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Oxadiazole-containing material with intense blue phosphorescence emission for organic light-emitting diodes

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2-(2-hydroxyphenyl)-5-phenyl-1, 3, 4-oxadiazole (**HOXD**), characteristic of excited state intramolecular proton-transfer (ESIPT), was synthesized and found to emit strong blue phosphorescence in the solid state at room temperature and at low temperature (77 K). The photoluminescent spectrum measurement in solution showed that there are two kinds of emission: fluorescence originated from the singlet state and phosphorescence derived from the triplet state in **HOXD** formed by ESIPT. For the photoluminescent spectrum in the solid state, only phosphorescence emission with the lifetime of 66 μs was observed. Multiple-layer light-emitting diodes with the configuration of ITO/NPB/**HOXD**/BCP/Alq₃/Mg:Ag were fabricated using **HOXD** as emitter and the maximum brightness of 656 cd/m^2 and the luminous efficiency of 0.14 lm/W was obtained. © 2002 American Institute of Physics. [DOI: 10.1063/1.1491288]

Organic light-emitting diodes (LEDs) have been extensively studied in the past several years.^{1,2} Very recently, some phosphorescent metal complexes containing Ir, Pt ions have attracted much attention,^{3–6} because the emission may result from both singlet and triplet states, and in principle, it should be possible to make use of 100% of electron-hole recombination, lifting the proposed 25% limit on electroluminescent efficiency. Nevertheless, the organic phosphorescent materials have been rarely developed, in particular, at room temperature, and there is a need for developing high efficient organic phosphorescent materials. In this letter, we report on an organic phosphorescent dye, 2-(2-hydroxyphenyl)-5-phenyl-1, 3, 4-oxadiazole (**HOXD**) and its photoluminescence (fluorescence and phosphorescence) and electroluminescence properties are presented. **HOXD** is chosen for the present study, because it is an example of a molecular system which undergoes excited-state intramolecular proton transfer (ESIPT) to yield an excited keto form of the original enol form. There are several kinds of proton-transfer dyes such as benzoxazole, benzothiazole, N-salicylidene aniline, benzimidazole.^{7–9} Among them, a few compounds such as 2-(2'-hydroxyphenyl)-benzothiazoles and 2-(2'-hydroxy-5'-fluorophenyl) benzimidazole emit quite strong ESIPT luminescence.^{10,11}

Compound **HOXD** is synthesized according to the procedure described in the literature.¹² It exhibits intense photoluminescence in the solid state under UV light irradiation. The control study demonstrates that 2-(4-hydroxyphenyl)-5-phenyl-1, 3, 4-oxadiazole and 2-(2-methoxyphenyl)-5-phenyl-1, 3, 4-oxadiazole (**MOXD**) without hydroxy group at 2-position of the phenyl ring shows very weak luminescence under the same conditions (see Fig. 1). This suggests

that the photoluminescence origin of **HOXD** must be associated with the intramolecular hydrogen bond and the ESIPT. Figure 2 shows the UV-visible absorption and emission spectra of **HOXD** and **MOXD** in CH_2Cl_2 solution. It is noticed that although their absorption spectra are very similar, the fluorescence spectra of **HOXD** and **MOXD** in solution are quite different. As can be seen from Fig. 2, the former absorption bands appear at 274 and 315 nm, the latter at 274 and 305 nm, respectively. The band at 274 nm is associated with the oxadiazole coupling with phenyl ring. The band at 305 or 315 nm is attributed to the oxadiazole coupling with substituted phenyl ring. From the emission spectra of **HOXD** in solution, we notice that there are two emission peaks at 365 and 489 nm, respectively. In contrast, only one emission at 358 nm is observed for **MOXD** as the nonproton transfer model compound. Thus, we can attribute the emission at 365 nm to the enol-tautomer form and the emission at 489 nm to the keto-tautomer form resulting from ESIPT, respectively. The 125 nm redshift of the **HOXD** between enol-form and keto-form can be attributed to a strong intramolecular hydrogen-bond formation in **HOXD**, which is commonly observed in many molecule systems with ESIPT.¹³ Surprisingly, no emission at 365 nm and only one emission at 489 nm is observed for **HOXD** in the solid state, indicating that ESIPT becomes more efficient in the solid state than in solution. In solid state, the torsional motion is virtually frozen so that the H-bonded conformer is preferred energetically. Furthermore, the disappearance of the short-wavelength emission at 365 nm also indicates that the energy of the single excited state transfers completely to the tautomers in the excited state.¹⁴

