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Synthesis of Two Blue-light – emitting Complexes with Schiff Base Calixarene as the Ligand

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Abstract: Two new blue luminescent zinc and beryllium complexes with Schiff base calixarene derivative as the ligand were prepared. Their luminescent properties were determined, which indicated that they had strong blue fluorescent properties. They also had good solubility and film formation. These new complexes can be used as blue organic electroluminescent materials (OELMs) in organic electroluminescent devices.

Keywords: Synthesis, calixarene, **S**chiff base, fluorescence, organic electroluminescent material.

Since the pioneering work of C. W. Tang *et al.*[1], which first demonstrated efficient electroluminescent (EL) devices based on organic materials, many efforts have been devoted to exploring new EL materials for display applications[2-6], but there are still some defects, such as: both the efficiency and stability of blue and red organic electroluminescent devices (OELDs) are not good. The design and synthesis of new blue and red OELMs and the design of better device structure were the key problems needed to be perfected.

Zinc complex with Schiff base as the ligand has excellent fluorescent property with high photoluminescence quantum efficiency and good thermal stability. Fabrication of EL devices employing this kind of zinc complexes as blue electroluminescent material was carried *via* thermal vacuum-deposition. As their poor solubility in normal organic solvents, these complexes cannot be easily doped in polymer and used to fabricate OELDs by spinning.

Calix[4]arenes are popular building blocks in supramolecular chemistry. The calixarene platform can be selectively functionalized both at the phenolic OH groups (lower rim) and at the *para* positions of the phenol rings (upper rim) which provide unique possibilities to organize several binding sites appropriately for complex of potential guests.

The new ligand was synthesized through reaction of salicyaldehyde- 2-hydroxy-ethylimine (**H_2SAE**) and *p*-t-butyl-calix[4]arene tetracarboxylic acid. This ligand maintains the cone conformation, which can form an intermolecular complex with Zn^{2+}

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or Be^{2+}. Complexation of zinc ion or beryllium ion in the molecular cavity can efficiently diminish the influence of external molecules to the fluorescence. We designed and synthesized zinc and beryllium complexes with Schiff base calix[4]arene ligand, the synthetic scheme was shown in **Figure 5.** The results indicated that they could emit pure blue light and have good solubility in normal solvents. Their photoluminescence properties were studied. Their strong PL intensity showed that they could be used as blue OELMs.

Results and Discussion

Zinc complexes with Schiff base as ligands have strong fluorescence and good thermal stability. OELDs using this kind of complexes as OELMs are often fabricated *via* thermal vacuum-deposition. The derivatives of calix[4]arene (complex **6**, **7**) had good solubility and could be dissolved in organic solvents such as $CHCl_3$, CH_2Cl_2, EtOH. Thus they can be easily doped in polymer such as PVK, PMMA, PC and so on. Because PL has almost the same mechanism to EL, we investigated fluorescent properties of **6** and **7** to predict their EL spectra. The fluorescence spectra of complex **6** and **7** were shown in **Figure 1**, **Figure 2**, **Figure 3** and **Figure 4.**

Figure 1 The fluorescence spectrum of complex **6** in EtOH (λ_{Exmax} = 360 nm)

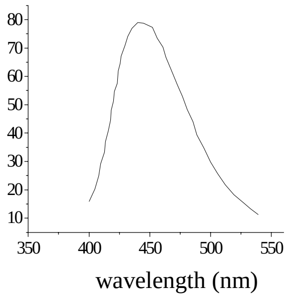


Figure 2 The fluorescence spectrum of the thin film of complex **6** doped in PMMA (λ_{Exmax} = 360 nm)

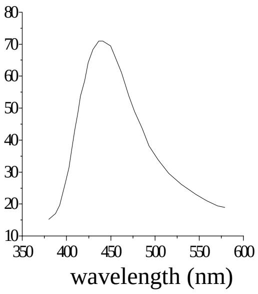


Figure 3 The fluorescence spectrum of complex **7** in EtOH (λ_{Exmax} = 422.5 nm)

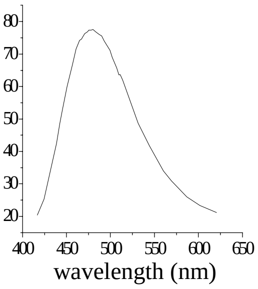
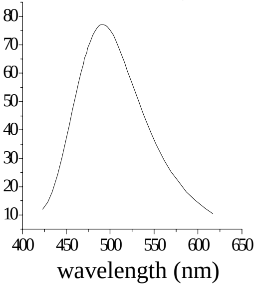


