A triphenylamine derivative as an efficient organic light color-conversion material for white LEDs

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Abstract

A novel efficient ($\Phi = 0.44$) organic yellow-emitting dye, 3-(4-(diphenylamino)phenyl)-1-phenylprop-2-en-1-one (DPPO), was synthesized. The compound was characterized by means of ^{1}H NMR and differential scanning calorimetry (DSC) and analyzed by quantum chemistry method. It was found that DPPO could be effectively excited by the InGaN-based blue LED. Photo-durability data of DPPO were studied. Bright white light of Commission International del' Eclairage (CIE) $x = 0.30$, $y = 0.33$ was obtained by using DPPO as a light color-conversion material (CCM).
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1. Introduction

Since Nakamura et al. [1] demonstrated blue-emitting InGaN light-emitting diodes (LEDs) in 1994, more and more interests have been focused on white light-emitting diodes (WLEDs) toward their enormous practical applications in solid state lighting, mainly due to high-efficiency, low-energy consumption, excellent reliability, long lifetime, etc. As introduced by Nichia, WLEDs were composed of near-ultraviolet-light-emitting chips and yellow-emitting phosphors to obtain white light output. Researchers worldwide have investigated many phosphors for potential applications in WLEDs. However, most of the efforts have been devoted to inorganic phosphors such as YAG:Ce^{3+}, etc. [2–4], in which the key performances are yet to be improved for practical applications, i.e. high cost, difficulty of color tuning and un-uniform dispersion [5]. Whereas, the utilization of organic color-conversion material (CCM) appears to be attractive with respect to low cost, easy

fabrication and color tuning. Organic phosphors usually possess strong absorptions in near-ultraviolet (UV) and UV wavelength region, which are caused by $\pi-\pi^*$ transitions and the emission colors can be easily adjusted via molecular design and structural modifications [5]. Unlike inorganic ones, organic phosphors can be doped into epoxy polymers on a molecular level owing to their perfect solubility in organic solvents and energies of the emissions are determined by the energy gaps between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the organic phosphors. Thus, another advantage of organic CCM over their inorganic counterparts is that emissions from organic phosphors are not sensitive to the bulk of the phosphors.

In order to realize those advantages mentioned above, we designed and synthesized a conjugated organic phosphor with a triphenylamine group. There exist charge transfer transitions in the triphenylamine group upon photon excitation [6], and the π-conjugated chain increases the probability of electron transitions. Therefore, the target molecule with highly efficient light emission under near-UV light excitation is expected.

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2. Experimental details

2.1. Synthesis

The synthetic route of the target molecule is shown in Scheme 1.

Triphenylamine (TPA): TPA was synthesized by modification of a literature procedure [7,8]. M.p.: 126 °C.

4-Diphenylamino-benzaldehyde (DPB): DPB was synthesized according to a literature procedure [9]. ^{1}H NMR (acetone-d$_6$, 500 MHz): 10.12 (s, 1H), 7.72 (d, $J = 7.2$ Hz, 2H), 7.43–7.37 (t, 4H), 7.24–7.17 (t, 6H), 6.96 (d, $J = 7.8$ Hz, 2H).