The phosphorescence spectra of **HOXD** at room temperature and at low temperature were measured in order to identify the existence of phosphorescence emission in **HOXD** molecular system, as shown in Fig. 4. It can be seen

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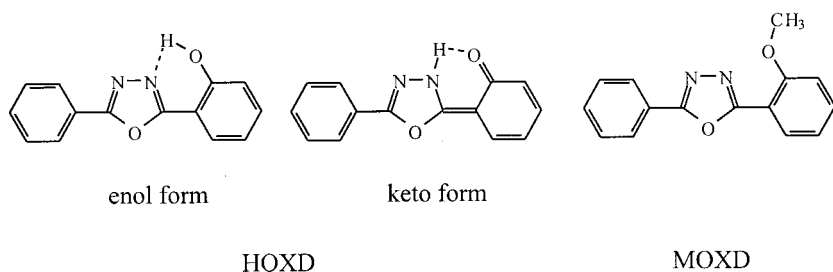


FIG. 1. Structure of **HOXD** and its corresponding keto-tautomer and methyl derivative.

that the phosphorescence emission at 77 K appears at 475 nm, almost the same with its photoluminescence spectrum in the solid state. At room temperature, its phosphorescence spectrum is also obtained and centered at 481 nm, but much broader than that in 77 K. It exhibits strong luminescence with the lifetime of 66 μ s at room temperature, consistent with emission from a triplet excited state.

The results of the *ab initio* calculations for the triplet state show that the stable triplet species of **HOXD** can be regarded as a kind of *cis*-keto form. Based on previous literature reports¹⁵ on keto-enol tautomerism in the metastable excited state and above luminescent properties, a schematic energy diagram is depicted (Fig. 3). This process is fast enough to accompany the short-lived first excited singlet state, the electronic excitation of a normal form (*N*) in the ground state yields a proton-transferred excited-state tautomer (*T*^{*}) of the much lower energy. This *T*^{*} relaxes radiatively or nonradiatively to the metastable ground state *T*, which reverts to *N* via reverse proton transfer. In the singlet electronic ground state of **HOXD**, ¹*E* is the more stable tautomer;¹⁶ In excited state ¹*K*^{*} is deactivated by three processes: fluorescence ¹*K*^{*} → ¹*K*, intersystem crossing ¹*K*^{*} → ³*K*^{*}, and a thermally activated process ¹*K*^{*} → ¹*E* not leading to ³*K*^{*}.^{16,17} In excited triplet state there is a fast proton transfer between enol form and keto form.¹⁸ Accordingly, **HOXD** should exhibit two kinds of luminescence behavior: singlet fluorescence and triplet phosphorescence.

Multiple-layer LED device was fabricated with the structure of ITO/NPB (40 nm)/**HOXD** (20 nm)/BCP (10 nm)/Alq₃ (40 nm)/Mg:Ag using **HOXD** as emitting material.

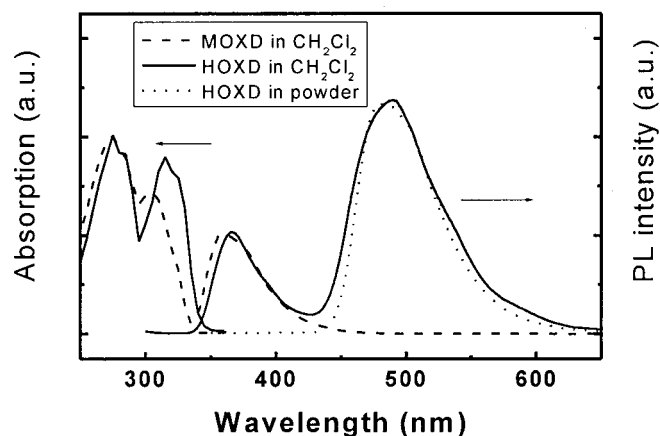


FIG. 2. The UV-visible and emission spectra of **HOXD** at room temperature.

