yield). 1 H NMR (400 MHz, Chloroform-d) δ 15.09 (s, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.07 (t, J = 8.0 Hz, 2H), 3.44 (t, J = 8.0 Hz, 2H), 3.31 (s, 3H), 2.60 (s, 3H), 2.38 (s, 3H), 1.89 (quint, J = 8.0 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) & 161.77, 160.28, 158.72, 138.60, 138.08, 130.64, 122.57, 117.21, 114.70, 101.21, 70.44, 58.74, 37.71, 27.94, 21.27, 16.62. HRMS ((FAB-MS), m/z): calcd. for, 340.3830; found 341.1620 [M]+.

2.2.2. Synthesis of 5,5'-((1E,1'E)-(methylenebis(4,1-phenylene))bis(diazene-2,1-diyl))bis(6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile), APY-D

4,4'-Methylenedianiline (1.98 g, 0.01 mol) was added to a mixture of ice (50 g), DI water (30 mL), and concentrated hydrochloric acid (5 mL, 35%), and the resulting solution was cooled to 0 °C. A solution of sodium nitrite (1.38 g, 0.02 mol) in 20 mL of DI water was then slowly added dropwise over 30 min while maintaining the temperature at 0 °C. After completion of the addition, the reaction mixture was stirred for an additional hour, keeping the temperature at 4–6 °C. In a separate step, a solution of 6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (3.0 g, 0.02 mol) in a mixture of ice (50 g), deionized water (40 mL), and sodium acetate (4.92 g, 0.06 mol) was prepared. This solution was then added dropwise to the initial reaction mixture over 1 h. After the addition, the mixture was stirred for 20 h. The resulting solid was collected by filtration under reduced pressure, washed with deionized water, and recrystallized from acetone, yielding APY-D as a solid (4.78 g, 92% yield). ¹H NMR (400 MHz, Tetrahydrofuran- d_8) δ 14.79 (s, 2H), 11.03 (s, 2H), 7.52–7.48 (m, 4H), 7.31–7.27 (m, 4H), 4.01 (s, 2H), 2.52 (s, 6H). ¹³C NMR (101 MHz, Tetrahydrofuran-d) δ 163.27, 161.01, 160.35, 142.70, 141.05, 131.20, 118.11, 116.22, 114.90, 41.61, 16.73. HRMS ((FAB-MS), m/z): calcd. for, 520.5090; found 521.1689 [M]⁺.

2.3. Fabrication of Film and Color Filters

Glass substrates (2.5 cm \times 2.5 cm) were ultrasonically washed in isopropyl alcohol for 10 min and then dried in an oven at 80 °C. A film containing a yellow colorant was fabricated by drop-casting a 1 \times 10⁻³ M solution of the colorant in propylene glycol monomethyl ether acetate (PGMEA) onto the substrate, followed by baking on a hotplate at 100 °C for 10 min. To assess the thermal stability of the image sensor, colorimetric measurements were conducted under specified conditions. The thickness of all drop-casting films was 20 µm, as shown in Figure S1.

3. Results and Discussion

To design a new yellow colorant with excellent optical and thermal properties, the azo pyridone group was chosen as the main core structure for developing a material suitable for color filter applications in image sensors. The azo pyridone chromophore group exhibits suitable optical properties for this purpose [21–24]. To enhance the absorption properties

while retaining the functional groups of the azo pyridone group, alkyl groups—acting as electron-donating groups—were introduced to the nitrogen atom of the main azo pyridone backbone, or hydrogen bonding was induced to improve thermal stability through intermolecular interactions in the NH form. Additionally, new yellow colorant molecules were synthesized by designing them in both monomer and dimer forms. The new compounds were designed considering the type of substituents and molecular size to ensure appropriate solubility. Dimerization is expected to improve thermal stability due to the increased molecular weight and the introduction of NH bonds compared to the monomer. Furthermore, electron delocalization is anticipated to partially enhance absorption. The final compounds were designated as APY-M and APY-D and were synthesized through Sandmeyer reactions, with their structures and synthesis pathways described in Schemes 1 and 2. The synthesized compounds were confirmed using NMR spectroscopy (Figures S2–S5).