3-(4-(Diphenylamino)phenyl)-1-phenylprop-2-en-1-one (DPPO): DPB [0.546 g (0.002 mol)] and NaOH [0.08 g (0.002 mol)] were added into the mixture of 30 mL of water and 25 mL of ethanol, then 0.24 g (0.002 mol) of 1-phenylethanone was added. The mixture was heated and stirred at 90 °C for 4 h. After cooling, the mixture was filtered and washed with plenty of water and then dried up at room temperature to produce 0.6 g of yellow powder, yield of 80%. ^{1}H NMR (CDCl$_3$, 500 MHz): 8.01 (d, $J = 7.5$ Hz, 2H), 7.77 (d, $J = 16.0$ Hz, 1H), 7.58–7.54 (t, 1H), 7.51–7.48 (m, 4H), 7.39 (d, $J = 16.0$ Hz, 1H), 7.34–7.29 (m, 4H), 7.18–7.09 (m, 6H), 7.03 (d, $J = 8.0$ Hz, 2H). M.p.: 129–130 °C. Anal. Calcd. for $C_{27}H_{21}NO$: C, 86.37%; H, 5.64%; N, 3.73%. Found: C, 86.32%; H, 5.69%; N, 3.69%.
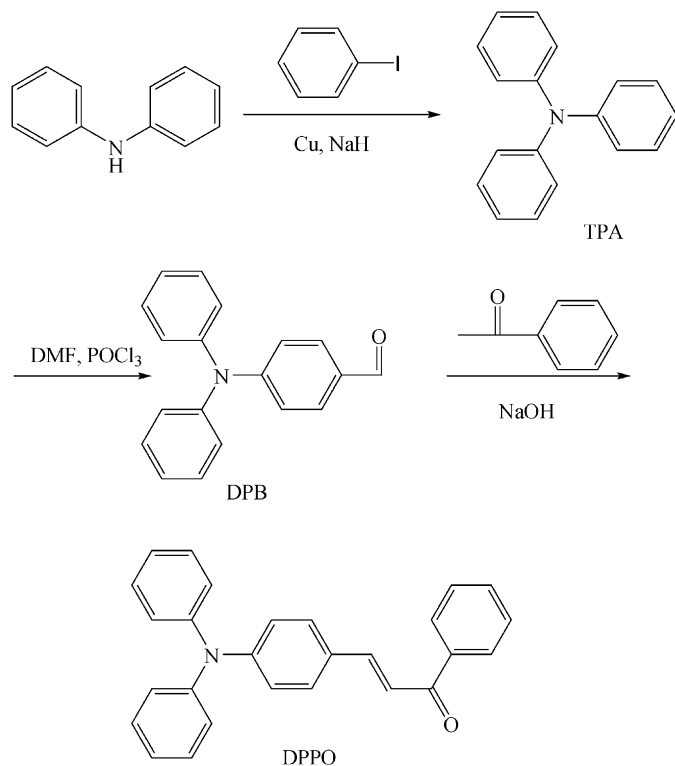
2.2. Fabrication of color-conversion film

One gram of polyethylene glycol-6000 (PEG-6000) and 0.01 g of DPPO were added into 10 mL of dichloromethane, the mixture was stirred for 10 min. Color-conversion film was formed by draw method on a quartz substrate and then dried up at room temperature.

2.3. Molecular orbital calculation of DPPO

The molecular and electronic structures of DPPO were calculated by density functional theory (DFT) calculations and geometry in the ground state was firstly optimized by MM2 method.

2.4. Instruments and photo-physical characterization

^{1}H NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer with chemical shifts relative to tetramethylsilane. Elemental analysis was performed on an ERBA-1106 instrument (Italy). All photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Decay data of DPPO were performed with F-4500 fluorescence spectrophotometer using the Repeat Time Scan mode (3600 s $\times 2$, interval $= 0.1$ min). Luminescence intensities were real time recorded from 0 to 7200 s, emission spectra were measured at 0, 3600, 7200 s and all these decay data were normalized for convenient comparison. Absorption spectra of organic films on quartz substrates were measured with a Shimadzu UV-3101PC spectrophotometer. Thermal properties were measured with Perkin-Elmer-TGA 7 under N$_2$ atmosphere. The Commission International del' Eclairage (CIE) chromaticity coordinates were measured with Photo Research PR650 spectrophotometer. The InGaN blue LED (rated driving bias $= 3.0$ V) was purchased from Xin He Ming Tech. All measurements were carried out in air at room temperature.

