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Facile synthesis and characterization of novel coronene chromophores and their application to LCD color filters

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ABSTRACT

New coronene derivatives, diphenylcoronene tetracarboxdiimide and monophenylbenzoperylene tetracarboxdiimide, were synthesized from N,N′-bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxdiimide via a one-step reaction. The suggested synthetic route is the simplest and most economical among the methods to extend the aromatic systems along the short molecular axis of perylene. The synthesized molecules exhibited superior stability and color strength as yellow chromophores. They were characterized by significant hypsochromic shifts of the absorption compared to perylene tetracarboxdiimide and high fluorescence quantum yields.

1. Introduction

Rylene tetracarboxdiimide derivatives including Perylene-3,4,9,10-tetracarboxdiimide are useful chromophores exhibiting exceptional chemical, thermal, and photochemical stability with high extinction coefficients [1]. They have a wide range of applications, such as reprographic processes [2], photovoltaic cells [3], fluorescent solar collectors [4], energy relaying dyes for solar cells [5], optoelectronic devices [6], light emitting diodes [7] as well as usual colorant usage. Therefore, diverse methodologies to functionalize the aromatic core of perylene tetracarboxdiimide have been reported to extend the range of application of these chromophores as functional dyes [8–13]. The extension of the aromatic systems along the long molecular axis of perylene usually induced bathochromic shifts of the absorption spectra with increasing extinction coefficients [8]. However, their absorption maxima shifted hypsochromically when the aromatic systems of those molecules were enlarged along the short molecular axis, such as coronenetetracarboxdiimides **1** (Fig. 1) [9]. These coronene derivatives can be extremely valuable because they are considerably stable and show high color strengths compared to other yellow chromophores. In general, stability and color strength of dye molecules often increase with increasing size of the aromatic system, which inevitably causes a bathochromic shift in absorption [10].

Several synthetic routes from perylene to coronene have been reported. The core extension of perylenediimides using a Diels–Alder reaction with maleic anhydride [11] and synthesizing bisalkynyl substituted perylenediimides and their successive cyclization to coronene were reported [9]. In addition, the further core expanded structure, dibenzocoronene **2** (Fig. 1), was synthesized by palladium-catalyzed dehydrobromination after Suzuki-coupling of 2-bromophenylboronic acid at the bay position of bromo-substituted perylene [12]. This is also possible by palladium-assisted cycloaddition of benzyne [8] or by the photocyclization of Suzuki-coupled phenylboronic acid [13]. However, all these synthetic methods were limited to some degree by the moderate yields, side reactions, and severe synthetic conditions.

In this study, new coronene derivatives were synthesized through a novel simple one-step synthetic route and their characteristics were discussed as well. In particular, their properties for yellow compensating dyes for color filters, which converts the white backlight into red (R), green (G) and blue (B) colored lights in LCD display panel, were investigated.

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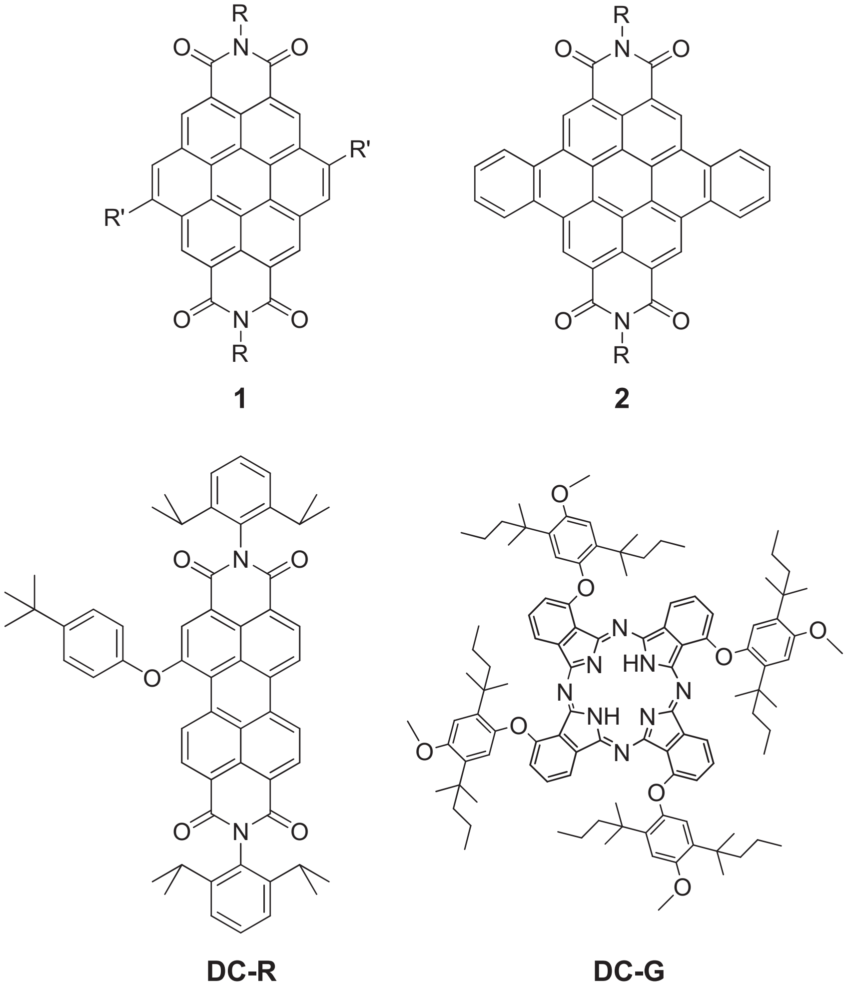