Scheme 1. Molecular structures of synthesized yellow materials and Disperse Yellow 241.



Scheme 2. Synthetic routes of the synthesized compounds.

The optical properties of the newly synthesized yellow colorants, APY-M and APY-D, in solution are presented in Figures 1 and 2, and Table 1. The absorbance and transmittance measurements of the synthesized azopyridone derivatives were conducted under conditions suitable for image sensor applications, using solutions of 1×10^{-5} M in PGMEA. The requirements for yellow colorants in color filter applications for image sensors include a molar extinction coefficient of at least 1.0×10^4 L/mol·cm and transmittance values of less than 5% at 435 nm and greater than 90% at 530 nm. The molar extinction coefficient values were calculated using the Beer–Lambert law, and the optical absorbance properties of the yellow colorants were evaluated accordingly.

 $A = \varepsilon cl$

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

The synthesized azo pyridone derivatives and Disperse Yellow 241 exhibited absorption in the range of 350–500 nm. In the field of colorant materials for image sensors, Disperse Yellow 241 has been used as a commercially available yellow colorant [25]. The maximum absorption wavelengths (λ_{max}) for APY-M and APY-D were 437 nm and 435 nm, respectively, while Disperse Yellow 241 had a λ_{max} of 425 nm. Both the synthesized materials and Disperse Yellow 241 showed very high molar extinction coefficient values, with

absorption intensities greater than 1 even at a diluted concentration of 1×10^{-5} M. The ε_{max} values at the maximum absorption wavelengths for APY-M and APY-D were 2.7×10^{5} and 3.0×10^{5} L/mol·cm, respectively. Compared to the molar extinction coefficient of Disperse Yellow 241, APY-D exhibited a 1.15-fold enhancement, while APY-M showed similar values. This improvement in APY-D is attributed to the addition of the azo pyridone dimer structure, which enhances the absorption characteristics [26]. All new compounds demonstrated excellent characteristics as yellow colorant candidates with molar extinction coefficients exceeding 1.0×10^{4} L/mol·cm in PGMEA solvent.



Figure 1. (a) UV-Visible absorption spectra and (b) normalized UV-Visible absorption spectra of Disperse Yellow 241 and azo pyridone derivatives in PGMEA solution (at 1.0×10^{-5} M).



Figure 2. Transmittance spectra of Disperse Yellow 241 and synthesized materials at a concentration of 1×10^{-5} M in PGMEA (inset image: photographs of the drop-cast films).

	λ _{max} [nm]	FWHM ^a [nm]	_{ق max} b [L/mol cm]
Disperse Yellow 241	425	72	2.6×105
APY-M	437	80	2.7 imes 105
APY-D	435	73	$3.0 imes 10^5$

Table 1. Optical properties of synthesized materials in 1.0×10^{-5} M PGMEA solution.

^a Full width at half maximum; ^b molar extinction coefficient.

To evaluate the transmittance properties of the newly synthesized materials, transmittance data were measured and are presented in Figure 2 and Table 2. The transmittance spectra were recorded at a concentration of 1×10^5 M in PGMEA. The transmittance criteria for commercial yellow colorants require values below 5% at 435 nm and above 90% at 530 nm. The transmittance values for APY-M were 0.21% at 435 nm and 99.9% at 530 nm, meeting the commercial standards. Similarly, APY-D exhibited transmittance values of 0.10% at 435 nm and 97.1% at 530 nm, also satisfying the commercial criteria. Comparing these results with those of the commercial yellow colorant Disperse Yellow 241, the newly synthesized materials showed relatively superior transmittance at 435 nm, confirming their excellent absorption properties at this wavelength. These results suggest that the newly synthesized compounds exhibit excellent optical properties suitable for commercialization, and they are expected to offer superior color purity when applied as yellow colorants in image sensors.

Table 2. Transmittance of Disperse Yellow 241 and synthesized materials at a concentration of 1×10^{-5} M in PGMEA.

