Appl. Chem. Eng., Vol. 34, No. 1, February 2023, 80-85
https://doi.org/10.14478/ace.2022.1121

Article

이미지 센서 컬러 필터용 다이온 성분을 포함하는 신규 황색 퀴놀린 유도체

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(2022년 12월 1일 접수, 2022년 12월 18일 수정, 2022년 12월 19일 채택)

New Yellow Quinoline Derivatives Including Dione Moiety for Image Sensor Color Filters

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(Received December 1, 2022; Revised December 18, 2022; Accepted December 19, 2022)

초 록

이미지 센서 컬러 필터에 사용하기 위해 새로운 노란색 퀴놀린-다이온 염료 파생물을 설계하고 합성했습니다. 합성된 화합물은 퀴놀린과 디온 그룹으로 구성된 기본 화학 구조를 가지고 있습니다. 새로운 재료는 상업적 장치 제조 공정을 모방한 조건에서 광학적, 열적 특성을 기반으로 평가되었습니다. 이들의 관련 성능을 비교한 결과, 제조된 두 화합물 사이에서 2-(3-hydroxyquinolin-2(1H)-ylidene)-1H-indene-1,3(2H)-dione (HQIDO)이 다음과 같은 우수한 성능을 나타냈습니다. 프로필렌 글리콜 모노메틸 에테르 아세테이트 용매에서 0.5 wt%보다 큰 용해도, 각각 298 °C의 높은 분해 온도를 포함하는 이미지 센서 컬러 필터 재료. 결과는 HQIDO가 이미지 센서 착색제에서 노란색 염료 첨가제로 사용될 수 있음을 시사합니다.

Abstract

New yellow quinoline-dione dye derivatives were designed and synthesized for use in image sensor color filters. The synthesized compounds have a basic chemical structure composed of quinoline and dione groups. New materials were evaluated on the basis of their optical and thermal properties under conditions mimicking those of a commercial device fabrication process. A comparison of their related performances revealed that, between the two prepared compounds, 2-(3-hydroxyquinolin-2(1H)-ylidene)-1H-indene-1,3(2H)-dione (HQIDO) exhibited the superior performance as an image sensor color filter material, including a solubility greater than 0.5 wt% in propylene glycol monomethyl ether acetate solvent and a high decomposition temperature of 298 °C, respectively. The results suggest that HQIDO can be used as a yellow dye additive in an image sensor colorant.

***Keywords**: Yellow colorant, Quinoline derivative, Dione group, Image sensor, Color filter*

1. Introduction

Recently, color filters have become critical in various electronic devices. In particular, they are used in liquid crystal displays, organic light-emitting diodes, and image sensors such as digital cameras and cameras incorporated into smart phones and tablet PCs. Image sensors can be classified as charge coupled device (CCD) types and complementary metal oxide semiconductor (CMOS) types. In the past, CCD image sensors led the market; however, the market for CMOS image sensors is now increasing because of their advantages of lower cost, lower power consumption, and easier integration than CCDs. The color-filter technology used in image sensors requires finer pixel sizes and higher contrast ratios to achieve higher-quality real images[1]. The pigment dispersion method is most widely used to make red, green, and blue color filters because of the high thermal-, chemical-, and photo-stability of pigments. However, this method is limited by the low solubility of pigments, which makes producing smaller particles difficult and leads to light scattering by aggregated particles[1-4]. To resolve these problems, dye-based color filters have been studied[5-8]. Because dyes are soluble in solvents, light scattering by particles is not

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observed and light transmittance is therefore improved. In addition, improved thermal and solvent stability in industrial solvents such as propylene glycol monomethyl ether acetate (PGMEA) must be realized for these dyes to be used in dye-based color filters[2,5-8]. If dyes are not stable in common industrial solvents such as PGMEA, then their application in color filters will be difficult[9-11]. Therefore, it is necessary to develop dyes with good thermal and solvent stability. In the present study, we designed and synthesized new yellow dyes based on quinoline-dione derivatives bearing phenyl or naphthyl groups and investigated their suitability for use in green color filters. Green colorants cannot perfectly absorb blue light, and yellow additives should be added to a green colorant mixture to achieve high color purity of green. The synthesized quinoline-dione derivatives were studied to optimize their optical, thermal, and solvent stabilities depending on the chemical structures, and their potential as yellow color-filter materials was evaluated.