Fig. 1. Coronene carboximide derivatives and prepared dyes for color filters.

2. Experimental

2.1. Materials and instrumentation

1-phenylvinylboronic acid, $Pd(PPh_3)_4$, and Na_2CO_3 purchased from Sigma–Aldrich were used as received. All the other reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Transparent glass substrates were provided by Paul Marienfeld GmbH & Co. KG. Commercial acrylic binder LC20160 was supplied by SAMSUNG Cheil industries Inc.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz using chloroform-d and TMS, as the solvent and internal standard, respectively. Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI-TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation with α-cyano-4-hydroxy-cynamic acid (CHCA) as the matrix. Elemetal analysis was done on CE Instrument EA1112. Absorption and transmittance spectra were measured using an HP 8452A spectrophotometer. Fluorescence spectra were measured using a Shimadzu RF-5301PC spectrofluorometer. Chromatic characteristics of the color filters were analyzed on a Scinco color spectrophotometer. Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10°C min^{-1} using a TA Instruments Thermogravimetric Analyzer 2050.

2.2. Synthesis

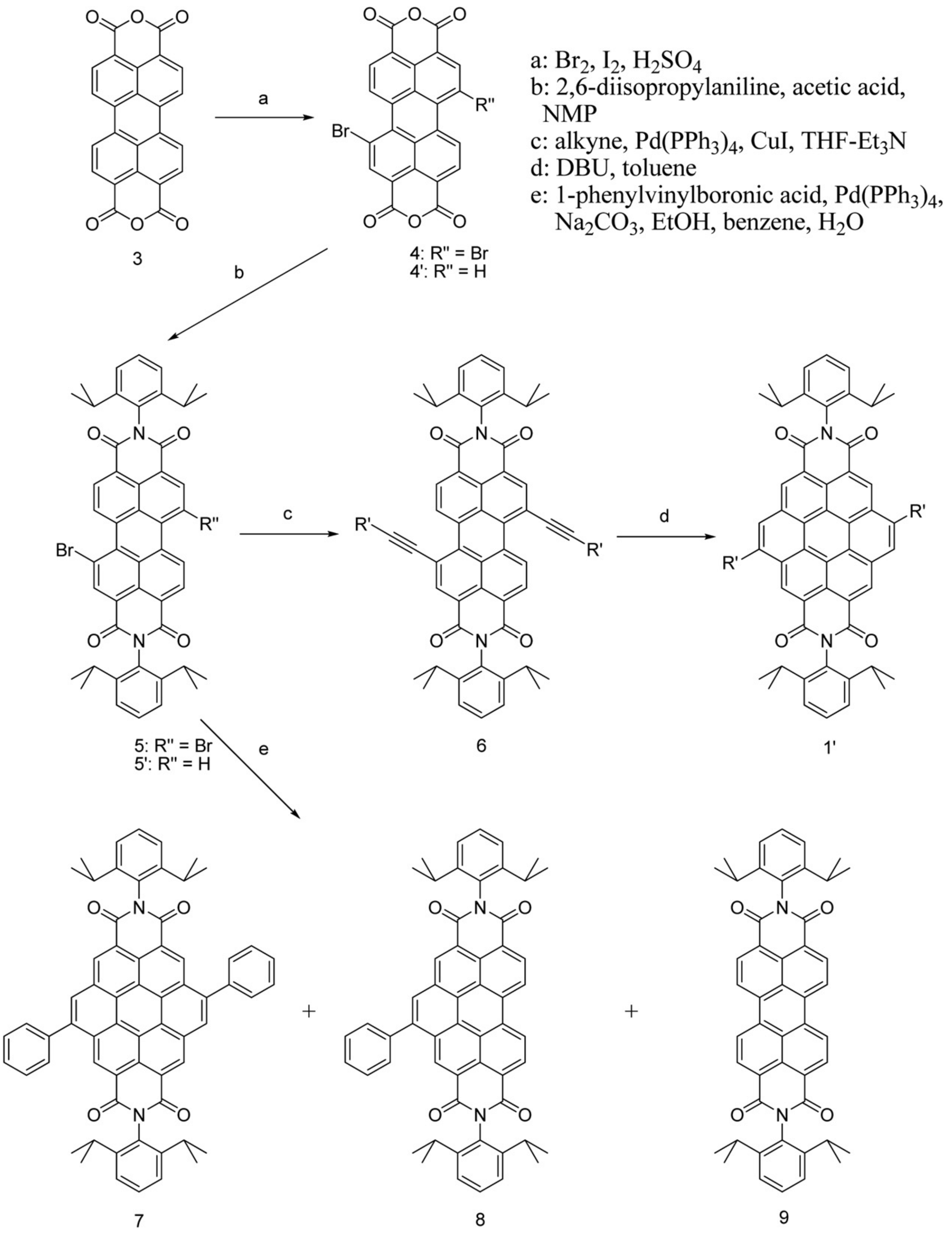
N,N′-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxdiimide **5**, N,N′-Bis(2,6-diisopropylphenyl)-1-bromoperylene-3,4,9,10-tetracarboxdiimide 5′, and DC-R were synthesized according to the previously reported procedures [14]. DC-G was synthesized according to the procedures reported elsewhere [15].