	Transmittance [%]		
	435 nm	530 nm	
Disperse Yellow 241	0.34	99.8	
APY-M	0.21	99.9	
APY-D	0.10	97.1	

The optimized structural and electronic properties of the newly synthesized yellow materials were analyzed through molecular calculations, and the results are summarized in Figures 3 and S6, and Table S1. The structure of Disperse Yellow 241 shows that the dihedral angles between the pyridine, azo, and dichlorobenzene moieties are approximately 0° , indicating a nearly planar conformation. For APY-M, the dihedral angle between the pyridone backbone and the phenyl ring is 1.5° , also indicating a planar structure. In the case of APY-D, the dihedral angles between the pyridone backbone and the phenyl rings are 1.8° and 2.0° , maintaining a similar planar configuration. Additionally, the methylene group connecting the left and right groups exhibits a twisted angle of 60.4° , which helps to effectively prevent intermolecular stacking, thereby inhibiting molecular packing and reducing particle aggregation during film formation. Consequently, this reduction in particle aggregation is anticipated to enhance the optical properties related to color quality by minimizing light scattering. The electron density distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the newly synthesized materials were similar, showing a uniform distribution over the entire molecule. Additionally, both materials exhibited similar band gap values. The experimental HOMO and LUMO values were measured using cyclic voltammetry [27,28]. Figure S7 presents the cyclic voltammogram of the synthesized materials, obtained at a scan rate of 100 mV/s to assess their electrochemical properties. The HOMO values of APY-M and APY-D, determined from the oxidation onset values, were found to be -5.89 eV and -6.00 eV, respectively (as shown in Figure S8). The optical band gap was derived from the $(\alpha h \nu)^2$ versus $(h \nu)$ plot, known as the Tauc plot, by determining the absorbance edge, where α , h, and ν represent the absorbance coefficient, Planck's constant, and the frequency of light, respectively, as shown in Figure S8. The optical band gaps of APY-M and APY-D were 2.58 eV and 2.55 eV, respectively. The LUMO values were calculated using the optical band gap, resulting in values of -3.31 eV for APY-M and -3.45 eV for APY-D. These values followed the same trend as those obtained from DFT calculations.

The solubility of the colorants in PGMEA, a solvent commonly used in the display and image sensor industries, was assessed for their suitability as color filter materials. The solubility of APY-M and APY-D in PGMEA was found to be 1.3 wt% and 1.0 wt%, respectively, as listed in Table 3. APY-M exhibited a solubility that is 1.3 times higher than that of APY-D. This improvement in solubility is attributed to the smaller molecular weight of APY-M and the presence of the methoxypropyl group, which allows for more flexible rotation. The solubility of the new yellow colorants was found to be comparable to that of the commercial yellow colorant Disperse Yellow 241. Additionally, we evaluated the solubility of the newly synthesized compounds in five common organic solvents: chloroform, tetrahydrofuran, acetone, methanol, and acetonitrile. For the solubility experiments, 0.1 g of the colorant was placed in a vial, followed by the addition of solvent, and sonicated for 10 min at room

temperature to measure solubility. APY-D was partially soluble in chloroform, while the new compounds were found to be insoluble in hexane. Both APY-M and APY-D showed improved solubility as the polarity of the solvent increased, with solubility increasing in the order of chloroform, tetrahydrofuran, methanol, and acetonitrile.



Figure 3. Pictorial presentation of the frontier orbitals and a plot of HOMO and LUMO energy levels for APY-M and APY-D (calculated at the B3LYP-D3/def2-TZVPP level of theory).

Table 3. The solubility of the synthesized materials in PGMEA solvent.

