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# Observation of red intraligand electrophosphorescence from a stilbene-containing Re(I) complex

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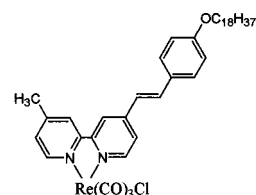
Red organic light-emitting diodes using a rhenium(I) bipyridyl complex, *fac*-[ClRe(CO)<sub>3</sub>(*trans*-4-methyl-4'-((2-4-octadecyloxyphenyl)vinyl)-2,2'-bipyridine)] (Re-mopvb), as an emitter were fabricated. The optimized device has a bilayer structure of indium-tin oxide/poly(*N*-vinylcarbazole): 2 wt. % Re-mopvb (80 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (50 nm)/LiF (1 nm)/Al (150 nm). Although no photoluminescence from Re-mopvb in the room-temperature solution appeared due to photoinduced isomerization, a bright red electrophosphorescence from an intraligand excited state of Re-mopvb was observed at room temperature, indicating the promising future of such a class of electroluminescent materials. The maximum luminance exceeding 120 cd/m<sup>2</sup> at 11 V and maximum efficiency of 0.75 cd/A at 7.5 V were obtained. © 2004 American Institute of Physics. [DOI: 10.1063/1.1818727]

Employment of transition metal complexes as emitters in organic light-emitting diodes (OLEDs) has become one of the most important subjects in the last few years,<sup>1–12</sup> since many of them have excellent photoluminescence (PL) properties and potential advantages of achieving maximum internal quantum efficiency up to 100%.<sup>1</sup> Highly efficient OLEDs based on the Ir complexes<sup>1</sup> and Pt complexes<sup>6</sup> have been extensively studied. In addition, recent research results indicate that Re(I) complexes can also serve as a class of electrophosphorescent materials,<sup>7–12</sup> because they feature high room-temperature (RT) phosphorescence quantum yield, relatively short excited state lifetime, and excellent thermal stability.<sup>13</sup> Most of these studies are focusing on the typical metal-to-ligand charge transfer (MLCT) emission of the tricarbonyl(diimine) rhenium(I) complexes.<sup>7–12</sup> However, the electroluminescent (EL) properties of the intraligand (IL) triplet excited state of the Re(I) complexes containing the stilbene, stilbazoles, or related olefin moieties, have not been reported. This could be attributed to efficient photoinduced isomerization in RT solutions upon photoexcitation, leading to nonemissive behavior. Comparing with the ligands, although the introduction of the heavy metal Re enhances the radiative relaxation of the triplets, the photophosphorescence from these kinds of Re(I) complexes can be observed only in low-temperature glass.<sup>14–16</sup> Because the EL mechanism is generally consistent with that of PL, people usually select highly efficient PL materials as emissive centers in OLEDs, and a number of highly efficient OLEDs based on the highly efficient PL materials have been obtained. Nevertheless, there are exceptional cases in which dominant mechanisms during electric and optical processes are different. It makes possible that some compounds without PL emission in the given conditions may also exhibit EL behavior. However, there are no reports on the usage of such compounds as emissive centers in OLEDs. Herein, we report a bright red EL device based on a stilbene-containing Re(I) complex which shows no photophosphorescence in a RT solution. It implies

that the EL can also be obtained from some non-PL materials at RT. Our finding is helpful to exploit some types of EL materials and understand the EL mechanism deeply.

Re-mopvb, which contains stilbene moiety, was selected in this study and prepared according to a literature procedure.<sup>16</sup> The chemical structure is depicted in Fig. 1. The introduction of a long hydrocarbon chain into the complex improves the solubility of Re-mopvb in the poly(*N*-vinylcarbazole) (PVK)-containing organic solvent, i.e., chloroform, and the compatibility between the complex and the PVK host, making Re-mopvb homogeneously disperse in the PVK film by spin casting.<sup>17</sup>

As shown in Fig. 2, the electronic absorption spectrum of Re-mopvb in CH<sub>2</sub>Cl<sub>2</sub> at RT exhibits a high-energy band centered around 297 nm and a low-energy absorption band centered at 367 nm with a shoulder centered at 400 nm. The high-energy absorption band is tentatively ascribed to a  $\pi$



Re-mopvb

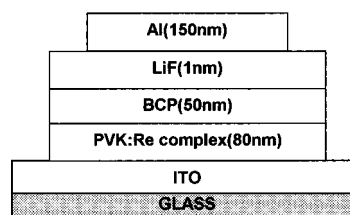


FIG. 1. Chemical structure of Re-mopvb and device configuration.