2. Experimental

2.1. Materials and instrumentation

All reagents used in these experiments were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), CK chem; their purity was 98% or higher, and they were used without further purification. 1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 400 spectrometer and high-performance liquid chromatography (HPLC) was carried out on a Shimadzu Nexera UHPLC. Ultraviolet–visible (UV–Vis) optical absorption spectra were recorded using a Lambda 1050 UV–Vis spectrophotometer (Perkin Elmer). Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q5000 IR/SDT Q600 with the sample under an air atmosphere. Transmission electron microscopy (TEM) images were acquired using a JEOL JEM-2100F.

2.2. Synthesis and characterization of the synthesized quinoline-dione derivatives

2.2.1. Synthesis of 2-(3-hydroxyquinolin-2(1H)-ylidene)-1H-indene-1,3(2H)-dione (HQIDO)

2-Methyl-3-hydroxyquinoline (3.8 g, 0.0238 mol), phthalic anhydride (1 g, 0.00675 mol), and benzoic acid (0.292 g, 0.00238 mol) were dissolved in 50 ml of 1,3,5-trichlorobenzene. The reaction mixture was refluxed at 180 °C for 2h and filtered and washed with ethanol. Washed compounds dried under vacuum oven at 120 °C for 1.5 hours and compound was obtained (1.54 g, yield 85%). 1H NMR (400 MHz, THF-d8) δ 7.75 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.56 – 7.50 (m, 2H), 7.43 – 7.38 (m, 1H).

2.2.2. Synthesis of 2-(3-hydroxyquinolin-2(1H)-ylidene)-1H-cyclopenta[b]naphthalene-1,3(2H)-dione (HQCNDO)

2-Methyl-3-hydroxyquinoline(1 g, 0.00628 mol), 2,3-naphthalenedicarboxylic anhydride (1.24 g, 0.00628 mol), methyl benzoate (8.55 g, 0.0628 mol), and benzoic acid (7.67 g, 0.0628 mol) were placed into reactor then heated to 220 °C under nitrogen condition for 12h. After completion of the reaction, it was cooled down to room temperature and was added with methanol, then stirred for 1 h and filtered and washed by methanol and acetone. The final product was obtained after vacuum drying (1.39 g, yield 65%). 1H NMR (400 MHz, THF-d8) δ 8.12 (d, J = 11.2 Hz, 2H), 8.03 (dd, J = 6.0, 3.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.71 (dd, J = 8.1, 1.2 Hz, 1H), 7.62 (s, 1H), 7.60 – 7.54 (m, 3H), 7.44 (td, J = 7.6, 7.1, 1.0 Hz, 1H).

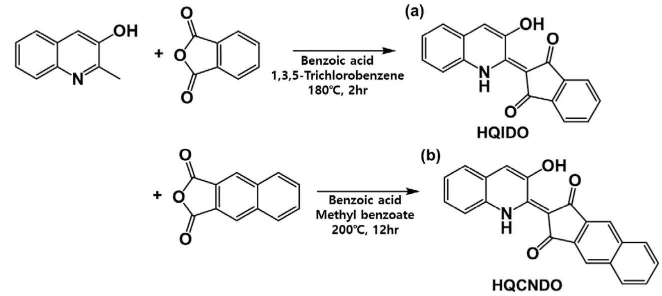
2.3. Fabrication and measurement of the dye-based color filters

Color resist solutions were prepared using the synthesized quinoline-dione derivatives and other components. The other components of the solutions included an acrylic binder consisting of methyl methacrylate groups, carboxylic acid groups, and benzyl methacrylate groups, a leveling agent, and PGMEA as a solvent. The solution was coated onto a 2.5 cm × 2.5 cm transparent glass substrate using a MIDAS SPIN-1200D spin-coater at 850 rpm for 10 s. All colorant films were baked at 220 °C for 3 min.