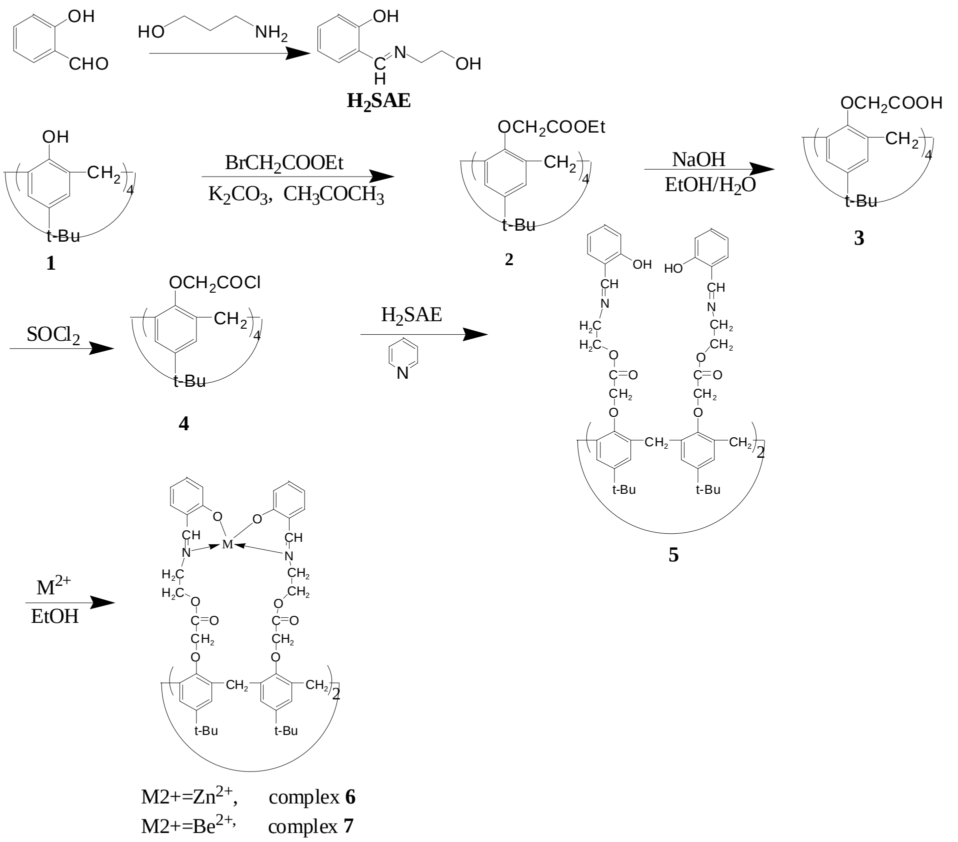
Figure 4 The fluorescence spectrum of complex **7** in solid state (λ_{Exmax} = 400 nm)



The complex **6** can emit blue light in EtOH solution as well as in the thin film doped in PMMA, but its fluorescence was quenched in solid state. The quenching of fluorescence may be caused by the interaction between molecules for the higher concentration in solid state. On the contrast, the complex **7** has strong fluorescence both in solution and in solid state. Their light emissions lie in blue region with λ_{Emmax}= 450 nm and λ_{Emmax}= 485 nm, so they may be prospective blue OELMs. When the solution of **6** doped in PMMA was cast, it could form a quite smooth and homogenous film. Using complex **6** as emission material doped in PVK, we had fabricated a double-layer-type electroluminescent device by spinning. By using a structure of ITO/ PVK/ PVK: complex **6** / Al, blue-light- emission was observed.

In summary, the Zn^{2+} and Be^{2+}complexes with ligand **5** have good fluorescence and film-forming ability. They can be used to fabricate OELDs by spinning.

Figure 5 Scheme of synthesis



Experimental

H_2SAE, **1**, **2**, **3** and **4** were synthesized according to literature 7, 8 and 9.

Synthesis of **5**: To the solution of acid chloride **4** (3.05 g, 3.2 mmol) in 20 mL of anhydrous CH_2Cl_2, the mixture of **H_2SAE** (2.114 g, 12.8 mmol) and pyridine (2.04 g, 26 mmol) was added dropwise at room temperature over 15 min. Then the reaction mixture was stirred for 12 h at room temperature. After the solution was concentrated, 10 mL ether was added to precipitate the compound **5**. mp: 208.5°C (decomp.). ESI－MS：1470（M^+）; IR（KBr，cm^{-1}）: 3426 (OH), 1654 (C=O), 1620 (C=N); ^{1}H-NMR ($CDCl_3$): 1.34-0.81 (36H, CH_3); 4.60-2.44 (32H, CH_2); 7.57-6.98 (24H, ph-H); 9.9 (4H, N=CH); 11.01 (4H, OH).

Synthesis of complex **6**: To 5 mL of 0.5 mol/L **5** in alcohol was added 1.25 mL of 2mol/L zinc acetate in alcohol. The reaction mixture was stirred and refluxed for 4h, then was cooled down to room temperature. After removement of the solvents, the residue was added into *n*-hexane to cause precipitation. The solid was filtered, washed thoroughly with water and dried in vacuum to yield complex **6**. mp: 281.6°C (decomp.). IR（KBr，cm^{-1}）: 1667 (C=O), 1635 (C=N).

Synthesis of complex **7**: To 5 mL of 0.5 mol/L **5** in alcohol was added 1.25 mL of 2 mol/L $BeSO_4$ in water. The reaction mixture was stirred and refluxed for 4h, then was cooled down to room temperature. After the removement of the solvents, the residue was added into *n*-hexane to cause precipitation. The solid was filtered, washed thoroughly with water and dried in vacuum to yield complex **7**. mp >250℃ (decomp.). IR（KBr，cm^{-1}）: 1663 (C=O), 1626 (C=N) .

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