	Disperse Yellow 241	APY-M	APY-D
Solubility [wt%]	1.2	1.3	1.0

To evaluate the thermal properties of the synthesized yellow colorant materials, the T_d corresponding to a 5% weight loss was measured using TGA. The T_d values for the newly synthesized APY-M and APY-D were found to be 248 °C and 266 °C, respectively, as summarized in Figure 4 and Table 4. Both compounds exhibited relatively high thermal stability compared to the commercial yellow colorant Disperse Yellow 241, which has a T_d value of 216 °C. The high thermal stability of these materials is generally associated with their ability to withstand temperatures above 230 °C, which is required for the manufacturing process of color filters for image sensors [29,30]. The higher thermal stability of APY-D, with a T_d value 18 °C higher than APY-M, can be attributed to its dimer structure, which involves two azo pyridone backbones and an increased molecular weight. Consequently, the thermal properties of the newly synthesized compounds are expected to be suitable for use in image sensor manufacturing processes.

Table 4. Decomposition temperature of the synthesized materials.

	$T_d^{a}[^{\circ}C]$	
Disperse yellow 241	216	
APY-M	248	
APY-D	266	

^a at 5% weight loss.



Figure 4. Thermo gravimetric analyzer (TGA) curves of the synthesized materials (scan rate: $10 \degree C/min$, nitrogen atmosphere).

To evaluate the applicability of the synthesized azo pyridone derivatives as color filters for image sensors, a solution containing PGMEA, an acrylic binder, the new colorant, and a photo-initiator was prepared and drop-casted onto a glass substrate to create a film. The coated color filter samples were pre-baked at 100 °C and then exposed to UV light at a wavelength of 365 nm. To assess the thermal stability of the manufactured color filters, the samples were treated at 220 °C for 10 min, and the transmittance before and after the treatment was measured, with the results shown in Figure 5 and Table 5. When applying yellow colorants to image sensors, they are typically used as additives to green colorants to enhance the optical properties of the green colorant. In particular, when applied to small image sensor pixel ranges, the following important characteristics are required to minimize color interference between pixels and achieve high color purity. First, the color filter should exhibit excellent transmittance properties, with transmittance below 5% in the blue region at 435 nm and above 90% in the green region at 530 nm. Second, the transmittance should be close to 0% in the blue region and close to 100% in the green region [31]. Before thermal stability testing, the transmittance of the films for APY-M and APY-D was 0.1% and 0.04%at 435 nm, and 99.9% and 92.3% at 530 nm, respectively. After thermal stability testing, the transmittance values for APY-M and APY-D films were 0.3% and 0.07% at 435 nm, and 99.9% and 93.1% at 530 nm, respectively. These results confirm that the optical properties remained at a similar level before and after the thermal stability tests. Additionally, there was no significant change in the slope of the band edge in the 450–575 nm range. In contrast, the commercial material Disperse Yellow 241 did not meet the transmittance requirements before and after thermal stability test. Particularly, APY-D was evaluated as an excellent yellow colorant for image sensor color filters due to its consistent transmittance spectrum and slope before and after thermal stability test. These results can be interpreted as indicating that the enhanced thermal stability of APY-D is due to the increased molecular weight associated with its dimer structure, which maintains its properties effectively. In contrast, while APY-M meets the necessary transmittance properties for commercialization, it exhibits slight changes in the spectrum before and after thermal stability test, with a partially reduced slope in the band edge range of 450–575 nm. This suggests a relative decrease in optical properties compared to APY-D. Consequently, the newly synthesized yellow colorant APY-D successfully meets the demanding requirements for yellow colorants in commercial image sensors. This material is considered to have potential for future applications in commercial image sensor technology.



Figure 5. Transmittance spectra of film (thickness: 20 um) after thermal stability test: (**a**) Disperse Yellow 241, (**b**) APY-M, and (**c**) APY-D.

Table 5. Transmittance values of Disperse Yellow 241 and azo pyridone derivatives after baking 220 $^{\circ}$ C 10 min on glass substrate.