3. Results and discussion

In order to develop high performance of optical property and thermal property, a new yellow colorant was designed based on quinoline-dione moiety as shown in Scheme 1. Two compounds of HQIDO and HQCNDO were purified by recrystallization and confirmed by NMR spectroscopy as shown in Figure 1 and 2.

Optical data of HQIDO and HQCNDO in solution state were shown in Figure 3 and Table 1. In the image sensor industry, 1×10^{-4} M propylene glycol monomethyl ether acetate (PGMEA) solution is required and the molecular extinction coefficient value should be more than 1.0×10^4 L mol^{-1} cm^{-1}. Especially for yellow colorant, transmittance value should be less than 5% at 435 nm and more than 90% at 530 nm because it can be added to green colorant mixture for high quality of image sensor application. As shown in Table 1, two compounds satisfied image sensor application requirements with high performance value. This result can provide small size image sensor pixels without color interference as well as highly qualified color purity based on high absorption in the blue wavelength region of 435 nm. The extinction coefficient value of HQIDO and HQCNDO was 3.86×10^4 L mol^{-1} cm^{-1} and 3.45×10^4 L mol^{-1} cm^{-1}, respectively. New synthesized quino-



Scheme 1. Synthetic routes and chemical structures of the quinoline-dione derivatives: (a) HQIDO, (b) HQCNDO.

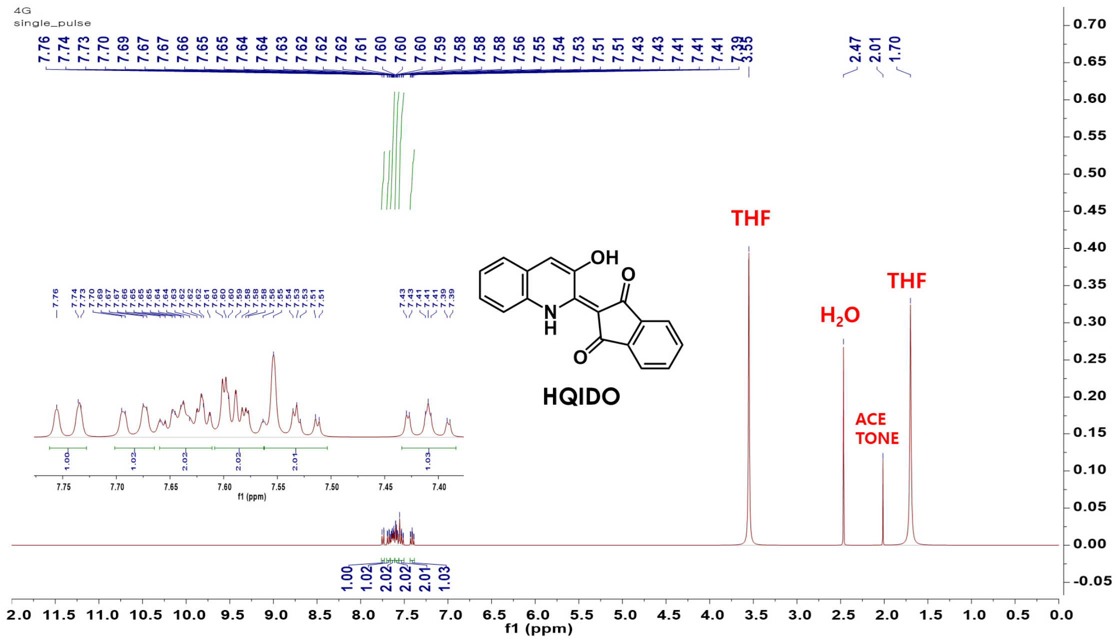


Figure 1. ^{1}H NMR spectrum of HQIDO.

