White LED light production by using dibromoperylene derivatives in down conversion of energy

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Abstract

Perylene derivatives of N,N'-bis(2,6-diisopropylphenyl)-1,6(7)-dibromoperylene-3,4,9,10-tetracarboxylic diimide (DBrPDI) and 1,7-dibromo perylene-3,4,9,10-tetracarboxylic acid butyl ester (DBrPTE) were synthesized, their structural and optical characterizations were performed. Both DBrPDI and DBrPTE, which were utilized as wavelength converters on a GaN/InGaN based blue LED, were singlet sensitizers and had molar absorptivity constants around 10^4 Lmol^{-1}.cm^{-1}. The blue LED that was used had Commission internationale de l'eclairage (CIE) coordinates of x,y=0.13, 0.06, power and luminous efficiencies of 2.7 lm/W and 6.6 cd/A @5mA, respectively. Since the fluorescence quantum yield of DBrPDI was much higher than that of DBrPTE, a meaningful white light efficiency was obtained with the diimide derivative. The use of DBrPDI resulted in white light with CIE coordinates of x,y=0.34,0.29 and luminous efficiency of 6.35 cd/A@5mA, respectively. Using DBrPDI in a resin matrix resulted in more than 3 orders of magnitude increase in the luminous efficiency value (23.0 cd/A@5mA) while the CIE coordinates remained the same. Whenever the applied current reached 20 mA, a CRI value of Ra = 90 was obtained.

Keywords: Organic phosphor; Perylene; PMMA; Downconversion; White light

1. Introduction

Light emitting diodes (LEDs) are known to have great potential as energy efficient lighting systems. Although electroluminescence (EL) abilities of inorganic semiconductors and devices similar to LEDs were known in 1950s, their potential in general lighting application was realized in 1990s when S. Nakamura developed the first nitride-based blue emitting LED [1,2]. Optimized combination of orange-red phosphor and blue emitting LED provides white light generation [3]. Although Cerium dopped Yttrium Aluminium Garnet (Ce:YAG) has many disadvantages [e.g. poor color rendering indices (CRI) of 75, high correlated color temperature (CCT) of 7756 K and cool white light with corresponding to Commission internationale de l'eclairage (CIE) chromaticity coordinates of (0.292, 0.325)] [4,5], it represents the most popular phosphor material used by the corresponding industry mostly because of the comfort of its well-known properties. Many research groups are working on developing alternative phosphor materials which would provide better CRI and CCT values and warm white light [5–8]. However, as Europium is used in most of them and because of the cost of this element, application of these efficient phosphors to industry remains limited.

Recently, not only because of their economic impacts but also because of their environmentally friendly natures, organic dyes started to gain attention [9–14]. Great photo and thermal stabilities, high molar absorptivity constants (ε) in the visible region and high fluorescence quantum yields (Φ_{PL}) of 3, 4, 9, 10-perylenetetracarboxylic-diimide (PDI) derivatives [15–17] make them one of the best organic dye alternatives for down conversion of energy produced by the blue LED. However, the Φ_{PL} value of PDIs decreases in film phase due to the π-π aggregation originating from the ring plane [18]. To overcome this problem, two main approaches can be followed; *i)* determining the optimum concentration of the dye to obtain maximum photoluminescence (high dye concentrations may induce self-quenching mechanism that maybe followed by aggregation induced quenched photoluminescence [19]) and *ii)* changing the intermolecular distance between the ring planes by the use of dopants, incorporation of the dye in a host matrix or deterioration of ring plane by bulky substituents. In order to interrupt π-π stacking between the perylene rings, second approach was followed in this study, i.e. functionalization of the perylene ring from its 1, 6 and/or 7 positions [20] and incorporation of the dye in polymethyl methacrylate (PMMA).