2.2.1. N,N′-Bis(2,6-diisopropylphenyl)-5,11-diphenylcoronene-2,3,8,9-tetracarboxdiimides 7

A deaerated mixture of EtOH (5.79 mL), benzene (33.12 mL), H_2O (8.13 mL) was added to a solid mixture of 5 (1.0 g, 1.15 mmol), 1-phenylvinylboronic acid (0.68 g, 4.6 mmol), $Pd(PPh_3)_4$ (66.57 mg, 5.0 mol%), and Na_2CO_3 (1.2 g, 11.5 mmol) under nitrogen. The mixture was reacted at 80 °C for 120 h. The reaction was quenched by the addition of water. The mixture was extracted with dichloromethane several times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to provide a crude solid. The crude solid was further purified by column chromatography on silica gel using dichloromethane as the eluent. The band containing a trace of compounds synthesized from tribrominated diimide could be separated firstly. Then, the second band containing yellow compound **7** was collected.

Yield 52.1%; Mp > 300 °C (decomp.). ^1H NMR(500 MHz, $CDCl_3$): $\delta = 1.24$ (d, $J = 6.5$ Hz, 24H), 2.99 (septet, $J = 40.0$ Hz, 4H), 7.42

(d, $J = 8.5$ Hz, 4H), 7.54 (t, $J = 9.2$ Hz, 2H), 7.70 (t, $J = 9.0$ Hz, 2H), 7.76 (t, $J = 13.5$ Hz, 4H), 7.97 (t, $J = 10.2$ Hz, 4H), 9.27 (s, 2H), 10.17 (s, 2H), 10.22 (s, 2H); ^{13}C NMR(126 MHz, $CDCl_3$): $\delta = 23.98$, 24.34, 29.52, 29.92, 122.20, 122.38, 124.00, 124.26, 124.39, 124.49, 125.21, 129.03, 129.35, 129.42, 129.93, 130.05, 130.37, 130.44, 131.15, 131.21, 131.46, 131.76, 139.38, 139.49, 142.93, 143.13, 145.96, 146.07, 164.99, 165.13; MALDI-TOF MS: m/z 911.07 (100%, $[M + H^+]$); Found: C, 84.52; H, 5.45; N, 3.10%. Calc. for $C_{64}H_{50}N_2O_4$: C, 84.37; H, 5.53; N, 3.07%.



Scheme 1. Synthesis of coronene carboximide derivatives.