		Transmittance [%]	
		435 nm	530 nm
Disperse Yellow 241	Before	11.0	97.2
	After	17.1	97.7
АРҮ-М	Before	0.1	99.9
	After	0.3	100
APY-D	Before	0.04	92.3
	After	0.07	93.1

4. Conclusions

New yellow colorant compounds, APY-M and APY-D, based on azo pyridone, have been successfully synthesized for use in image sensors. The synthesized materials were evaluated for their optical and thermal properties. The molecules were designed to enhance absorption characteristics by introducing an electron-donating alkyl group to the N atom, or to improve intermolecular interactions through hydrogen bonding. The dimer compound APY-D, compared to the monomer, not only exhibits improved optical properties but also maintains excellent optical characteristics even at high processing temperatures of 230 °C, due to its increased molecular weight and the introduction of NH bonds. Among the synthesized compounds, APY-D demonstrated a solubility of 1.0 wt% in PGMEA and its optical properties, such as band edge, maximum absorption wavelength, and transmittance, were found to be comparable to or superior to the commercial yellow colorant Disperse Yellow 241. Additionally, the newly synthesized compounds showed high thermal stability with T_d values exceeding 248 °C. These results indicate that APY-D, with its outstanding absorption, transmittance, and thermal properties, is an excellent candidate not only for image sensors but also for future applications in various organic display and semiconductor fields.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/photonics11100989/s1. Figure S1: Thickness profiles of films using the synthesized materials; Figure S2: ¹H NMR spectrum of APY-M; Figure S3: ¹³C NMR spectrum of APY-M; Figure S4: ¹H NMR spectrum of APY-D; Figure S5: ¹³C NMR spectrum of APY-D; Figure S6: Optimized molecular structures calculated using B3LYP-D3/def2-TZVPP of Disperse Yellow 241 and synthesized yellow materials; Figure S7: Cyclic voltammetry curves of (a) APY-M and (b) APY-D (scan rate = 100 mV/s); Figure S8: Plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for synthesized materials; Table S1: HOMO-LUMO energy levels by DFT calculation; Table S2: Solubility of the synthesized materials and Disperse Yellow 241. **Author Contributions:** Conceptualization, S.P. (Sunwoo Park), H.K., C.Y. and J.P.; methodology, H.K. and C.Y.; validation, C.Y., H.L. and J.P.; formal analysis, S.P. (Sunwoo Park), S.P. (Sangwook Park) and K.L.; investigation, S.P. (Sangwook Park) and S.O.; resources, J.P.; writing—original draft preparation, S.P. (Sunwoo Park), H.L. and J.P.; writing—review and editing, S.P. (Sunwoo Park), H.L. and J.P.; visualization, S.P. (Sunwoo Park), S.P. (Sangwook Park) and S.O.; supervision, J.P.; project administration, J.P.; funding acquisition, J.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2020R1A6A1A03048004). This research was supported by Basic Science Research Capacity Enhancement Project through Korea Basic Science Institute (National research Facilities and Equipment Center) grant funded by the Ministry of Education (No. 2019R1A6C1010052). This work was partly supported by the GRRC program of Gyeonggi province [(GRRCKYUNGHEE2023-B01); development of ultra-fine process materials based on the sub-nanometer class for the next-generation semiconductors].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- 1. Ren, S.; Zhang, W.; Wang, Z.; Yassar, A.; Chen, J.; Zeng, M.; Yi, Z. Preparation of Dye Semiconductors via Coupling Polymerization Catalyzed by Two Catalysts and Application to Transistor. *Molecules* **2023**, *29*, 71. [CrossRef]