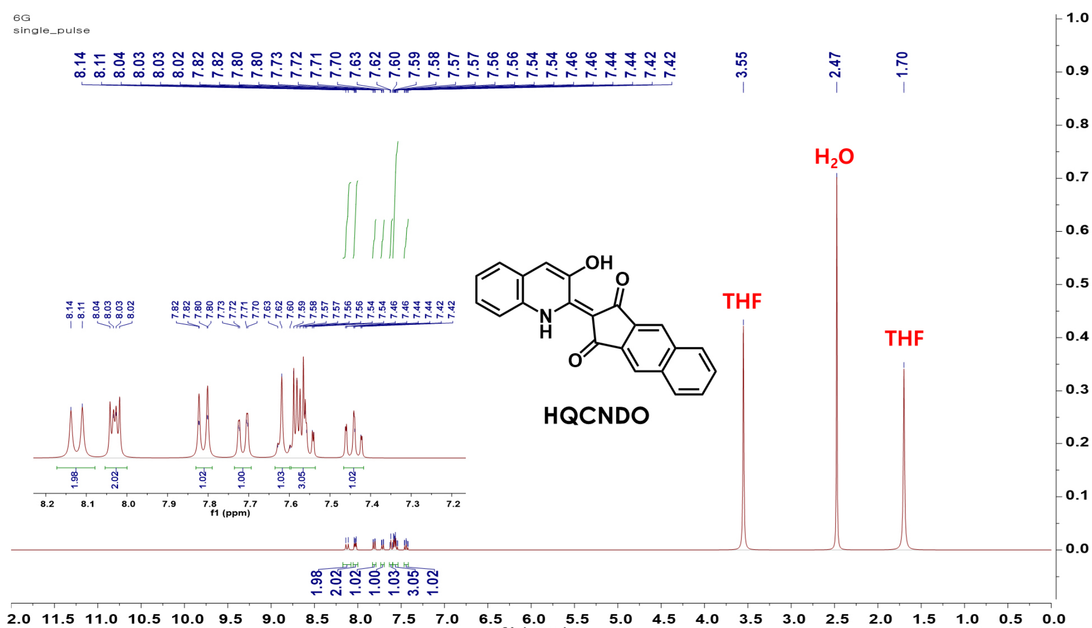


Figure 2. ^{1}H NMR spectrum of HQCNDO.

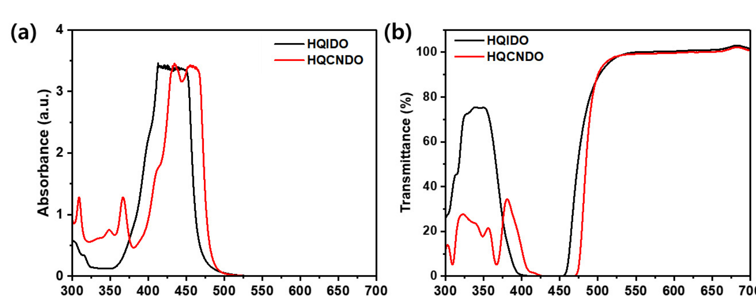


Figure 3. UV-Vis spectra: (a)The absorbance spectra and (b) The transmittance spectra of synthesized materials in 1 × 10^{-4} M PGMEA solution.