Two perylene derivatives of N,N'-bis(2,6-diisopropylphenyl)-1,6(7)-dibromoperylene-3,4,9,10-tetracarboxylic diimide (DBrPDI) and 1,7-dibromo perylene-3,4,9,10-tetracarboxylic acid butyl ester (DBrPTE) were synthesized and used as wavelength

converters on a Gallium Nitride/Indium Gallium Nitride (GaN/InGaN) based blue LED. DBrPDI presented better performance because of its higher photoluminescence quantum yield. Whenever this derivative was incorporated in PMMA matrix and applied on the blue LED, white light with CIE coordinates of x,y=0.34,0.29 and CRI of 90 was obtained.

2. Experimental

Materials and Instruments

2,6-diisopropylaniline, potassium carbonate, 1-iodobutane and 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) were from Acros Organics, VWR Chemicals, ABCR Chemicals and TCI Chemicals, respectively. Ethanol absolute, hydrochloric acid, bromine, iodine, 1-butanol, methanol, acetonitrile (ACN), hexane, chloroform, dichlorometane (DCM), N,N-dimethyl-formamide (DMF), acetic acid, 1-methyl-2-pyrrolidinone, silica gel 0.040-0.063 mm were obtained from Sigma-Aldrich and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) was purchased from Fluka. The blue LED based on GaN/InGaN and polymethyl methacrylate (PMMA) were purchased from PROLED and Ossila, respectively.

^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer. Infrared (FTIR) spectra were obtained by using a PerkinElmer Spectrum BX-FTIR spectrophotometer. UV-Vis absorption spectra were recorded by using Analytik Jena S 600 UV-Vis spectrophotometer. Photoluminescence (PL), absolute photoluminescence quantum yield (Φ_{PL}) and life time (τ_f) measurements were performed by using Edinburgh Instruments FLS920P spectrophotometer. EL characteristics of the devices were measured by Keithley 2400 source meter and Hamamatsu C9920-12 external quantum efficiency measurement system utilizing an integrating sphere.

Synthesis of perylene derivatives

Perylene derivatives of 1,7-Dibromoperylene-3,4,9,10-tetracarboxytetrabutylester (DBrPTE) and N,N′-Bis(2,6-diisopropylphenyl)-dibromoperylene-3,4,9,10-tetracarboxybisimide (DBrPDI) were synthesized by following the procedure in literature [21]. The synthetic pathway is summarized in Scheme 1 and below:
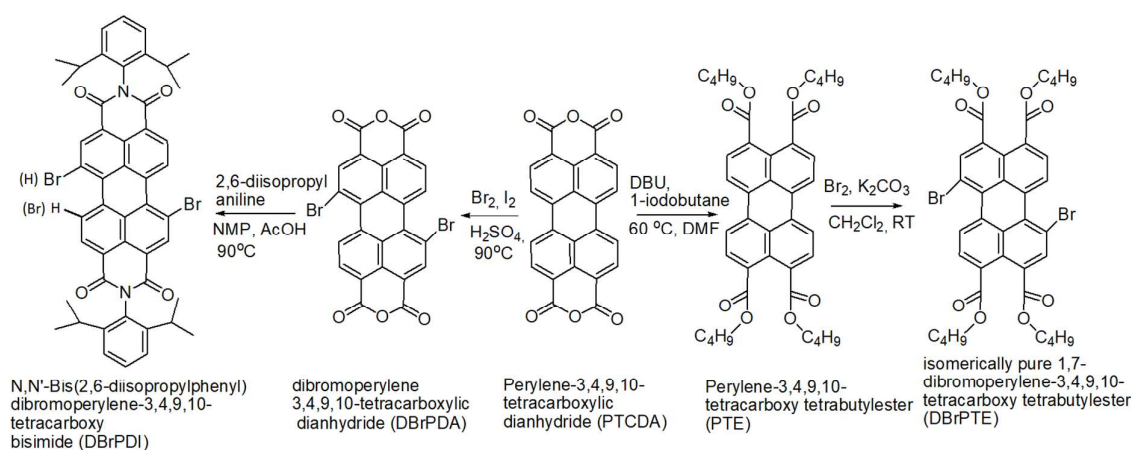
Scheme 1 Synthetic route of brominated perylene derivatives.