2.2.2. *N,N′-Bis(2,6-diisopropylphenyl)-5-phenylbenzoperylene-2,3,8,9-tetracarboxdiimides* ***8***

8 was synthesized in the same manner with **7** using **5′** (1.0 g, 1.27 mmol), 1-phenylvinylboronic acid (0.38 g, 2.54 mmol), $Pd(PPh_3)_4$ (66.57 mg, 5.0 mol%), and Na_2CO_3 (1.2 g, 11.5 mmol).

Yield 66.8%; Mp > 300 °C (decomp.). ^{1}H NMR(500 MHz, $CDCl_3$): $\delta = 1.21$ (d, $J = 7.0$ Hz, 24H), 2.84 (septet, $J = 38.5$ Hz, 4H), 7.38 (dd, $J = 26.2$ Hz, 4H), 7.52 (m, $J = 18.4$ Hz, 2H), 7.61 (t, $J = 9.9$ Hz, 1H), 7.67 (t, $J = 14.5$ Hz, 2H), 7.77 (t, $J = 9.4$ Hz, 2H), 8.81 (s, 1H), 9.22 (d, $J = 8.2$ Hz, 2H), 9.49 (d, $J = 10.8$ Hz, 2H), 9.56 (s, 1H), 9.63 (s, 1H); ^{13}C NMR(126 MHz, $CDCl_3$): $\delta = 24.25$, 24.32, 29.55, 29.92, 122.41, 122.60, 123.22, 123.62, 123.71, 124.30, 124.42, 124.49, 124.73, 124.88, 126.08, 128.02, 128.10, 128.93, 129.03, 129.31, 129.72, 129.86, 129.88, 130.00, 130.25, 130.75, 130.92, 130.96, 131.10, 133.50, 133.94, 134.29, 135.21, 138.91, 143.15, 145.91, 145.96, 164.17, 164.26, 164.35; MALDI-TOF MS: m/z 811.09 (100%, $[M + H^+]$); Found: C, 83.12; H, 5.58; N, 3.42%. Calc. for $C_{56}H_{46}N_2O_4$: C, 82.94; H, 5.72; N, 3.45%.

2.3. *Preparation of dye-based inks and color filters*

The dye-based ink for a color filter was composed of the cyclohexanone (3.2 g), acrylic binder (1.4 g), and dye (0.1 g).

The prepared dye-based inks were coated on a transparent glass substrate using a MIDAS System SPIN-1200D spin coater. The coating speed was initially 100 rpm for 5 s, which was then increased to 500 rpm and kept constant for 20 s. The wet dye-coated color filters were then dried at 80 °C for 20 min, prebaked at 150 °C for 10 min, and postbaked at 230 °C for 1 h. After each step, the coordinate values of the color filters were measured.

2.4. *Measurement of thermal stability*

Thermal stability of the synthesized dyes was evaluated by thermogravimetry (TGA). The prepared dyes were heated to 110 °C and held at that temperature for 10 min to remove residual water and solvents. The dyes were then, heated to 220 °C and held at that temperature for 30 min to simulate the processing thermal conditions of color filter manufacturing. The dyes were finally heated to 400 °C to determine their degradation temperature. The temperature was raised at the rate of 10°C min^{-1} under nitrogen atmosphere.

To check the thermal stability of the dyes in color filters, the fabricated color filters were heated to 230 °C for 1 h in a forced convection oven (OF-02GW Jeiotech Co., Ltd.). The color difference values (ΔE_{ab}) before and after heating were measured on a color spectrophotometer (Scinco colormate) in CIE L'a'b' mode.