Table 1. The Transmittance Values of the Synthesized Yellow Materials at 435 nm and 530 nm in 1 × 10^{-4} M PGMEA Solution

	HQIDO	HQCNDO
435 nm	0.04%	0.04%
530 nm	98.63%	98.60%

Table 2. The Solubility of Synthesized Materials in PGMEA Solvent

	HQIDO	HQCNDO
Solubility (wt%)	0.5	0.4

line-dione derivatives showed molecular extinction coefficient values of more than 3.0 × 10^4 L mol^{-1} cm^{-1} which is higher than 1.0 × 10^4 L mol^{-1} cm^{-1}. Comparing the band edge value of HQIDO and HQCNDO, it had 466 and 479 nm, respectively. It can be explained by that HQCNDO has an extended conjugation length based on chemical structure. As a result, HQIDO and HQCNDO exhibited about 0.04% transmittance at 435 nm and more than 98% transmittance at 530 nm as well as maximum absorption wavelengths of 415 and 434 nm, respectively. It means that it can be applied to green color image sensor application as the yellow additives.

In order to use color materials for the image sensor and display applications, it is desirable for the organic colorant materials to be solved in PGMEA solvent. The solubility of HQIDO and HQCNDO was 0.5 and 0.4wt% as shown in Table 2.

Thermal property for the industry application is needed under the 5% weight loss in TGA experiment, which is defined as the decomposition temperature (T_d). Figure 4 and Table 3 show the related graph and data. HQIDO and HQCNDO exhibited Td values of 298 °C and 390 °C, which is due to the increased molecular weight from 289.29 g/mol to 339.35 g/mol. It can be also explained by the inserted phenyl ring because flat chemical structure can increase the thermal stability. Industry application requires more than 250 °C of T_d value.

In order to prepare the color resist (CR) mixture, the pigmentation process should be followed after colorant synthesis and then dispersion additives should be mixed to provide mill-base (MB) mixture. After mixing MB material with monomer, photo initiator, and solvent, CR mixture can be finally prepared. When the nano pigmentation was applied to the synthesized HQIDO and HQCNDO average particle size was 45 nm and 350 nm as shown in Figure 5, respectively. Before pigmentation, HQIDO and HQCNDO exhibited rod like shape morphology having the width and the length in the range of 100~600 nm (HQIDO) and 120~1,000 nm (HQCNDO). After pigmentation, two compounds maintain the similar morphology shape but the particle size was decreased. Also, HQIDO average particle size was relatively small as 45 nm. It can be explained by that before pigmentation, HQIDO was already synthesized with the relatively small width and the length in the range of 100~600 nm, which might come from the small size of molecular structure.

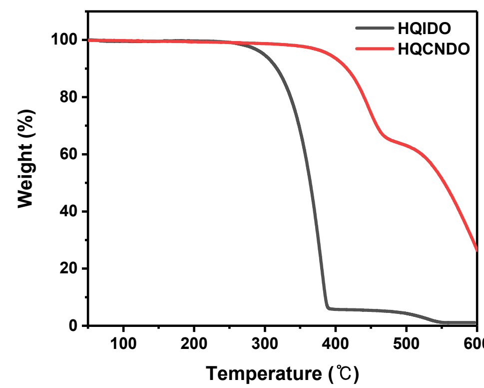


Figure 4. Thermogravimetric analysis (TGA) curves of the synthesized the quinoline-dione derivatives.

Table 3. The Decomposition Temperature and Molecular Weight of Newly Synthesized Compounds