3. Results and discussion

3.1. Thermal stability of DPPO

Thermal properties of DPPO were studied by differential scanning calorimetry (DSC). Temperature increased from 20 °C with a rate of 10 °C/min. As shown in Fig. 1, there exist two weak absorption of heat at 34 and 100 °C, respectively. The first one is ascribed to the vitrification absorption of DPPO, and the latter one corresponds to the vaporization heat absorption of water. A sharp absorption of heat peaks at 130 °C, indicating that the melting process of DPPO occurs. Since normal working temperature of white LEDs is below 100 °C [10], it is clear that DPPO is thermal stable enough for practical applications.
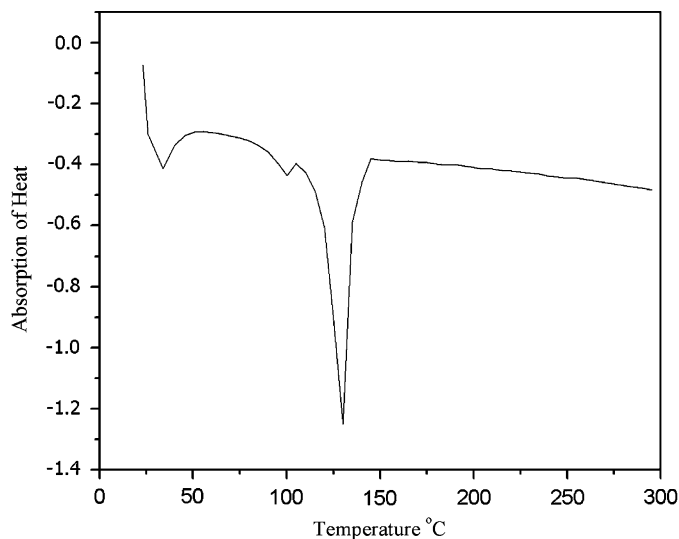

Scheme 1. Synthetic route of the target material.

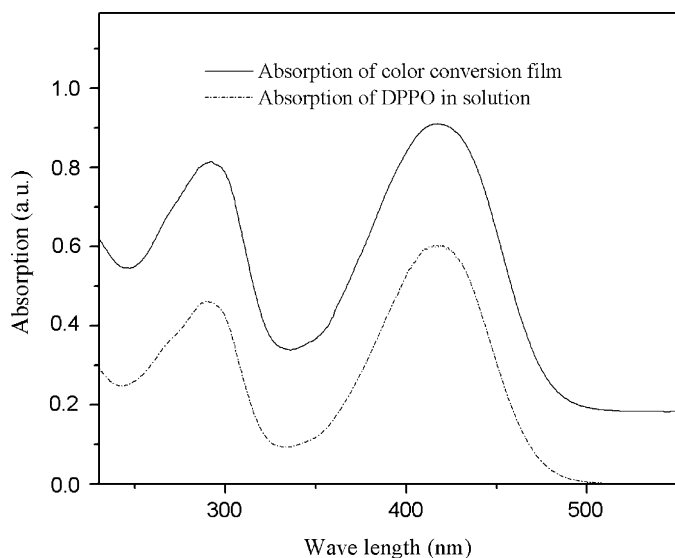Fig. 1. DSC curve of DPPO from 20 to 300 °C with a ratio of 10 °C/min.

Fig. 2. Absorption spectra of DPPO in CH_2Cl_2 (10^{-4} mol/L) solution and polymer film.

3.2. Photo-physical properties and molecular orbits of DPPO

The absorption spectra of DPPO in CH_2Cl_2 (10^{-4} mol/L) and in the PEG-6000 film are shown in Fig. 2. It can be found that there is no significant influence of matrix on the absorption of DPPO. There are two strong broad absorption bands at 290 and 420 nm, respectively, which are ascribed to the $\pi-\pi^*$ transitions of conjugated chain [6,11]. Compared with the absorption spectrum of *N,N*-diphenyl-4-styrylaniline which possesses a molecular structure similar to that of DPPO [6], the $\pi-\pi^*$ transitions of DPPO shift to visible region owing to enlargement of π-conjugated chain and introduction of strong electron donor, the triphenylamine group.

Fig. 3 depicts the calculated HOMO and LUMO of DPPO molecule, and the coefficients are shown in Table 1. It shows that atomic orbits of 17 N contribute the most to the HOMO, and contributions from atomic orbits of 1 C, 3 C and 4 O are much higher than those of any other atoms in the LUMO. Under photo-excitation, it can be predicted that an intramolecular charge transfer process from 17N to π^* of 1C, 3C and 4O occurs. The calculated E_g between HOMO and LUMO is 0.09217 hartree (2.52278 eV), the corresponding wavelength is 490 nm, adjacent to the absorption band centered at 465 nm, confirming the intramolecular charge transfer transition process upon 465-nm excitation.

