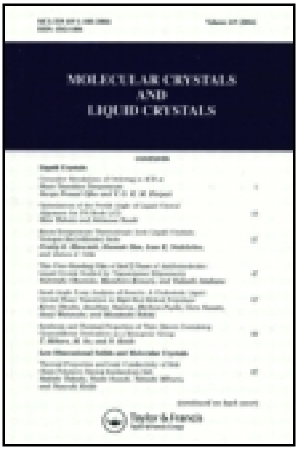

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A Novel Phenothiazine Derivative for Application in High Performance Red Emitting Electroluminescent Device

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The new red emitting materials based on phenothiazine and DCM were synthesized by Knoevenagel condensation following Vilsmeyer-Haack formulation. The obtained materials showed good thermal stability and amorphous property. The ITO/CuPc/NPB/Alq_3:KSR-1 (0.2%)/Alq_3/LiF/Al device showed 3.5 cd/A of efficiency and CIE color coordinate of (0.46, 0.47) at 10 mA/cm^2 and 29000 cd/m^2 of maximum brightness at 11 V and 512 mA/cm^2. In the device using the Alq_3:KSR-1 (0.5%) as emitting material device, 1.5 cd/A of efficiency and CIE color coordinate of (0.55, 0.42) at 10 mA/cm^2 and 19200 cd/m^2 of maximum brightness at 12 V and 702 mA/cm^2 were observed.

Keywords: amorphous; phenothiazine; red emitting

INTRODUCTION

Organic light emitting devices (OLEDs) have received much attention because of their potential applications in flat panel displays [1,2]. Since the initial works on high efficiency OLEDs, many research efforts have focused on the development of full color diaplays. For full

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color applications, it is essential to have RGB (red-green-blue) materials with good color purity and high efficiency. After intensive studies in the past decade, efficient blue and green materials have been developed to meet the requirement of commercial OLED applications. However, there is still a lack of red materials with good color purity, high efficiency, and good stability. Many known and new red fluorescent dyes have been tried and more recently some red phosphorescence dyes have also been introduced [3,4]. Among these, one prominent example is the development of 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyrane (DCJTB), which is arguably the state of the art red dopant, by modifying the well known laser dye 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyrane (DCM). However, for OLEDs doped with DCJTB, device efficiency and color purity are usually traded and compromised. For rare-earth complexes, the color purity is excellent, but the efficiency and chemical stability is much below the requirement of commercial applications. Recently, triplet emitters have been developed to obtain very efficient red devices. However, due to the long lifetime of the triplet state, the density of the triplet state can be more easily saturated for high brightness applications [5]. As a result, the efficiency of triplet red emitter usually decreases very quickly as brightness increases. This will pose a potential problem for applications requiring high excitation density such as in passive dot matrix displays. Thus, new high performance red dyes are still much in demand.

In the present work, we designed and synthesized the new red emitting phenothiazine derivatives, which are expected to have inhibited intermolecular reaction due to bulky t-butyl group and to have high efficient red emitting due to introduction of sulfur having low band gap [6]. We also investigated the spectral and photo physical behaviors of novel phenothiazine derivatives and the electroluminescent (EL) performance of the compound as the red dopant in OLED.

EXPERIMENTAL

N-(4-tert-butylphenyl)-3-Formylphenothiazine

The Vilsmeyer-Haack formulation was used to synthesize C. 0.4 mol of phosphoryl chloride was added dropwise over a period of 0.5 h to a mixture solution of 0.04 mol of N-(4-tert-butylphenyl)-phenothiazine which is obtained from the phenothiazine and 4-tert-butyl-iodobenzene, and 0.4 mol of dimethylformamide in 15 mL of 1,2-dichloroethane at –15°C. After refluxing at 83°C for 72 h, the solution was cooled to room temperature. The solution was poured into a sodium acetate aqueous solution and then stirred for 4 h. to complete the hydrolysis. The resulting mixture was concentrated under reduced pressure and poured into acetone. Insoluble salts in acetone were filtered off, and the filtrate was concentrated. The residue was extracted with water and dichloromethane, and organic layer was concentrated. The purification was carried out by silica gel column with hexane as eluent.