3. Results and discussion

3.1. *Synthesis*

Different types of linear alkyl chains were introduced selectively at the R′ position of coronenetetracarboxdiimides **1** through reactions c and d of Scheme 1 as described in literature [9]. In this reference, sterically demanding substituents, such as *tert*-butyl or a phenyl group, could not be introduced because the bulky substituents at the C–C triple bond restricted the cyclization reaction. However, as shown in the experimental section of this paper, phenylvinylboronic acid, inherent with an aryl group, was reacted successfully with bromo-substituted perylenediimides **5**, and **5′** under similar conditions to Suzuki-coupling and spontaneously cyclized to afford two novel compounds diphenylcoronene tetracarboxdiimide **7** and monophenylbenzoperylene tetracarboxdiimide **8**. The conveniences of this synthesis are that the 1,6-isomer of 1,7-dibromoperylene tetracarboxdiimide **5** does not have to be removed because both isomers react with phenylvinylboronic acid to form the same desired product **7**, and 1,7-dibromoperylenediimide **5** and mono-bromoperylenediimide **5′** could be obtained from the same crude product after column chromatography [14]. The yield of monophenylbenzoperylene **8** (66.8%) was higher than that of diphenylcoronene **7** (52.1%) because there were more side products such as mono-substituted compound when diphenylcoronene **7** was synthesized. In column chromatography process of diphenylcoronene **7**, the first band of the eluent was carrying the impurity reacted from the trace of tribrominated diimide, and the second band was for diphenylcoronene **7**. Monophenylbenzoperylene **8** was also obtained as a side product at the fourth band of the eluent, and the sixth band was for N,N′-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-tetracarboxdiimide **9**, all bromines were removed. The described synthetic route is the simplest and most economical method with a considerable yield under mild conditions.

3.2. *Photophysical properties of dyes*

Both coronene derivatives **7** and **8** are highly soluble in most organic solvents, such as dichloromethane, hexane, and toluene since the aggregation between dyes is suppressed by steric hindrance of the phenyl groups at the bay positions as well as the diisopropylphenyl groups at the terminal positions, which are distorted from the plane of the main body of the coronene derivatives [14]. Monophenylbenzoperylene **8** shows the main absorption maximum at 472 nm (Fig. 2), which originated from the typical vibronic structure of perylene, giving this chromophore a very strong and vivid yellow color. The shape of this characteristic main peak is analogous to that of dibenzocoronene **2**, but hypsochromically shifted by approximately 22 nm [12]. Monophenylbenzoperylene **8** is an ideal yellow chromophore since its main peak is very sharp and there is no absorption over 500 nm. The extinction coefficient of monophenylbenzoperylene **8** at 472 nm ($\varepsilon = 65{,}688$ M^{-1} cm^{-1}) is similar to that of dibenzocoronene **2** at 494 nm ($\varepsilon = 66{,}000$ M^{-1} cm^{-1}) and higher than that of coronene **1** at 428 nm ($\varepsilon = 62{,}000$ M^{-1} cm^{-1}) [12]. Diphenylcoronene **7** shows its main absorption maximum at a much shorter wavelength (426 nm, $\varepsilon = 59{,}988$ M^{-1} cm^{-1}) with minor absorption at approximately 512 nm (Fig. 2). The shape of these absorption peaks is similar to that of coronene **1**, which has an alkyl chain introduced at the R′ position, but the distance between the two absorption maxima is slightly different [9]. The minor absorption around

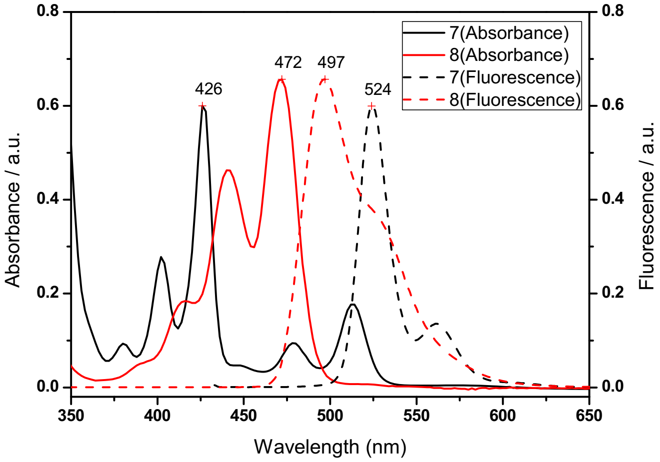


Fig. 2. Absorption and fluorescence spectra of compounds **7** and **8** in CH_2Cl_2 (10^{-5} mol L^{-1}).

Table 1
Transmittance of the spin-coated color filters.

Prepared dyes	λ_{max}(nm)	Transmittance(%)
DC-R	626	95.89
DC-R + 8	628	94.78
DC-G	498	85.05
DC-G + 8	524	85.39

512 nm gives diphenylcoronene **7** a somewhat dull color in solution compared to the much brighter and greener color of monophenylbenzoperylene **8**. The absorption spectra of these molecules make them very suitable as yellow compensating dyes for LCD color filters. In particular, monophenylbenzoperylene **8** can be used to cut off the undesirable transmittance in short wavelength range of red color, and extremely useful for making the green color with narrow half-band width [16].