Efficient energy transfer from source light to phosphors is one of the key issues for CCM. Poor superposition between source light emission spectra and excitation spectra of phosphors leads to inefficient energy transfer between source light and phosphors. So, although there are so many organic molecules and polymers absorbing light in near-UV region and emitting light in 550-nm region, many of them cannot be used as CCM due to their inefficient energy transfer. The excitation and emission spectra of DPPO and the emission spectrum of InGaN LED are shown in Fig. 4. It is found that the maximum excitation of DPPO overlaps perfectly with the emission spectrum of InGaN LED (465 nm), which means that DPPO can be efficiently excited by the emission of InGaN LED. Efficient energy transfer between blue source light and DPPO can be generated and that can be attributed to the perfect superposition between emission spectrum of blue LED and excitation spectrum of DPPO as shown in Fig. 4. Comparing the excitation spectrum of DPPO with its absorption spectrum, it can be found that the maximum excitation (465 nm) is not consistent with the maximum absorption (420 nm). This phenomenon can be explained by the electron transition type of DPPO between HOMO and LUMO. As mentioned above, HOMO centralizes at 17N, and π^* orbits of 1C, 3C and 4O contribute the most to the LUMO, so the transition between the HOMO and LUMO can be considered to be $n-\pi^*$ transition, whose molar absorption coefficient (10–100 L/mol cm) is much smaller than that of $\pi-\pi^*$ transition (1000–100,000 L/mol cm). As a result, the maximum excitation appears with relative low molar absorption coefficient. That is, the emission of InGaN LED cannot be totally absorbed by DPPO-dispersed polymer films, and the excess blue emission and yellow emission from DPPO consist of the white light output.

3.3. Quantum yield of DPPO

PL quantum yield is defined as the ratio of the number of photons emitted to the number of photons absorbed. Absolute luminescence quantum yield of DPPO was determined by the method of Demas and Crosby with quinine sulfate in 1.0 M sulfuric acid ($\Phi_r = 0.546$) as reference standard [12]. Sample and
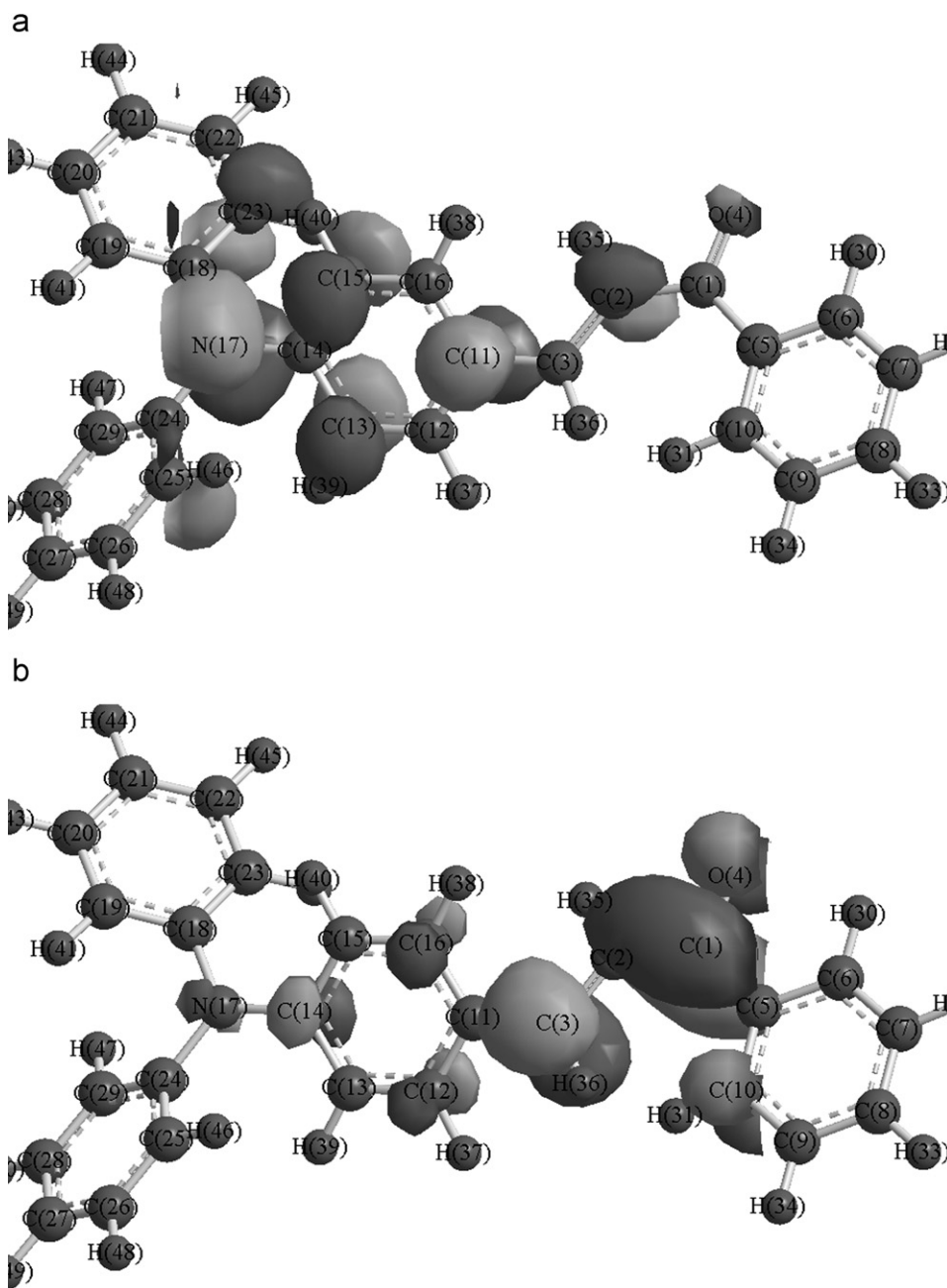
Fig. 3. (a) HOMO of DPPO, (b) LUMO of DPPO.