4-(Dicyanomethylene)-2-Tert-Butyl-6-[N-(4-tert-butylphenyl)-phenothiazylene] (KSR-1)

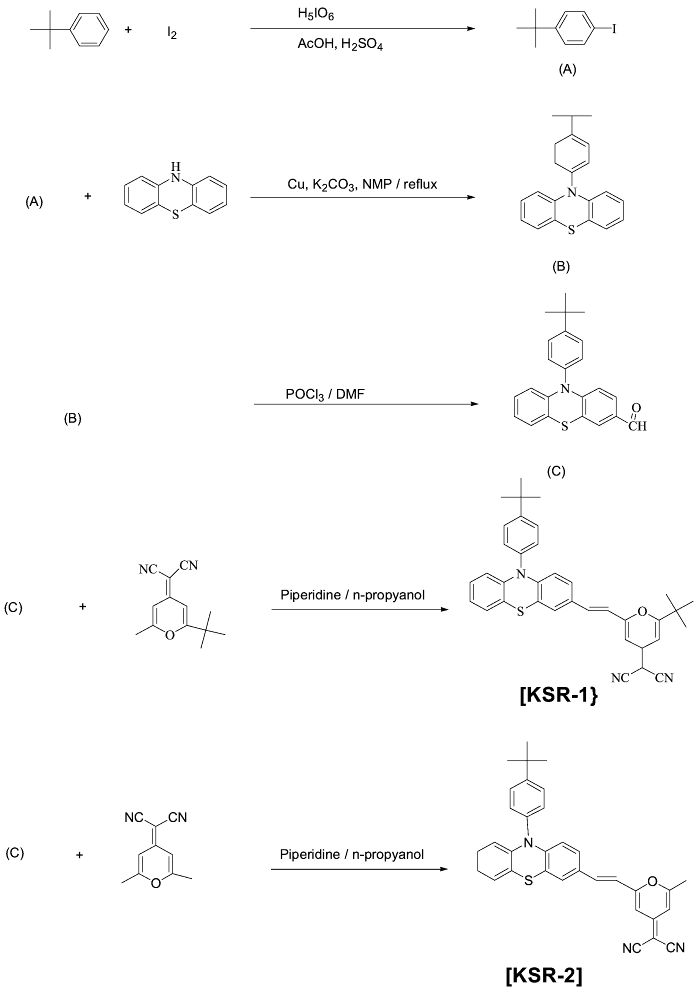
The synthesis is based on Knoevenagel condensation of 2.1 mol of N-(4-tert-butylphenyl)-3-formylphenothiazine and 2-methyl-6-tert-butyl-4H-pyrane-4-ylidine)propanedinitryl. The Knoevenagel condensation was carried out in the 1-propanol. After reaction was finished, the crude product was purified by column chromatography using methylene chloride as eluent. ^{1}H-NMR ($CDCl_3$) δ 7.6 (d, 2H), 7.3 (d, 2H), 7.5 (m, 3H), 7.0 (d, 1H), 6.8 (m, 1H), 6.6 (m, 3H), 6.2 (n, 2H), 1.4 (s, 9H), 1.3 (s, 9H). FT-IR (KBr pellet, cm^{-1}): 3050 (aromatic & vinylic C$-$H), 2964 (aliphatic C$-$H), 2207 ($C\equiv N$).

4-(Dicyanomethylene)-2-Methyl-6-[N-(4-tert-butylphenyl)-phenothiazylene] (KSR-2)

The synthesis was similarly carried by above procedure. ^{1}H-NMR ($CDCl_3$) δ 7.6 (d, 2H), 7.3 (d, 2H), 7.5 (m, 3H), 7.0 (d, 1H), 6.8 (m, 1H), 6.6 (m, 3H), 6.2 (n, 2H), 2.1 (s, 3H), 1.3 (s, 9H), FT-IR (KBr pellet, cm^{-1}): 3050 (aromatic & vinylic C$-$H), 2964 (aliphatic C$-$H), 2207 ($C\equiv N$).

RESULTS AND DISCUSSION

The synthesis of new red emitting materials are showed in the Scheme 1. The new red emitting materials are obtained by Knoevenagel condensation following Vilsmeyer-Haack formulation. The obtained materials are confirmed by various spectroscopic methods. The thermal property of synthesized materials were evaluated by the means of TGA under nitrogen atmosphere. TGA curve shows that the materials showed 5% weight loss at 300°C for KSR-2 and 360°C for KRS-1, respectively. The DSC measurement showed the glass transition at around 215°C for KSR-2. However, for KSR-1, Tm and Tg were not observed even heating up 250°C. From the results, the obtained new



SCHEME 1 Synthetic routes of KSR-1 and KSR-2.

red emitting materials had amorphous property, which can increase the device longevity.