Synthesis of perylene-3,4,9,10-tetracarboxytetrabutylester (PTE): 1g (2.54 mmol) of perylene-3,4,9,10-tetracarboxylic dianhydride was placed in a 50 mL two-neck round bottom flask, DBU (1.52 mL), n-butanol (1.86 mL) and DMF (13 mL) were added to the reaction flask and they were stirred in Ar atmosphere at 60 ºC for 30 min. Then 1-iodobutane (1.84g , 10 mmol) mixed with DMF (10 mL) was added. The mixture was stirred at 60 ºC for a further 3 hours and then cooled to room temperature. The reaction mixture was slowly added into distilled water (100 mL) and the solid was filtered. The solid material was dried (80ºC) and purified by column chromatography (silica gel, DCM). Yield: 1.52g (92%). FTIR (KBr) (Figure 1): U_{max} = (C_{Ar}-H): 2959 cm^{-1}; (C-H): 2872 cm^{-1}, (C=O): 1724 cm^{-1}, (C-O): 1276-1172 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d, TMS/ppm) δ: 7.92 (d, *J*: 2.0 Hz, 4H), 7.84 (d, *J*:2.0 Hz, 4H), 4.36 (t, *J*: 2.0 Hz, 8H), 1.85-1.78 (m, *J*: 2.0 Hz, 8H), 1.57-1.48 (m, *J*: 2.0 Hz, 8H), 1.02 ppm (t, *J*: 2.0 Hz, 12H).

Synthesis of regioisomerically pure 1,7-dibromoperylene-3,4,9,10-tetracarboxytetrabutylester (DBrPTE): PTE (0.35 g, 0.53 mmol), DCM (5 mL) and K_2CO_3 (0.75g, 5.4 mmol) were added into a 10 mL round bottom flask. The reaction mixture was stirred at room temperature for 30 min, and then bromine (0.35 mL) was added slowly and stirred for 24 hours at room temperature. Excess bromine was removed by passing air through the reaction flask in the fume hood. The solid mixture was dissolved with DCM and ACN and then allowed to crystallize. Yield: 0.1g (25%). FTIR (KBr) (Figure 1): U_{max} = (C_{Ar}-H): 2956 cm^{-1}; (C-H): 2869 cm^{-1}, (C=O): 1717 cm^{-1}, (C-O): 1300-1175 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d, TMS/ppm) (Figure 2) δ: 8.88 (d, *J*: 2.0 Hz, 4H), 8.27 (s, 4H), 8.36 (d, *J*: 2.0 Hz, 8H), 4.35 (t, *J*: 2.0 Hz, 8H), 1.83-1.76 (m, *J*: 2.0 Hz, 8H), 1.55-1.46 (t, *J*: 2.0 Hz, 8H), 1.00 ppm (t, *J*: 2.0 Hz, 12H).

Synthesis of N,N'-Bis(2,6-diisopropylphenyl)-dibromoperylene-3,4,9,10-tetracarboxybisimide

(DBrPDI): PTCDA (5g, 12.7 mmol) was added to a 250 mL two-neck round bottom flask. Then, H_2SO_4 was added slowly and stirred at room temperature for 24 hours. After iodine (0.2g, 0.78 mmol) was added into the reaction flask, the reaction temperature was increased to 85 ºC and kept for an hour. Bromine (3.9 mL) addition was performed and allowed mixing for 15 hours. The reaction mixture was cooled to room temperature and poured into pure water. The crude material was filtered, washed with distilled water and dried. The product was named as DBrPDA but could not be characterized by NMR because of its solubility problem and was used as crude product in the synthesis of DBrPDI. DBrPDA (0.46 g) was added into a reaction flask. Acetic acid (0.3 mL), NMP (10 mL) and 2,6-diisopropylaniline (1mL) was added to the flask in Ar atmosphere and the mixture was stirred under reflux for 4 days at 120 °C. The mixture was cooled to room temperature and then poured into pure water. The crude material was filtered and washed with pure water. Purified by column chromatography (silica gel, DCM:Hexane 2:1. *Note that the product was 1,6- and 1,7- dibromine mixture. Regioisomerically pure derivatives could not be obtained*). Yield: 0.43g (60%). FTIR (KBr) (Figure 1): U_{max} = (C_{Ar}-H): 2960, 2928 cm^{-1}; (C-H): 2866 cm^{-1}, (C=O): 1709,1669 cm^{-1}, (C_{Ar}-C_{Ar}): 1588 cm^{-1}, (HC=C): 1386, 1333 cm^{-1}, (C-N): 1242 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d, TMS/ppm) (Figure 3) δ 9.58-9.56 (d, J: 8 Hz, 2H), 9.03 (s, 2H), 8.82-8.80 (d, J: 8 Hz, 2H), 7.52 (t, J: 8 Hz, 2H), 7.38 (d, J: 8 Hz, 4H), 2.75 (m, 4H), 1.20-1.19 ppm (d, 24H).