standard solutions were degassed with no fewer than four freeze-pump-thaw cycles. Quantum yield is determined according to

$$\Phi_s = \Phi_r \left(\frac{B_r}{B_s}\right)\left(\frac{n_s}{n_r}\right)^2\left(\frac{D_s}{D_r}\right), \tag{1}$$

where the subscripts s and r refer to sample and reference standard solution, respectively, n is the refractive index of the solvent, D the integrated intensity, and Φ the luminescence quantum yield. The quantity B is calculated by $B = 1 - 10^{-AL}$, where A is the absorption coefficient at the excitation wavelength and L is the optical length. PL quantum yield of DPPO under 465-nm excitation was

calculated to be as high as 0.44. Thus, highly efficient color conversion can be realized.

3.4. Photo-durability of DPPO

Not only the quantum yield, but also the photo-durability of organic phosphors is an important factor for practical applications. Generally, organic compounds and polymers are unstable when exposed to the UV light. However, the maximum excitation of DPPO is blue light (465 nm), whose energy is smaller than that of UV light, organic compounds are usually more stable when exposed to blue light. Fig. 5 shows the normalized luminescence

Table 1
Summary of coefficients of HOMO and LUMO, and E_g between HOMO and LUMO

HOMO		LUMO	
−0.17955 hartree		−0.08684 hartree	

LUMO–HOMO = 0.09217 hartree = 2.52278 eV (1 hartree = 27.2 eV)