Figure 1 shows the UV-vis absorption and photoluminescence spectra of the new red emitting materials in $CHCl_3$ solution. The absorption spectrum of solution of KSR-2 showed the absorption maximum at 487 nm. For KSR-1, the absorption maximum was observed at 488 nm. And absorption cutoff wavelength was similarly observed at 580 nm in both KSR-1 and KSR-2 regardless of substituents. However,

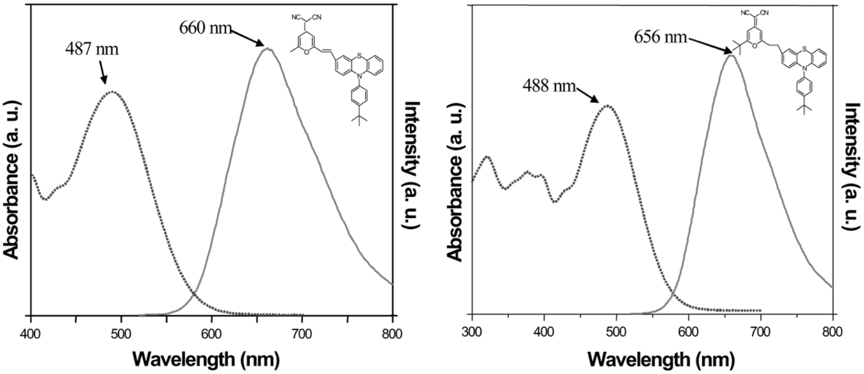


FIGURE 1 UV-vis absorption and photoluminescence spectra in $CHCl_3$.

in the photoluminescence, the emission maximum of KSR-1 and KSR-2 was observed at 656 nm and 660 nm, respectively. It can be explained that tert-butyl group for KSR-1 inhibits the planarity, and the photoluminescence spectrum was slightly blue shifted.

The LED devices with configuration ITO/CuPc (200)/NPB (500)/ Alq_3:KSR/Alq_3/LiF (10)/Al (1500) were fabricated, where CuPc as hole injection, NPB as hole transporting, Alq_3 as host and electron

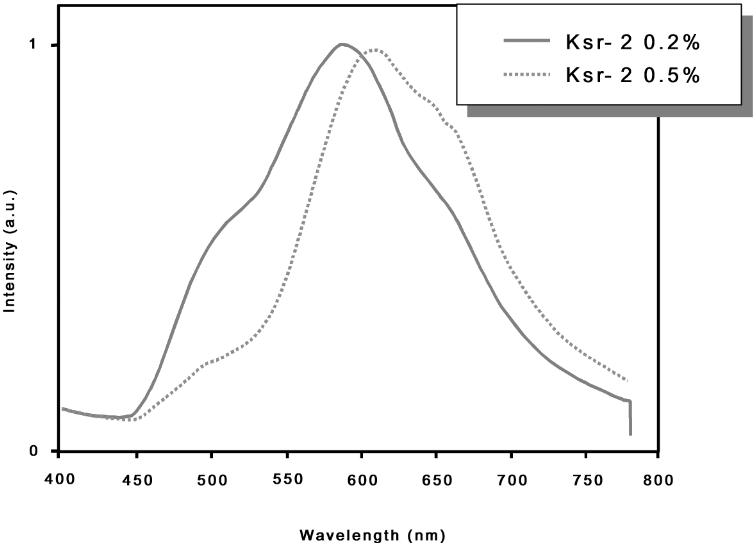


FIGURE 2 Electroluminescence (EL) spectra of the devices.

TABLE 1 The Summary of Characteristics of Devices

Structure	@10 mA/cm^2			@100 mA/cm^2				
Alq$_3$:KSR-2/ Alq$_3$	Turn-on (V)	Efficiency (cd/A)	CIE (x, y)	Turn-on (V)	Efficiency (cd/A)	CIE (x, y)	EL$_{max}$	Max brightness (cd/m^2)
300:0.2%/300	6.9	3.5	(0.462, 0.475)	8.9	3.2	(0.458, 0.478)	587	29,000 (11 V, 512 mA/cm^2)
300:0.5%/300	7.2	1.5	(0.545, 0.422)	9.6	1.2	(0.554, 0.417)	605	19,000 (12 V, 702 mA/cm^2)

transporting, LiF as electron injection and Al as cathode were used. Since the color of LEDs with red dopants was expected to be dependent on the concentration dye, LEDs with different dye concentration were fabricated. The electroluminescence (EL) spectra of the devices, which were fabricated with different dye concentrations, are shown in Figure 2. The results and brightness are summarized in Table 1. The results showed that the color purity was increased as doping level of red dopant, however, the efficiency and maximum brightness was decreased.

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