	HQIDO	HQCNDO
T_d (5wt loss)	298 °C	390 °C
M.W (g/mol)	289.29	339.35

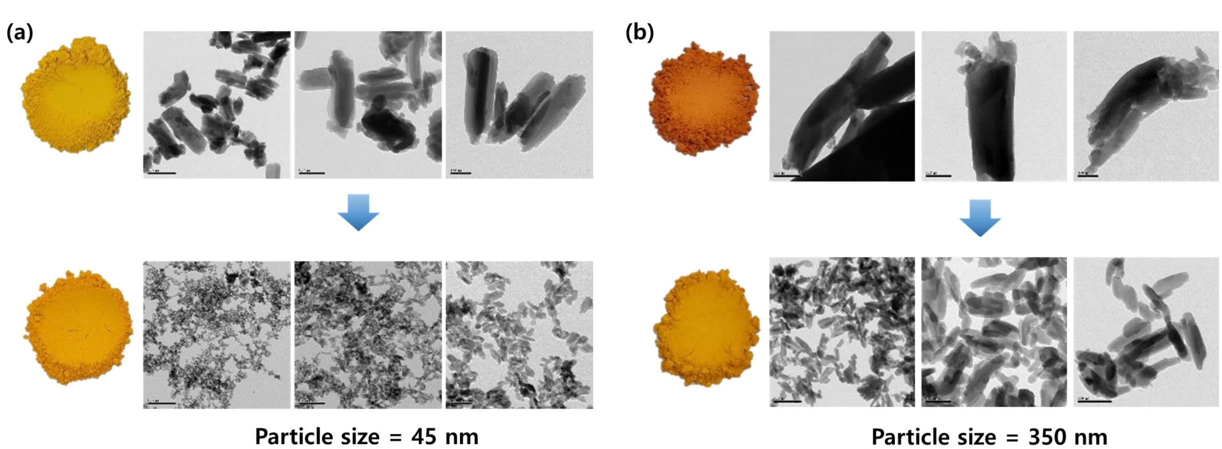


Figure 5. Transmission electron microscope (TEM) images of (a) HQIDO, and (b) HQCNDO.

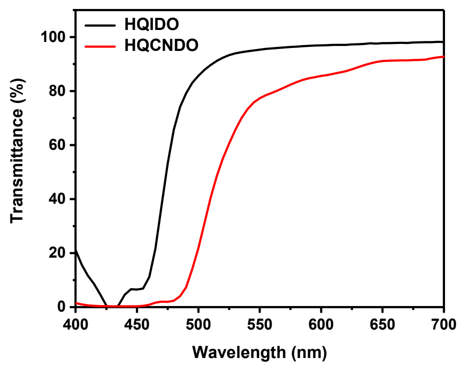


Figure 6. The transmittance spectra of the synthesized materials on CR Filml.

Table 4. The Transmittance Values of the Synthesized Yellow Materials at 435 nm and 530 nm on CR Film

	HQIDO	HQCNDO
435 nm	0.76%	0.30%
530 nm	93.92%	65.60%

The optical property of thin film after CR preparation is summarized in Figure 6 and Table 4. Although other additives were mixed with pure yellow colorant, the transmittance was maintained with less than 5% at 435 nm as well as more than 90% at 530 nm. Especially, HQIDO showed the transmittance value of 0.76% and 93.9% at 435 nm and 530 nm, and HQCNDO had the value of 0.30% and 65.6% at 435 nm and 530 nm, respectively. The reason why HQCNDO showed low transmittance of 65.6% is that compound has longer conjugation length and the red-shifted absorption band edge based on the chemical structure.

As a result of transparent property, HQIDO satisfied the commercial image sensor yellow requirement. This result can be made by the fine particle size of 45 nm in case of HQIDO.

4. Conclusion

New quinoline-dione dye compounds were successfully synthesized as image sensor colorant additives. Two materials were proposed and evaluated on the basis of their optical, thermal properties. Between the two investigated compounds, HQIDO showed superior solubility in PGMEA (greater than 0.5 wt%), and HQIDO and HQCNDO exhibited optical properties similar to those of the commercialized yellow colorant in terms of the transmittance. A comparison of the related performance of the two compounds revealed that HQIDO exhibited optimized optical and thermal properties, including a transmittance of less than 5% at 435 nm and greater than 90% transmittance at 530 nm, and a T_d greater than 250 °C. The results indicate that HQIDO can be used as an image sensor application colorant.

Acknowledgements

This research is (partially) funded by the BK21 FOUR program of National Research Foundation of Korea. This work was supported by the ITECH R&D program of MOTIE/KEIT [project No. 20009872, Development of high throughput colorimetric chemical materials]. 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 work was supported by the Korea Institute for Advancement of Technology (KIAT) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. P0017363). 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).

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