| Coefficient of HOMO		Coefficient of LUMO	
17N	2PX 0.07957	1C	2PY −0.23122
	2PZ 0.38384		2PZ −0.11896
	3PZ 0.31929		3PY −0.16940
18C	2PZ −0.11745		3PZ −0.09386
19C	2PZ −0.15779	2C	2PY −0.16315
	3PZ −0.13682		2PZ −0.10113
21C	2PZ 0.19070		3PX −0.20873
	3PZ 0.15923		3PY −0.12043
23C	2PX −0.10805	3C	2PY 0.24464
	2PZ −0.13816		2PZ 0.13685
	3PX −0.10894		3PY 0.26478
	3PZ −0.10576		3PZ 0.17236
24C	2PZ −0.12104	4O	2PY 0.24332
25C	2PZ −0.16733		2PZ 0.12285
	3PZ −0.13835		3PY 0.22401
27C	2PZ 0.20587		3PZ 0.11771
	3PZ 0.17222	5C	3S −0.12677
29C	2PZ 0.20587	6C	2PY 0.11742
	3PZ 0.17222	8C	2PY −0.13157
			3PY −0.13889
		10C	2PY 0.11737
			3PY 0.13344
		11C	2PY 0.11498
			3PY 0.11606
		12C	2PY −0.13675
			3PY −0.12894
		14C	2PY 0.18530
			3PY 0.17688
		16C	2PY −0.15486
			3PY −0.16105
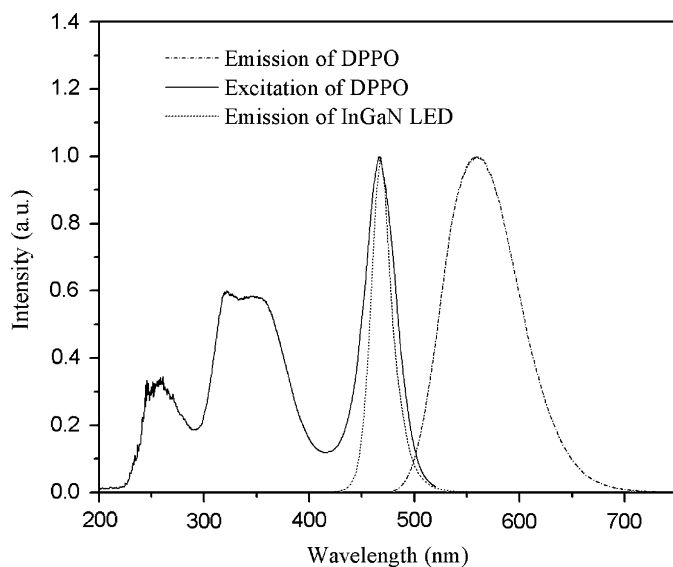
Fig. 4. Excitation and emission spectra of DPPO and emission spectrum of InGaN LED.

decay curves of DPPO when exposed to the blue light (465 nm) and UV light (365 nm). It is found that the luminescence intensities decrease with the increase of irradiation time. Luminescence spectra of DPPO under the blue irradiation are similar despite of different luminescent intensities, but the spectra under UV irradiation demonstrate blue shift tendency. These results indicate that photons with higher energy can break down the π-conjugated molecular structure. Decay curves confirm the fact that luminescence intensity of DPPO under blue light decreases slower than that under UV light. As shown in Fig. 5, it takes about 3200 s for decay-curve-365 to lose 30% of its initial luminescence intensity and the corresponding time of decay-curve-465 is about 6600 s, two times longer than that of decay-curve-365. So it is safe to say that the decay process of DPPO under blue excitation source light (465 nm) is much slower than that under UV light (365 nm), confirming that decay process can be sharply slowed by utilizing lower energy excitation light.

3.5. Energy band gap of DPPO

Generally, the relationship between energy gap (E_g) and UV absorption corresponding to the direct HOMO-to-LUMO transitions can be described as [13]

$$\alpha h v = B(h v - E_g)^n, \qquad (2)$$

where α, h, v, B are the absorption coefficient, Planck constant, frequency of light and the constant related to the nature of material itself, respectively. It is assumed that the transition between HOMO and LUMO is a direct transition because of the high quantum yield. Then n is chosen to be 0.5. Fig. 6 shows the $(\alpha h v)^2$ vs. $h v$ curve of DPPO in CH_2Cl_2 (10^{-4} mol/L). Extend the linear $(\alpha h v)^2$ through $h v$ axis, the E_g can be determined to be 2.52 eV. The absorption band of DPPO ends at 500 nm, the corresponding energy is 2.48 eV. The calculated value of E_g is similar to that obtained from UV absorption spectrum, indicating that the luminescence process of DPPO can be seen as direct transition. Thus high PL efficiency is obtained.