Preparation of downconversion solution and experimental setup

DBrPDI and DBrPTE were dissolved in chloroform with a concentration of 10 mg/ml and drop casted on GaN/InGaN based blue LED which had a peak emission wavelength of 465 nm, CIE co-ordinates of (0.13, 0.06) and power and current efficiencies of 2.7 lm/W and 6.6 cd/A@5mA, respectively. DBrPDI solution was further mixed with PMMA resin with a ratio of 1:2 and kept in ultrasonic bath for 30 min. This homogeneous mixture was also drop casted on the blue LED. The blue LED used and prepared samples were named as InGaN and InGaN/DBrPTE, InGaN/DBrPDI, InGaN/DBrPDI:resin, respectively.

3. Results and Discussion

Absorption and Photoluminescence Studies

Absorption and PL spectra of synthesized perylene derivatives are provided in Figure 4 and their properties are summarized in Table. DBrPDI has a red shifted absorption compared to DBrPTE due to its approximately 6 kcal/mol lower singlet energy (E_s) state. Both have absorption and PL peaks which are typical for the tetraester and diimide perylene derivatives;

maximum absorption wavelengths (λ_{abs}) correspond to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions (Figure 4a) and maximum emission wavelengths (λ_{ems}) are assigned to the $S_1\rightarrow S_0$ relaxation (Figure 4b) [22].

The absolute Φ_{PL} values of both of the synthesized dyes are measured by using an integrating sphere attached to the spectrophotometer. The measured absolute values are lower than the relative Φ_{PL} values reported in literature [21]. This situation was expected because following the exact conditions of the Φ_{PL} reference (e.g. using the same excitation wavelength, making solvent or environment correction) occasionally escape from the attention of researchers while reporting the relative Φ_{PL} values, and most commonly, relative Φ_{PL} values reported in one study is accepted as the reference in calculation of other materials' relative Φ_{PL} [21,22]. The measured fluorescence life times (τ_f) are at ns scale and the molar absorptivity constants (ε) are around 10^4 M^{-1} cm^{-1} for both of them. Although the absorption spectrum of DBrPTE exhibits a better overlap with a higher ε value at the corresponding wavelength (λ_{EL}^{LED}=465 nm, λ_{abs}^{DBrPTE} =468 nm and λ_{abs}^{DBrPDI} =528 nm) for efficient excitation with the electroluminescence of blue LED (Figure 4a), the Φ_{PL} of it is almost 20% of DBrPDI (Table).

White light properties

Drop casting the DBrPDI directly on blue LED produced white light with CIE coordinates of x=0.34, y=0.29, luminous and power efficiency values of 6.35 cd/A and 2.22 lm/W@5 mA, respectively and CRI value of 60. However, drop casting DBrPTE on blue LED produced only yellow-green light with a peak maximum of 550 nm, CIE coordinates of x= 0.41 y= 0.57 and efficiency values of 0.81 lm/W and 2.20 cd/A@5mA (Figure 5). When compared with the bare DBrPTE PL wavelength range of 450 nm to 650 nm (Figure 4b), approximately 50 nm of red shift is obtained in InGaN/DBrPTE (Figure 5). This implies an aggregation induced emission [15,23,24] and shows that 1,7-dibromination of perylene-3,4,9,10-tetracarboxytetrabutylester could not interrupt π-π stacking between the DBrPTE rings. Additionally, obtaining only yellow-green light suggests an efficient energy transfer resulting from the overlap between the EL spectrum of the LED and absorption of DBrPTE (Figure 4a) and that the entire EL energy is used in the excitation of ground state electrons of DBrPTE. Therefore, only DBrPDI derivative is mixed with the PMMA resin and applied on the blue LED. Although the current density (J)-voltage (V) characteristics of InGaN/DBrPDI and InGaN/DBrPDI:resin were almost identical (Figure 6a), InGaN/DBrPDI:resin sample presented much better white light efficiency values (Figure 6b-d). InGaN/DBrPDI:resin presented efficiency values of 23 cd/A and 8.5 lm/W@5mA whereas these values were 6.35

