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Studies on synthesis and EL properties of several novel squaraines

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Abstract

Several novel squaraines were synthesized and their structures were elucidated by IR, HNMR, MS and elementary analysis. Their photoluminescent (PL) and electroluminescent (EL) properties have been studied, which indicated that all of them had electron-transporting properties, and some had both electron- and hole-transporting properties. One of the squaraines was inserted between a cathode and an anode, and the single-layer-sandwiched device processed a red-light-emitting ability under both low negative and low positive driven bias. It was regarded as one kind of promising material.

Keywords: Electroluminescence; Squaraines

1. Introduction

Organic electroluminescent devices (OELDs) have attracted much interest and have been regarded as promising and sophisticated devices, as they have many advantages [1,2] superior to other display devices and light sources.

In this paper, we designed and synthesized several novel squaraines whose structures have never been reported [3], and selected three of them (**S1**, **S2** and **S3**) to be used as EL materials according to their better photoluminescent (PL) properties. Their structures have been elucidated by IR, H NMR, MS and elementary analysis. Both their PL properties in solid and solution have been studied together with their EL properties. They were expected to be new red light-emitting-layer (EML) materials and electron-transporting-layer (ETL) materials with low driven voltages.

2. Experimental

All of the reagents ($SOCl_2$, CH_2Cl_2, n-butanol, morpholine, DMF) were dried and redistilled before use. Squaric acid, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4' diamine) (TPD) and tri(8-hydroxyquinoline) aluminum (Alq_3) were prepared and purified according to the literature [4,5]. Intermediate compounds **1** and **2** were prepared according to the literature [6,7].

The synthesis route of the materials is shown in Fig. 1. Synthesis of **S1** was carried out as follows. Compound **2** (400 mg, 1.834 mmol) and morpholine (160 mg, 1.834 mmol) were dissolved in DMF (15 ml) and refluxed for 2 h. The reactant was cooled down and filtered; the final compound of orange–red needle crystals was obtained with a yield of 76%; m.p. 330 °C (decomposition temperature).

S2 was obtained in the same way as **S1** with a yield of 80%; it was red crystals; m.p. 300 °C (decomposition temperature).

S3 was also obtained in the same way as **S1** with a yield of 73%; it was orange crystals; m.p. 300 °C (decomposition temperature).

Studies of EL properties have been done on **S2**, while **S1** and **S3** were studied only to determine their transporting properties. Devices with thin organic films sandwiched between indium–tin oxide (ITO) and Al electrodes were fabricated, the thickness of each organic layer being 50 nm, and that of the Al layer about 150 nm. The vacuum was about 2×10^{-6} Torr.

3. Results and discussion

Squaraines had electron-defect centres and could capture electrons, so they could probably be used as electron-transporting-layer materials (ETLMs). We designed an alteration in their conjugation systems so that they could emit light in the visible region, and they were expected to be light-emis-

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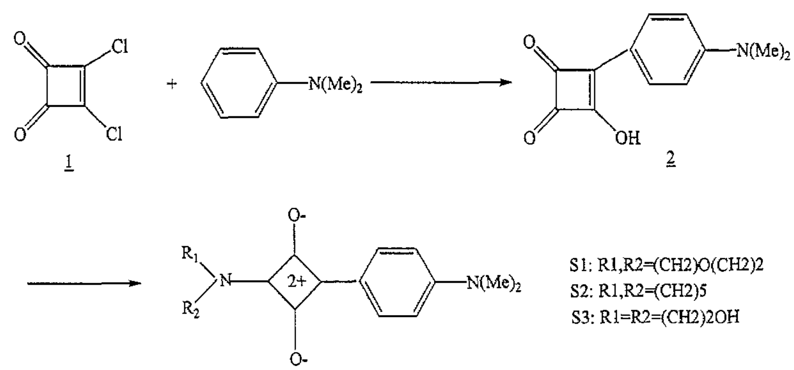

Fig. 1. Synthesis route and structures of squaraines.

Table 1
PL properties of **S1**, **S2** and **S3**

	S1	S2	S3
λ_{EM1} (nm)	628	630	610
λ_{EM2} (nm)	508	497	490

sion-layer material (EMLM) for their good PL intensities. Research on their EL properties showed that the results were in conformity with our design. PL data of these materials are shown in Table 1 (λ_{EM1} is EM wavelength of the solid; λ_{EM2} is EM wavelength of 10^{-5} M solution in $CHCl_3$).

Studies on EL properties indicated that:

(1) Device ITO/**S2**/Al could emit red light under both low negative and positive bias, the lowest driven voltages being 1 V; generally, the device could emit stable light under 2 V with a current of 4 mA (positive) and 2 mA (negative). The wavelength of the emission was in conformity with its solid photoluminescence. Further observations showed that the colour of the combination part of Al and **S2** turned from silver to purple–silver. It was assumed that a cathode complex was formed or that **S2** had both electron- and hole-transporting abilities and was a kind of special material which perhaps could lower the driven voltage and simplify the structure of the device. The device could emit light with only a slightly increased driven bias after it was exposed to atmosphere at room temperature for 24 h. The luminance was weak and was observed with the naked eye.

(2) Device ITO/TPD/**S2**/Al could emit light from red to blue–purple with increased voltages. The red light was due to **S2** and the blue–purple to TPD. This confirmed that **S2** had electron-transporting abilities. The device had light-emitting properties after 24 h exposure to the atmosphere.

(3) Device ITO/TPD/Alq_3/**S2**/Al could emit green light which was emission of Alq_3. Electron-transporting abilities were investigated. The device had a lifetime of more than 24 h when exposed to the atmosphere and the green light emission was bright.

All of the above devices had good durability; their *I–V* curves are shown in Fig. 2. Further studies will be carried out

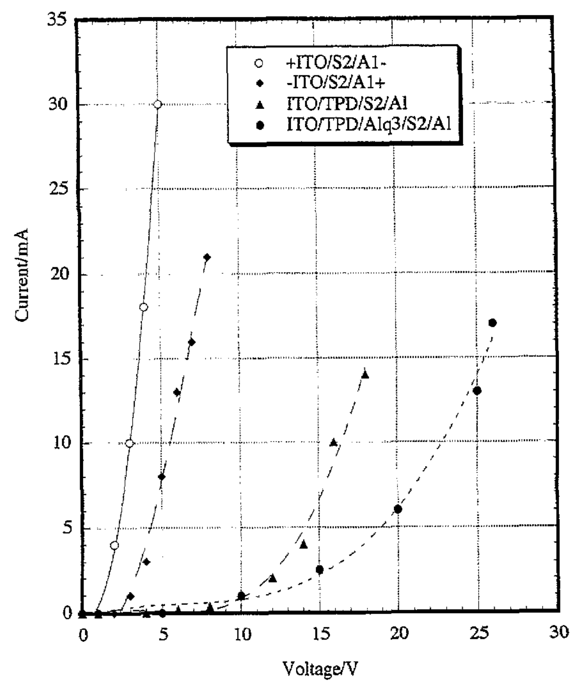

Fig. 2. *I–V* curves of the devices.

and their *B–I* (*B–V*) curves and EL spectra will be reported in subsequent papers.

S1 and **S3** were investigated in the same way. They did not appear to form a cathode complex and the single-sandwiched device did not give the same phenomena as **S2**. They also could emit red light and transport electrons.

We can conclude that **S1**, **S2** and **S3** are ETLMs and EMLMs in the EL device. Probably **S2** also has hole-transporting ability. **S2** has special EL properties and is expected to be a new useful kind of material.

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