3.6. White light from CCM film and spectral luminous efficiencies

The emission spectra of DPPO-dispersed polymer film combined with InGaN LED at different bias voltages (from 2.6 to 3.2 V) are shown in Fig. 7. It is obvious that the light output consists of both blue emission of InGaN LED and color-conversion emission from DPPO excited by blue emission. White light output was obtained when the bias voltage increased from 2.7 to 3.2 V, as shown in Fig. 7. Under the bias voltage of 2.6 V, blue light is relatively weak and most of blue light is absorbed by DPPO and converted to yellow light. So the output light centers at yellow region. Relative intensity of yellow light in the output light decreases with the increment of source blue light and
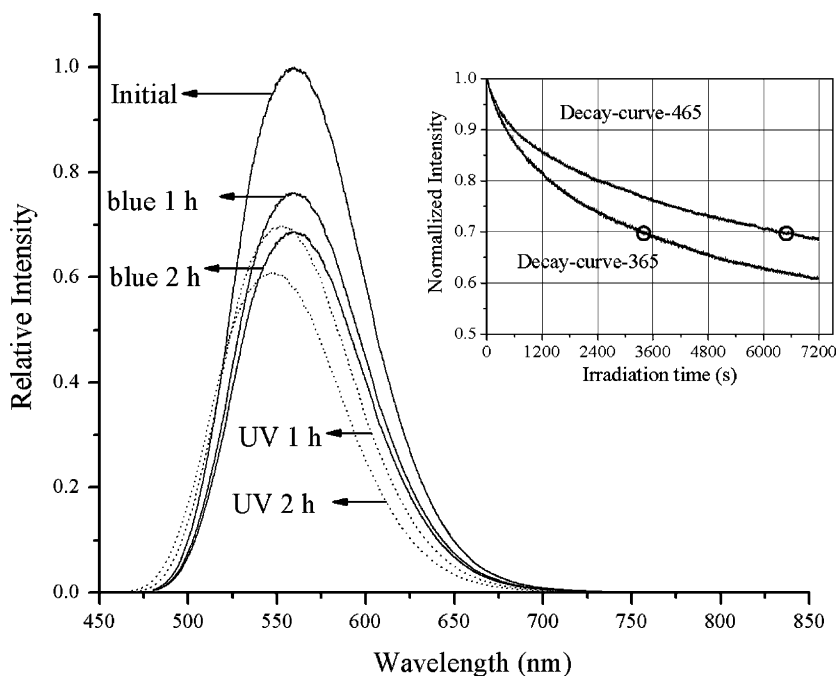
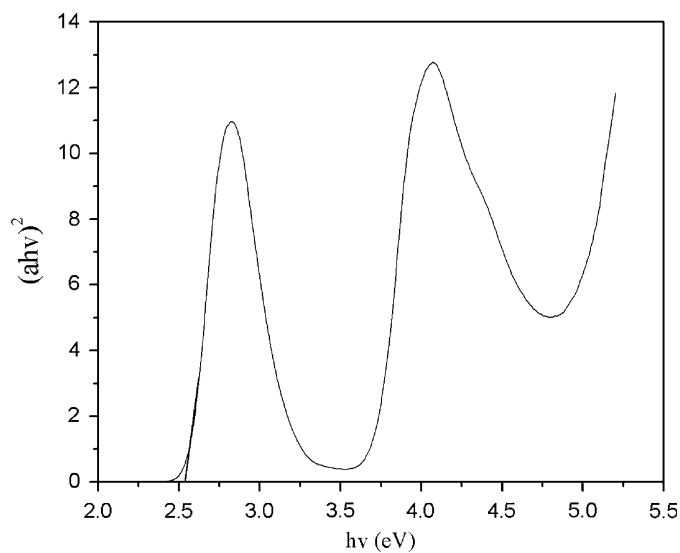Fig. 5. Normalized decay curves of DPPO under blue light (465 nm) and UV light (365 nm).