Diphenylcoronene **7** and monophenylbenzoperylene **8** show fluorescence maxima at 524 and 497 nm, respectively (Fig. 2). Their quantum yields are 82 and 86%, respectively, which are much higher than other yellow fluorophores, e.g. acridine yellow, which has a fluorescence quantum yield of 47% [17]. In particular, diphenylcoronene **7** can be an excellent donor dye for DSSCs using Förster resonance energy transfer (FRET) because the emission of diphenylcoronene **7** is strong and barely overlaps with the absorption range [18].

3.3. Spectral and chromatic properties of spin coated color filters

Currently, dyes are extensively investigated to replace pigments in LCD manufacturing process since there are growing needs for enhancing the picture quality [14]. The dye-based color filters have superior transmittance compared to the pigment-based one because dyes dissolved in the media have a smaller particle size, which leads to less light scattering [19]. Monophenylbenzoperylene **8** can make ideal transmittance spectra of red and green color filters when used as a yellow compensating dye, shown at Table 1, Fig. 3, and 4. The common red dyes, such as DC-R, which have undesirable transmittance under 500 nm as shown in Fig. 3 can not be solely used to color filters without yellow compensating dye [14]. Monophenylbenzoperylene **8** absorbing under 500 nm intensively without any residual absorption over 500 nm can cut off undesirable transmittance of given red dye effectively with maintenance of the desired transmittance range. This kind of compensation effect is more prominent in green color. The main dyes for green color, such as DC-G, transmit wide range of wavelength to have dull bluish green color. However, the dye composite including monophenylbenzoperylene **8** exhibited sharp transmittance spectrum cut off under 500 nm as shown in Fig. 4. Therefore, vivid and clear green color could be realized by blending monophenylbenzoperylene **8**. With less amount of the green dye in the mixture with the yellow dye, λ_{max} of the color filter red shifted about 20 nm to be closer to the green color for conventional LCD color filters [16].

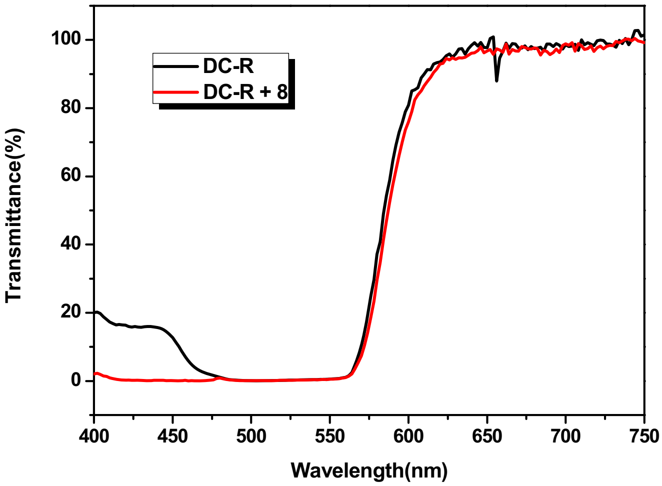


Fig. 3. Transmittance spectra of red spin coated color filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

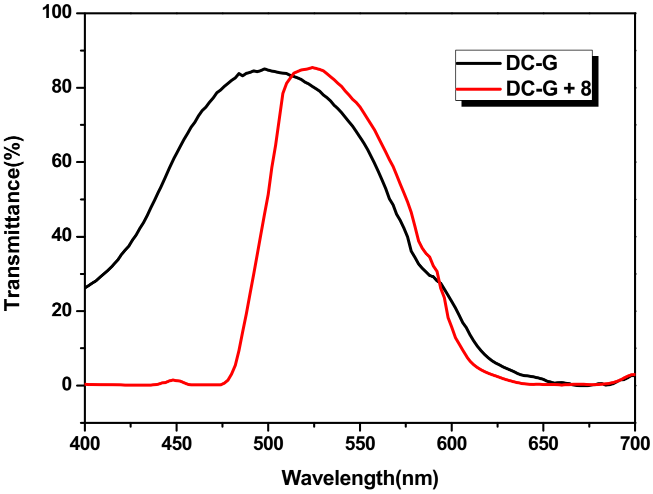


Fig. 4. Transmittance spectra of green spin coated color filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2 and Fig. 5 shows the coordinate values of spin coated color filters. The coordinate values of DC-R were rarely affected by blending of monophenylbenzoperylene **8**, but the *x* value of DC-G was increased to be close to the conventional green coordinate (0.274, 0.572) of the LCD color filters.