- 2. Taguchi, H.; Enokido, M. Technology of color filter materials for image sensor. *Red* 2017, 10502, 3216.
- 3. Hunger, K. Industrial Dyes: Chemistry, Properties, Applications; John Wiley & Sons: Hoboken, NJ, USA, 2007.
- 4. Gürses, A.; Açıkyıldız, M.; Güneş, K.; Gürses, M.S. Dyes and Pigments; Springer: Berlin/Heidelberg, Germany, 2016.
- 5. Ashida, T. Development of color resists containing novel dyes for liquid crystal displays. Sumitomo Kagaku 2013, 1, 521–523.
- 6. Fontaine, R. In The state-of-the-art of mainstream CMOS image sensors. In Proceedings of the International Image Sensors Workshop, Vaals, The Netherlands, 8–11 June 2015; International Image Sensors Society: Vaals, The Netherlands, 2015; pp. 6–12.
- Chen, Q.; Hu, X.; Wen, L.; Yu, Y.; Cumming, D.R. Nanophotonic Image Sensors. *Small* 2016, *12*, 4922–4935. [CrossRef]
 Kim, C.; Hong, J.; Jang, J.; Lee, G.-Y.; Kim, Y.; Jeong, Y.; Lee, B. Freeform metasurface color router for deep submicron pixel image
- sensors. *Sci. Adv.* 2024, *10*, eadn9000. [CrossRef]
 Li, S.; Gao, C.; Xue, J.; Xin, H.; Li, H.; Zhang, J. Red phenanthrenequinone dyes with high thermal and photo-stability for LCD color filters. *Dye. Pigment.* 2024, *224*, 112023. [CrossRef]
- 10. Kelley, A.T.; Alessi, P.J.; Fornalik, J.E.; Minter, J.R.; Bessey, P.G.; Garno, J.C.; Royster, T.L., Jr. Investigation and application of nanoparticle dispersions of pigment yellow 185 using organic solvents. *Acs Appl. Mater. Interfaces* **2010**, *2*, 61–68. [CrossRef]
- 11. Kim, T.-H.; Lee, B.-J.; An, S.-O.; Lee, J.-H.; Choi, J.-H. The synthesis of red dyes based on diketo-pyrrolo-pyrrole chromophore to improve heat stability and solubility for colour filter fabrication. *Dye. Pigment.* **2020**, *174*, 108053. [CrossRef]
- 12. Do Kim, Y.; Kim, J.P.; Kwon, O.S.; Cho, I.H. The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters. *Dye. Pigment.* **2009**, *81*, 45–52. [CrossRef]
- Kim, H.M.; Lee, H.J.; Lee, H.K.; Hwang, T.G.; Namgoong, J.W.; Lee, J.M.; Kim, S.; Kim, J.P. A study of the diimmonium dyes employing bis (fluorosulfonyl) imide anions for NIR absorbing film of CMOS image sensor. *Dye. Pigment.* 2021, 190, 109288. [CrossRef]
- 14. Namgoong, J.W.; Kim, H.M.; Kim, S.H.; Yuk, S.B.; Choi, J.; Kim, J.P. Synthesis and characterization of metal phthalocyanine bearing carboxylic acid anchoring groups for nanoparticle dispersion and their application to color filters. *Dye. Pigment.* **2021**, *184*, 108737. [CrossRef]
- 15. Jang, S.H.; Lee, G.; Lee, S.Y.; Kim, S.H.; Lee, W.; Jung, J.W.; Kim, J.P.; Choi, J. Synthesis and characterisation of triphenylmethine dyes for colour conversion layer of the virtual and augmented reality display. *Dye. Pigment.* **2022**, *204*, 110419. [CrossRef]
- 16. Lee, H.K.; Kim, H.M.; Kim, S.; Kim, W.; Kim, M.S.; Yoon, J.H.; Choi, W.J.; Jeong, D.H.; Kim, J.P. Development of thermally-stable NIR absorbing films based on heptamethine cyanine dyes with bistriflimide anion. *Prog. Org. Coat.* 2023, *178*, 107473. [CrossRef]
- 17. Sokolova, N.; Kovzhina, L.; Dmitrieva, N.; Karsakova, T. Lightfastness of polymeric color filters with metal-containing dyes and heterocyclic azo dyes as absorbing agents. *Russ. J. Appl. Chem.* **2003**, *76*, 114–116. [CrossRef]
- Oliveira, E.; Bértolo, E.; Núñez, C.; Pilla, V.; Santos, H.M.; Fernández-Lodeiro, J.; Fernández-Lodeiro, A.; Djafari, J.; Capelo, J.L.; Lodeiro, C. Green and red fluorescent dyes for translational applications in imaging and sensing analytes: A dual-color flag. *ChemistryOpen* 2018, 7, 9–52. [CrossRef]