cd/A and 2.22 lm/W@5mA for the InGaN/DBrPDI sample. The resulted 3 orders of magnitude increase is attributed to the fabulous optical properties of PMMA and its ability to provide an inert matrix for homogenous distribution of perylene derivative in the matrix [25,26]. A maximum brightness value of 33450 cd/m^2 is obtained (Figure 6b). EL vs wavelength spectrum is provided in Figure 6e. EL peak maximum of 465 nm for the blue LED is observed and the PL wavelength range of DBrPDI is preserved (Figure 4b vs Figure 6e). CIE coordinates of blue LED deviated with the applied current whereas a negligible shift (Δx,y=0.02, 0.01) is observed from InGaN/DBrPDI:resin (Figure 6f). Increasing the applied current resulted in an increase in CRI from 60@5mA to 90@20mA. White light with CIE coordinates of x= 0.34, y= 0.29, CRI value of 90 and temperature of 4700 K could be obtained with the applied current of 20mA.

Above discussed results show that by simply bromination of the perylene diimide ring from 1, 6 and/or 7 positions, performance values comparable with the perylene derivatives presented for down conversion in literature, which need at least one more synthetic step [9,11–13,27] and commercially available BASF Lumogen F Yellow 083 [13] can be obtained.

4. Conclusion

In this study two perylene derivatives DBrPDI and DBrPTE were synthesized and used as wavelength converters on a GaN/InGaN based blue LED. While the use of DBrPTE, presented only the PL characteristic of DBrPTE itself, using DBrPDI enabled obtaining white light. CRI values and CIE coordinates of the InGaN/DBrPDI:resin sample were comparable with its commercial analogs. Color temperature of 4700 K points out that it may mimic daylight and can be utilized in security lighting, display areas, etc. The 1, 6 (7) functionalized perylene derivatives used in this study hold the advantage of relatively easy modification to gain longer wavelength emitting perylene derivatives, those of which may allow obtaining color temperatures between 3100-4500 K and even 2000-3000 K.

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Figure Captions

Figure 1. FTIR spectra of PTE, DBrPTE and DBrPDI

Figure 2. ^{1}H NMR spectrum of regioisomerically pure 1,7-dibromoperylene-3,4,9,10-tetracarboxytetrabutylester (DBrPTE)

Figure 3. ^{1}H NMR spectrum of N,N′-Bis(2,6-diisopropylphenyl)-dibromoperylene-3,4,9,10-tetracarboxybisimide (DBrPDI)

Figure 4. a) Normalized EL and absorbance and b) Normalized EL and PL spectra of blue LED and synthesized perylene derivatives, respectively.