3.4. Thermal stability of dyes and spin coated color filters

Although the dyes have superior optical properties than the pigments, they were hardly applied for LCD color filters owing to their inferior thermal stability. For dyes to be used as color filters, they should endure temperature of 220 °C, which is the current highest temperature in the LCD manufacturing process, without significant weight loss [20,21]. The synthesized novel dyes **7** and **8** have more rigid structures than other yellow chromophores to be suitable for the colorants of LCD color filters. However, their thermal stabilities are somewhat different according to the degree of substitution. In our earlier report, the 1,7-di(substituted) perylenediimides exhibited lower thermal stability than the monosubstituted one due to the higher core twisting of their main body resulted from bulky aryl substituents at both side bay

Table 2
The coordinate values corresponding to the CIE 1931 chromaticity diagram and the color difference values of the spin coated color filters.

Prepared dyes	*Y*	*x*	*y*	ΔE_{ab}
DC-R	25.01	0.640	0.334	0.752
DC-R + 8	24.33	0.631	0.339	1.04
DC-G	54.28	0.205	0.572	1.69
DC-G + 8	58.54	0.286	0.563	1.77

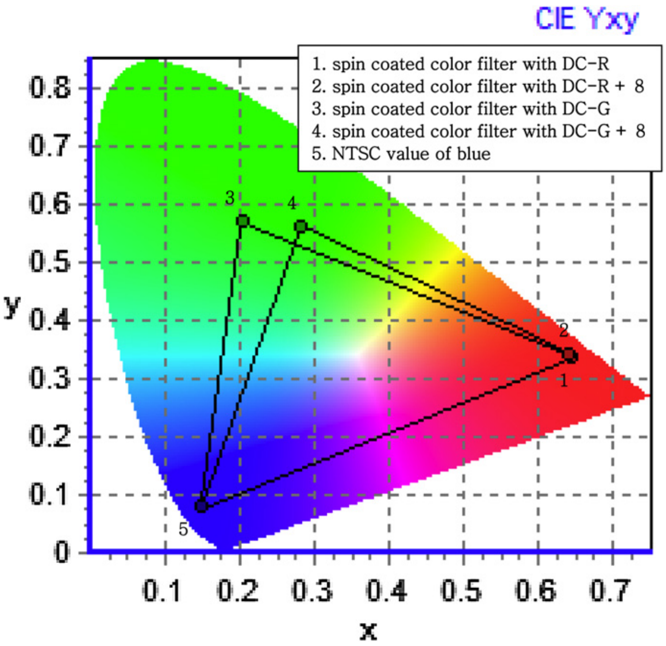


Fig. 5. CIE 1931 chromaticity diagram of the spin coated color filters.

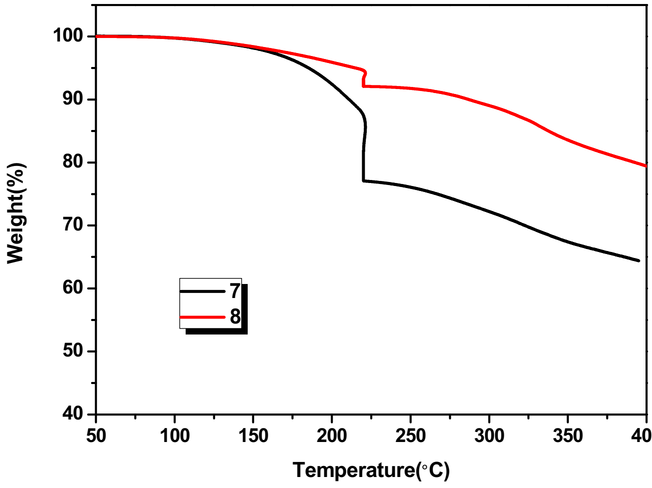


Fig. 6. Thermogravimetric analysis (TGA) of the synthesized dyes.

positions [14]. Similarly, whereas the monophenylbenzoperylene **8** showed less than 3% of weight loss in isothermal section which is sufficient for LCD color filters, diphenylcoronene **7** showed much more weight loss as shown in Fig. 6. The thermal stability of the spin coated color filters is estimated by the color difference (ΔE_{ab}) value. The ΔE_{ab} values of the color filters should be less than 3 after heating for 1 h at 230 °C for commercial applications [16]. The ΔE_{ab} values of the color filters with monophenylbenzoperylene **8** were less than 3 desired for LCD manufacturing process, as shown in Table 2.

