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Synthesis of Pyrazolines Used as Blue Organic Electroluminescence Materials

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Abstract: Three kinds of pyrazolines were designed and synthesized. Their structures were elucidated by IR, ^{1}HNMR, MS, UV and elemental analysis. Their luminescent properties were determined, which indicated that they had strong blue fluorescent properties. One of them was designed to have good film formation. All the three kinds of pyrazolines can be used as blue organic electroluminescence materials (OELMs).

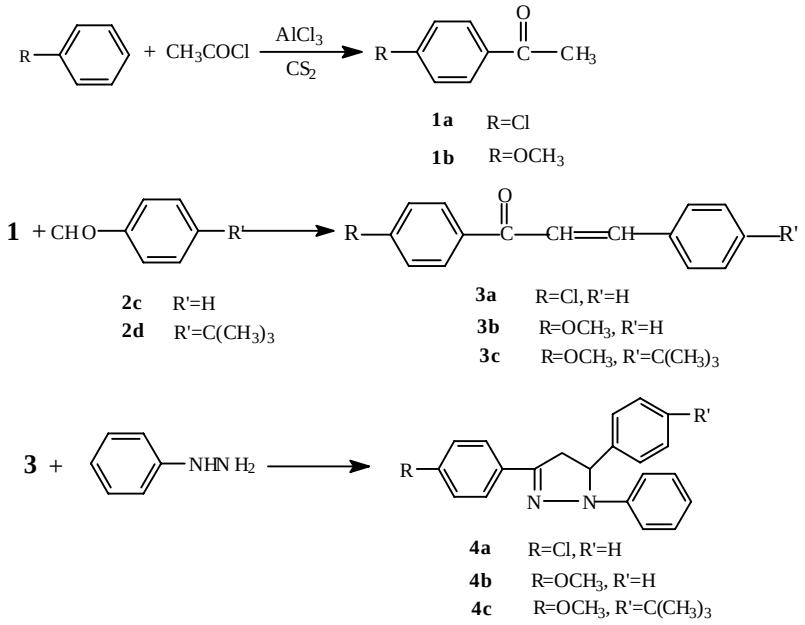
Keywords: Synthesis; pyrazolines; fluorescence; blue organic electroluminescence materials.

Since Tang *et al.* developed a novel two-layer organic electroluminescent device (OELD) in 1987 successfully[1], OELD has attracted much interest all over the world. It is regarded as "having brought the third revolution to flat panel display "[2], because it has so many advantages superior to Cathode Ray Tube (CRT) and Liquid Crystal Device (LCD). It has low driven voltage (<10V), high brightness (>100,000 cd/m^2), high luminescent efficiency (15 lm/w), good stability (50,000 h), and it has simple structure and is easy to fabricate[3]. Compared to inorganic ELD, OELD is easier to realize blue light-emission.

Although much progress has been achieved on OELD, there are still some defects, such as: both the efficiency and stability of blue and red OELDs are not good. The key problem needed to perfect is to design and synthesize new blue and red OELMs and to design better device structures as well.

Pyrazoline, which is well-known as fluorescent brightening agent, has excellent fluorescent property[4]. It can absorb light of 300-400 nm and emit blue fluorescence. There is a heterocyclic ring in the structure of pyrazoline containing two nitrogen atoms, one of which forms an electron-donating p-π conjugated system, so it is able to function as hole-transporting material[5] used in OELD[6]. Its excellent carrier-transporting ability and fluorescent property makes it possible to be used as a kind of good OELM. We designed and synthesized pyrazolines. It was shown that they can emit blue light, and the film formation was improved by adding some groups on their structures. Their photoluminescence (PL) properties were studied, their strong blue solid PL showed that they could be used as blue OELMs.

Scheme.



Results and Discussion

Pyrazolines have strong fluorescence in solution. As to OELMs, we hope to obtain those having excellent fluorescent properties in solid state. Pyrazoline has a five-membered ring in which there are two nitrogen atoms and three carbon atoms. The conjugated system contains two nitrogen atoms and one carbon atom, while the other two carbon atoms are sp^3 hybridized. Both the conjugated system and the two sp^3 hybridized carbon atoms make a rigid and discoplanar five-member ring. This meets the qualification of materials that have good solid photoluminescence (PL) property.