Figure 5. EL intensity spectra of InGaN/DBrPTE

Figure 6. a) Current density – potential, b) brightness– potential, c) power efficiency–potential, d) luminous efficiency– potential curves of InGaN, InGaN/DBrPDI and InGaN/DBrPDI:resin samples, e) EL intensity-Wavelength curve of InGaN/DBrPDI:resin sample and f) CIE coordinate deviations of blue LED and InGaN/DBrPDI:resin between the applied currents of 5 mA and 37 mA.
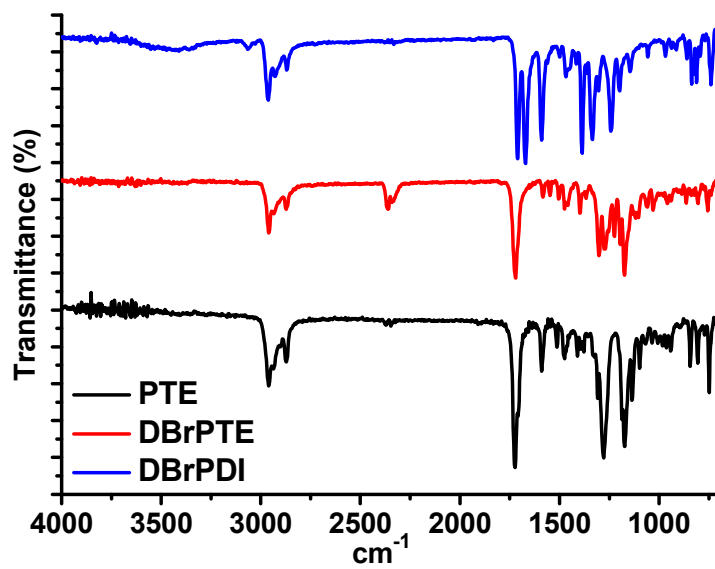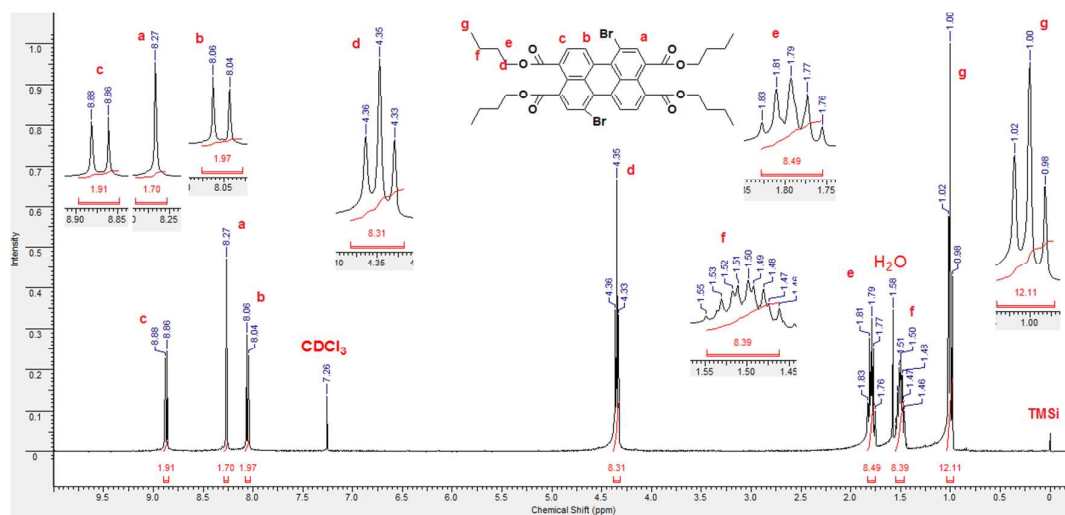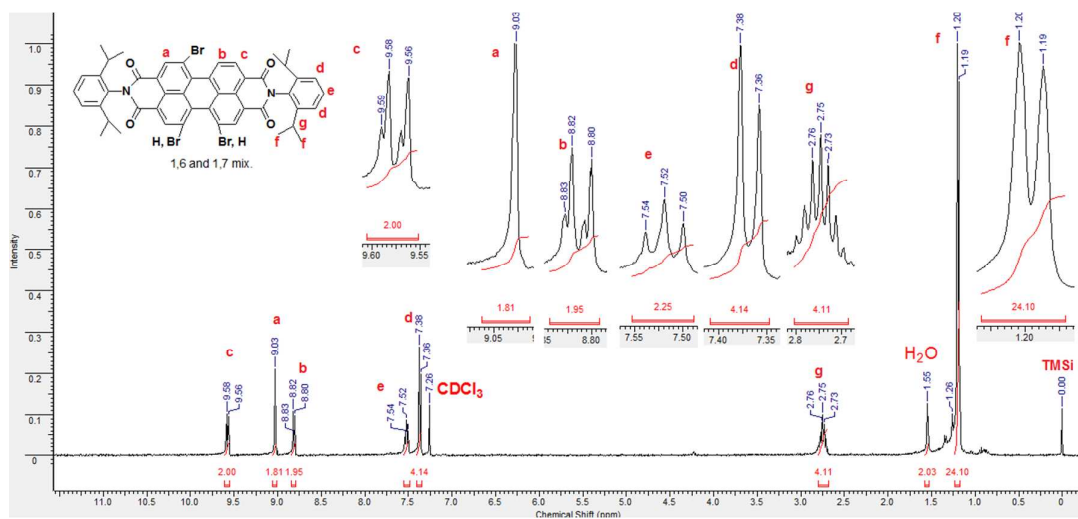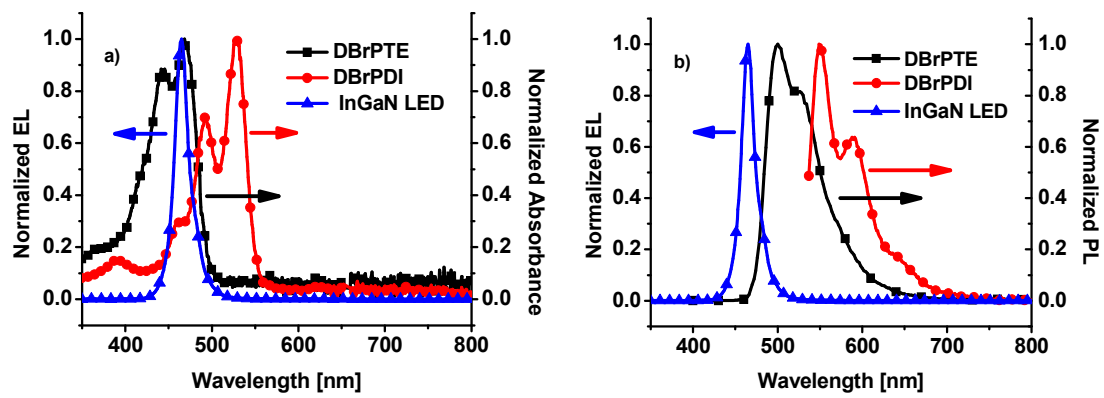
Figure 1.