4. Conclusions

In summary, we have successfully synthesized two novel compounds diphenylcoronene **7** and monophenylbenzoperylene **8** by a simple one-step reaction. These chromophores are stable, have largely hipsochromic shifted absorption peaks compared to perylene-3,4,9,10-tetracarboxdiimide and exhibit strong, bright emission. They can be used as good yellow chromophores or fluorophores for a wide range of applications according to their characteristic range of absorption and emission peaks. While diphenylcoronene **7** draws attention to be applied for energy relaying dye of DSSC, monophenylbenzoperylene **8** was successfully applied as a yellow compensating dye for LCD color filters.

Acknowledgments

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References

[1] Nagao Y, Misono T. Synthesis and properties of N-alkyl-N'-aryl-3,4:9,10-perylenebis(dicarboximide). Dyes Pigm 1984;5:171–88.
[2] Loufty HO, Hor AM, Kazmaler P, Tarn MJ. J Imaging Sci 1989;33:151–9.
[3] Schlettwein D, Wöhrle D, Kaarmann E, Melville U. Conduction type of substituted tetraazaporphyrins and perylene tetracarboxylic acid diimides as detected by thermoelectric power measurements. Chem Mater 1994;6:3–6.
[4] Seybold G, Wagenblast G. New perylene and violanthrone dyestuffs for fluorescent collectors. Dyes Pigm 1989;11:303–17.
[5] Hardin BE, Hoke ET, Armstrong PB, Yum JH. Increased light harvesting in dye-sensitized solar cells with energy relay dyes. Nat Photonics 2009;3:406–11.
[6] Hernando J, de Witte PAJ, van Dijk EMHP, Korterik J, Nolte RJM. Investigation of perylene photonic wires by combined single-molecule fluorescence and atomic force microscopy. Angew Chem Int Edit 2004;43:4045–9.
[7] Angadi MA, Costola D, Wasielewski MR. Organic light emitting diodes using poly(phenylenevinylene) doped with perylenediimide electron acceptors. Mater Sci Eng B 1999;B63:191–4.
[8] Avlasevich Y, Müller S, Erk P, Müllen K. Novel core-expanded rylenebis(dicarboximide) dyes bearing pentacene units: facile synthesis and photophysical properties. Chem Eur J 2007;13:6555–61.
[9] Rohr U, Kohl C, Müllen K, van de Craats A, Warman J. Liquid crystalline coronene derivatives. J Mater Chem 2001;11:1789–99.
[10] Zollinger H. Color chemistry. VCH Weinheim; 1987.
[11] Langhals H, Kirner S. Novel fluorescent dyes by the extension of the core of perylene-tetracarboxylic bisimides. Eur J Org Chem; 2000:365–80.
[12] Müller S, Müllen K. Facile synthetic approach to novel core-extended perylene carboximide dyes. Chem Commun (camb) 2005;32:4045–6.
[13] Li Y, Zheng H, Li Y, Wang S, Wu Z, Liu P, et al. Photonic logic gates based on control of FRET by a solvatochromic perylene bisimide. J Org Chem 2007;72:2878–85.
[14] Choi J, Sakong C, Choi JH, Yoon C, Kim JP. Synthesis and characterization of some perylene dyes for dye-based LCD color filters. Dyes Pigm 2011;90:82–8.
[15] Lee W, Yuk SB, Choi J, Jung DH, Choi SH, Park JS, et al. Synthesis and characterization of solubility enhanced metal-free phthalocyanines for liquid crystal display black matrix of low dielectric constant. Dyes Pigm 2012 (DYPI 3432).
[16] Kim YD, Kim JP, Kwon OS, Cho IH. The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters. Dyes Pigm 2009;81:45–52.
[17] Olmsted J. Calorimetric determinations of absolute fluorescence quantum yields. J Phys Chem 1979;83:2581–4.
[18] Basham JI, Mor GK, Grimes CA. Förster resonance energy transfer in dye-sensitized solar cells. ACS Nano 2010;4:1253–8.
[19] Tilley RJD. Colour and optical properties of materials. Chichester: John Wiley & Sons Inc; 2000. pp 108–110.
[20] Ohmi T. Manufacturing process of flat display. JSME Int J Ser B (Jpn Soc Mech Eng) 2004;47:422–8.
[21] Takamatsu T, Ogawa S, Ishii M. Color filter fabrication technology for LCDs. Sharp Tech J 1991;50:69–72.