Fig. 6. The $(\alpha h v)^2$ vs. $h v$ curve of DPPO in CH_2Cl_2 (10^{-4} mol/L).

output light moves close to pure white light when the driving bias increases, output light shows a blue-region shift tendency in the CIE coordinates when driving bias increases to 3.2 V. Under the bias voltage of 3.0 V, a typical white light of $x = 0.30$ and $y = 0.33$ is observed, which is quite close to pure white light ($x = 0.33$, $y = 0.33$). The color temperature is calculated by

$$T = -437n^3 + 360\,1\text{n} \times 686\,1\text{n} + 5514.31, \qquad (3)$$

where $n = (x-0.3320)/(y-0.1858)$. The emission color temperature of color-conversion film excited by InGaN LED (bias voltage = 3.0 V) is calculated to be 5700 K, close

to that of sunlight (5500 K), which means that this white light output is an ideal indoor lighting source.

Luminous efficiency is also an important factor for practical applications of WLEDs. The spectral luminous efficiencies are calculated by [14]

$$\eta_{\text{LM}} = \frac{C \int_b^a E(\lambda) \times V(\lambda)\,\mathrm{d}\lambda}{\int_b^a E(\lambda)\,\mathrm{d}\lambda}, \qquad (4)$$

where the constant $C = 683$ lm/W, $E(\lambda)$ is the spectral energy distribution, $V(\lambda)$ the spectral luminous efficiency function and b, a are the beginning and end of wavelength of spectrum, respectively. The spectral luminous efficiencies of white light output were calculated to be 287 lm/W (2.7 V), 290 lm/W (2.8 V), 275 lm/W (3.0 V), 255 lm/W (3.2 V), respectively. These spectral luminous efficiencies are close to the limit spectral luminous efficiency of WLEDs utilizing blue LED and yellow-emitting phosphor (320 lm/W) [14,15]. All those data confirm that DPPO is a promising candidate for CCM in the WLEDs.

4. Conclusion

We report the synthesis, characterization, thermal and PL properties of DPPO as a high-efficiency organic CCM. Molecular orbital and energy band of DPPO were studied by quantum chemical method and UV absorption spectra. In addition, white light emission with CIE $x = 0.30$ and $y = 0.33$ was obtained by integrating a DPPO-dispersed polymer film with blue InGaN LEDs, indicating that DPPO is an excellent organic CCM for WLEDs.
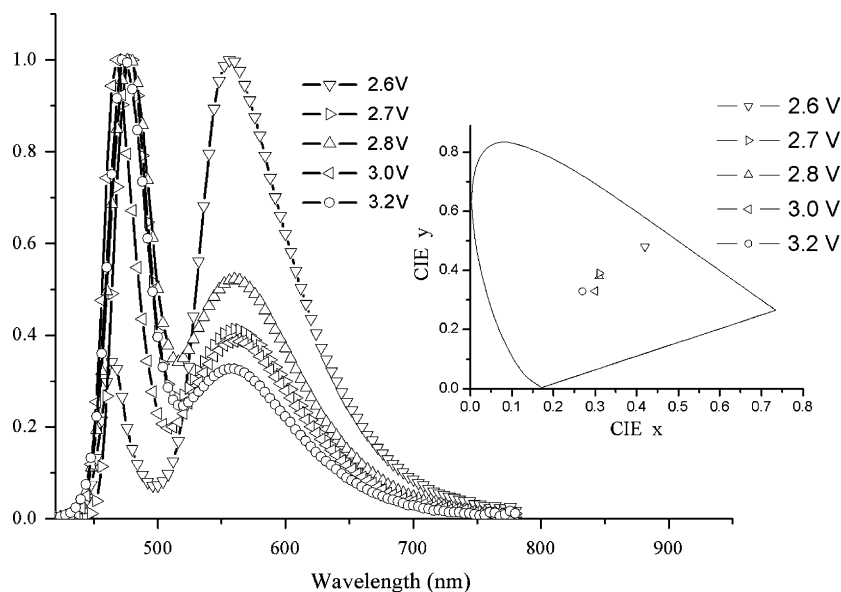
Fig. 7. Normalized emission spectra from the WLED consisting of DPPO-doped film and InGaN LED under bias voltages from 2.6 to 3.2 V.

Acknowledgments

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