Figure 2.

Figure 3.

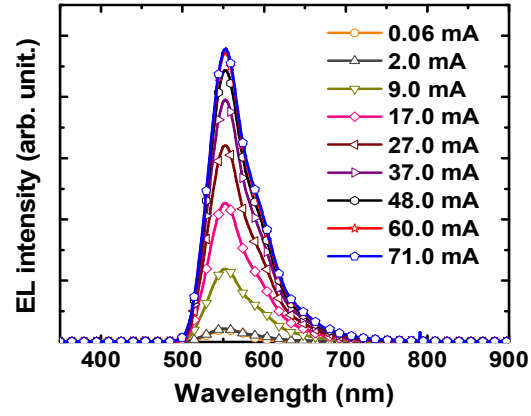**Figure 4.**

Figure 5.

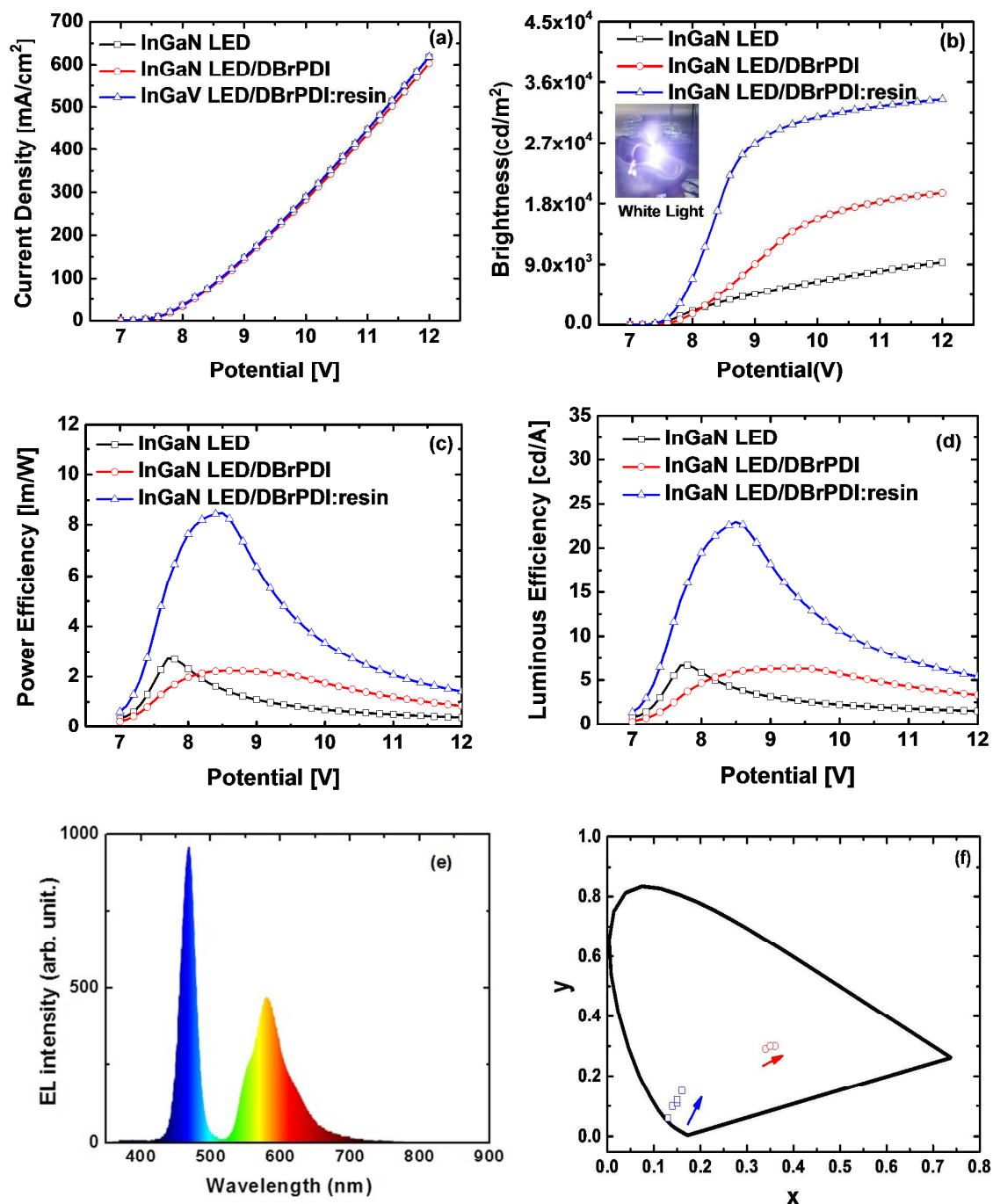**Figure 6**.

Table. Absorption wavelengths (λ_{abs}, nm), molar absorptivity constants (ε, M^{-1} cm^{-1}), singlet energies (E_s, kcal/mol), excitation wavelengths (λ_{exc}, nm), photoluminescence quantum yields (Φ_{PL}) and fluorescence life times (τ_f, ns) of perylene derivatives.

Perylene derivatives	λ_{abs} (nm)	$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})	E_s [a] (kcal/mol)	λ_{exc} (nm)	λ_{ems} (nm)	Φ_{PL}		τ_f (ns)	
DBrPTE	445	2.40	60.90	468	500	0.11	0.26 [b]	1.63 [c]	1.78 [b]
	468	2.75			526				
DBrPDI	462	1.21	54.89	528	550	0.50	0.79 [b]	5.8 [c]	4.36 [b]
	492	3.18			589				
	528	5.04			642				

[a] calculated from the onset wavelength of photoluminescence curves

[b] ref [21] (relative Φ_{PL} determined by the comparative method using perylene-3,4,9,10-tetracarboxylictetramethyl ester (Φ_f =0.95 in CH_2Cl_2) as a reference [22])

[c] 472.4 nm excitation laser is used