Otherwise, as OELMs, they need to have good carrier-transporting abilities so that they can form electron traps in the light-emitting layer. Pyrazoline derivatives has been reported to be used as hole-transporting material (HTM)[6] for it has one nitrogen atom in the ring forming a electron-donating p- π conjugated system.

Because PL has almost the same mechanism to EL, we investigated fluorescent properties of these compounds to estimate their EL spectra.

Table 1. Photoluminescence property of **4a**, **4b** and **4c**
(λ_1:10^{-3}M in chloroform solution ; λ_2:solid state)

	4a		**4b**		**4c**	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
λ EXmax (nm)	341	290	341	288	405	290
λ EMmax (nm)	448	452	432	448	446	446

We can draw the conclusion that all the three kinds of pyrazolines have good PL properties in both solution and solid states. The light emission lies in the blue region. So they can be used as blue OELMs. We synthesized **4a** first and found that its solid PL was not quite good. Then we changed the -Cl group into -OMe group (**4b**) because halogen atoms would decrease the intensity of fluorescence[7]. The result showed that **4b** had better solid PL property than **4a** but the film-forming ability is poor. In order to improve it, we add the t-butyl group into the structure to get **4c**. When they were vacuum-deposited, **4c** could form a quite smooth and good film while **4a** and **4b** could not. This result is in conformity with our design.

In summary, all the three kinds of pyrazolines could be used as blue OELMs, and have hole-transporting abilities. One of them has good film-forming ability and can be used to fabricate vacuum -deposit OELDs, while **4a** and **4b** can be used as dopants in polymer ELDs. This is the first time these compounds are used as OELMs.

Experimental

All of the reagents (ethanol, carbon disulfide, glycol monoethyl ether, acetyl chloride, methoxyl benzen, chlorobenzene) were dried and distilled before use.

Intermediates **1a** and **1b** were synthesized according to literature[8]. Yield. **1a** 93.7%; **1b** 80%. b.p. **1a**:158-159℃/50 mmHg; **1b**:154-156℃/5o mmHg (lit.[9]**1a**: b.p.236℃, 1b: b.p.258℃). Intermediate **2d** was prepared according to literature[10]. Yield. 82%. b.p.84-100℃/0.5 mmHg (lit.[9], b.p.100-115℃/11 mmHg). Intermediates **3a**, **3b** and **3c** were synthesized according to literature[11]. Yield. **3a** 42.5%; **3b** 62.7%; **3c** 30%.

Synthesis of 4a, 4b and 4c.

2.5 g (0.01 mol) **3a**, 1.4 g phenylhydrozine (0.01 mol) and 52 mL glycol monoethyl ether were mixed and refluxed for 2 hours. The yellow crystal was obtained after cooling. It was recrystallized from ethanol to give pale yellow needle crystal **4a**. Yield. 43.8%. m.p.152-153℃. Found: C%: 75.76. H%: 5.18. N%: 8.38(Required: C%: 75.78. H%: 5.15. N%: 8.41), ^{1}HNMR ($CDCl_3$,ppm): δ 1.55 (1H,CH), 3.6 (2H,CH_2), 7.25 (14H,C_6H_5, C_6H_4), m/z: 332 (m^+).

4b and **4c** were synthesized in the same way as **4a**.

4b: white needle crystal. Yield. 30%. m.p.144-145℃. Found: C%: 80.28. H%: 6.19. N%: 8.43. (Required: C%: 80.46. H%: 6.14. N%: 8.52.), ^{1}HNMR ($CDCl_3$, ppm): δ 1.55 (1H,CH), 3.6 (5H, CH_2, OCH_3), 7.25 (14H, C_6H_5, C_6H_4), m/z: 328 (m^+).

4c: pale yellow needle crystal. Yield. 27%. m.p.151-152℃. Found: C%: 80.6. H%: 7.39. N%: 7.16. (Required: C%: 81.2. H%: 7.34. N%: 7.16.) ^{1}HNMR ($CDCl_3$,ppm): δ 1.4 (10H, CH, CH_3), 3.9 (5H, CH_2, OCH_3), 7.25 (14H, C_6H_5, C_6H_4), m/z: 384 (m^+).

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