- Kim, J.Y.; Hwang, T.G.; Kim, S.H.; Namgoong, J.W.; Kim, J.E.; Sakong, C.; Choi, J.; Lee, W.; Kim, J.P. Synthesis of high-soluble and non-fluorescent perylene derivatives and their effect on the contrast ratio of LCD color filters. *Dye. Pigment.* 2017, 136, 836–845. [CrossRef]
- 20. Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. J. Chem. Phys. 2020, 152, 224108. [CrossRef]
- 21. Kim, S.H.; Jang, C.K.; Jeong, S.H.; Jaung, J.Y. Synthesis and characterization of novel blue azo-dye derivatives containing acrylate group for dye-based color filters. *J. Soc. Inf. Disp.* **2010**, *18*, 994–1009. [CrossRef]
- Porobić, S.J.; Božić, B.D.; Dramićanin, M.D.; Vitnik, V.; Vitnik, Ž.; Marinović-Cincović, M.; Mijin, D.Ž. Absorption and fluorescence spectral properties of azo dyes based on 3-amido-6-hydroxy-4-methyl-2-pyridone: Solvent and substituent effects. *Dye. Pigment.* 2020, 175, 108139. [CrossRef]
- 23. Mijin, D.Ž.; Ušćumlić, G.S.; Valentić, N.V. History, Synthesis and Properties of Azo Pyridone Dyes. In *Textiles: History, Properties and Performance and Applications*; Nova Publishing: Hauppauge, NY, USA, 2014; pp. 157–186.
- 24. Matijević, B.; Mrđan, G.; Lađarević, J.; Valentić, N.; Mijin, D.; Apostolov, S.; Vaštag, D. Synthesis and solvatochromism of some hydroxy substituted phenyl azo pyridone dyes. *Zaštita Mater.* **2023**, *64*, 444–451. [CrossRef]
- 25. Lee, J. Development of Color Photoresist Material and Color Filter Technology for Image Sensor; The Ministry of Trade, Industry & Energy (MOTIE, Korea): Seoul, Republic of Korea, 2022.
- 26. Park, S.; Kim, J.H.; Park, S.; Mahendra, G.; Lee, J.; Park, J. New Yellow Aromatic Imine Derivatives Based on Organic Semiconductor Compounds for Image Sensor Color Filters. *Appl. Chem. Eng.* **2023**, *34*, 590–595.
- 27. Ren, S.; Wang, S.; Chen, J.; Yi, Z. Design of Novel Functional Conductive Structures and Preparation of High-Hole-Mobility Polymer Transistors by Green Synthesis Using Acceptor-Donor-Acceptor Strategies. *Polymers* **2024**, *16*, 396. [CrossRef]
- Ren, S.; Habibi, A.; Ni, P.; Zhang, Y.; Yassar, A. Tuning the Photophysical Properties of Acceptor-Donor-Acceptor Di-2-(2-oxindolin-3-ylidene) Malononitrile Materials via Extended pi-Conjugation: A Joint Experimental and Theoretical Study. *Materials* 2023, *16*, 6410. [CrossRef]
- 29. Kim, W.S.; Yoon, H.I.; Lee, J.M.; Hwang, T.G.; Kim, H.M.; Lee, H.K.; Kim, S.; Choi, W.J.; Kim, J.P. Substituents effects on properties of perylene dyes for spectrum conversion film. *Dye. Pigment.* **2023**, 209, 110845. [CrossRef]
- 30. Park, J.M.; Jung, C.Y.; Yao, W.; Song, C.J.; Jaung, J.Y. Synthesis of yellow pyridonylazo colorants and their application in dye–pigment hybrid colour filters for liquid crystal display. *Color. Technol.* **2016**, *133*, 158–164. [CrossRef]
- Park, S.; Godi, M.; Khairnar, N.; Dae, S.; Kwon, H.; Park, S.; Lee, H.; Lee, K.; Park, J. Enhanced Optical and Thermal Properties of a Novel Yellow Quinophthalone Derivative for Color Filter Colorants in Image Sensors. *Phys. Status Solidi* (A) 2024, 2300888. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.