NPB (*N,N'*-Di-[naphthalenyl]-*N,N'*-diphenyl)-(1,1'-biphenyl)-4,4'-diamine) was introduced between the emitting **HOXD** and the ITO layer as hole-transporting layer. BCP [4,4'-(*N,N'*-dicarbazole)biphenyl] was used as hole-blocking layer to block holes in the **HOXD** layer, and Alq₃ [tris (8-quinolinolato) aluminum] for electron-transporting layer. Bright blue electroluminescence was observed under normal day light. As shown in Fig. 4, its electroluminescence (EL) spectrum shows a main peak at 451 and two shoulders at 480 and 516 nm, almost similar to the phosphorescence spectra at 77 K and at room temperature except the main peak at 451 nm, implying that the electroluminescence emission may be originated from the triplet state of the enol-form¹⁶ and/or the singlet state of the keto-form of **HOXD** after undergoing an ESIPT. Figure 5 shows typical luminance-voltage (*L-V*) and *I-V* curves. The maximum brightness of the EL devices is about 656 cd/m² at a driving voltage of 25 V. The turn on voltage is 7 V. The current efficiency of 0.44 cd/A and the luminous efficiency of 0.14 lm/W were gained.

In conclusion, we have designed and synthesized an organic light-emitting material exhibiting excited-state intramolecular proton transfer—2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole (**HOXD**), and found its unusual luminescent properties in both solution and the solid state. The intense blue phosphorescence emission is observed in the solid state at room temperature and at 77 K. Its electrolu-

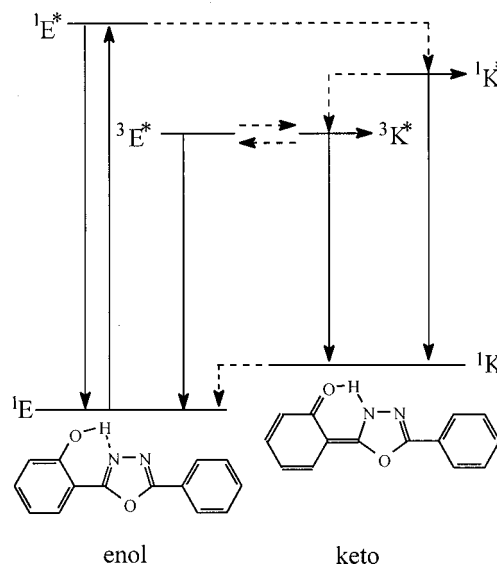


FIG. 3. Schematic energy diagram of **HOXD**.

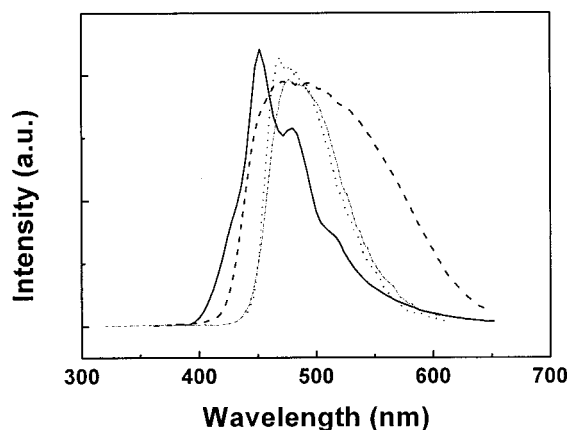


FIG. 4. The phosphorescence (room temperature, dashed line; 77 K, dotted line), the photoluminescence (dash dotted line), and electroluminescence (solid line) spectra.

miniscence emission may originate from the triplet state of the enol-form and/or the singlet state of the keto-form of **HOXD** after undergoing an ESIPT, with the maximum brightness of 656 cd/m^2 and the luminous efficiency of 0.14

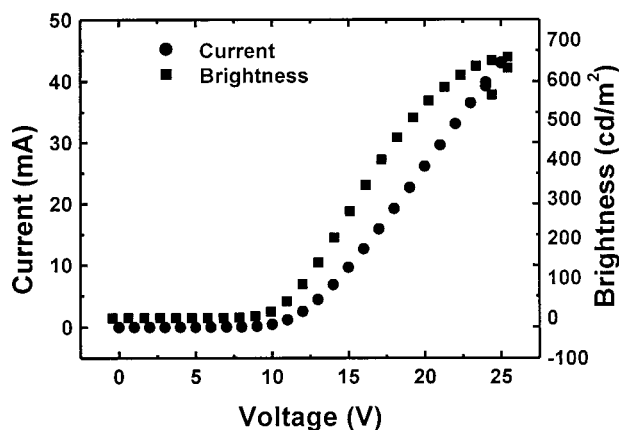


FIG. 5. The $V-I$ and $V-L$ characteristics of a device with structure of ITO/NPB/**HOXD**/BCP/Alq₃/Mg:Ag.

lm/W. This molecular system appears to be representative for developing the organic light-emitting materials for the phosphorescence emission.

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