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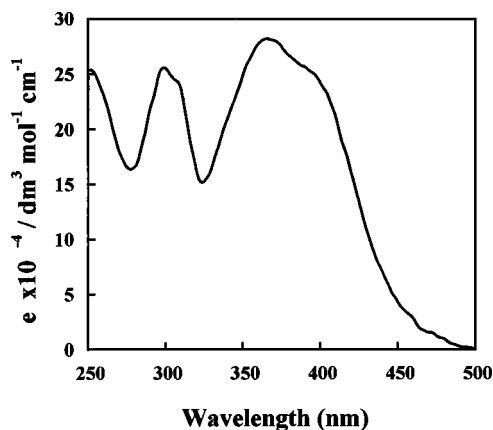


FIG. 2. The absorption spectrum of Re-mopvb in  $\text{CH}_2\text{Cl}_2$  solution.

$\rightarrow \pi^*$  IL transition of mopvb, and the low-energy absorption band is assigned to the  $d\pi(\text{Re}) \rightarrow \pi^*$  (mopvb) MLCT transition.<sup>16,18</sup> However, the extinction coefficient of the low-energy absorption band in the order of  $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  is much larger than those for typical MLCT transitions ( $\sim 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), so the low-energy absorption band of Re-mopvb is accordingly assigned as an admixture of the  $d\pi(\text{Re}) \rightarrow \pi^*$  (mopvb) MLCT transition and  $\pi \rightarrow \pi^*$  IL transition of ligand mopvb.

Re-mopvb was found to be nonemissive in degassed dichloromethane solution at RT upon irradiation at different wavelength but emissive in frozen glass at  $\lambda > 330 \text{ nm}$  due to efficient *trans-cis* isomerization process in RT solution.<sup>16,19</sup> The emission spectrum of Re-mopvb in EtOH/MeOH (4:1 v/v) glass at 77 K showed vibronic structures with vibrational progression spacings of  $\sim 1260 \text{ cm}^{-1}$  (Fig. 3), typical of the ring C—H deformation vibrations in the ground state. Therefore, the emission of Re-mopvb in 77 K was assigned to the  $^3\text{IL}$  excited state. It was proposed that the presence of an efficient photosensitization pathway, i.e., intramolecular energy transfer from the  $^3\text{MLCT}$  state to the  $^3\text{IL}$ , should be responsible for such an observation.

The EL properties of Re-mopvb were studied using bilayer structure of indium-tin oxide/PVK:  $x \text{ wt. \%}$  Re-mopvb (80 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline [(BCP) 50 nm]/LiF (0.5 nm)/Al (150 nm) shown in Fig. 1. The PVK film-doped Re-mopvb acted as the light-emitting layer. PVK has the advantages of excellent film-forming

properties and compatibility, and also guarantees the sufficient dispersion of metal complexes to avoid “concentration quenching”. BCP is the hole-blocking and electron-transporting layer that confines charge recombination zone within the doped PVK layer. The BCP and electrode layers LiF/Al were deposited on the PVK film in a chamber under  $10^{-4} \text{ Pa}$  during one pump down.

It was found that the doping concentration of Re-mopvb in PVK significantly affected the EL performance, such as emission spectra, and charge injection. The optimization of the doping concentration was first carried out. When the concentration of Re-mopvb was higher than 4 wt. %, maybe due to aggregation or serious triplet-triplet annihilation of Re-mopvb,<sup>9</sup> merely very low luminance was observed. 1 wt. % concentration of Re-mopvb resulted in a purplish-blue fluorescence peak at around 420 nm, which came from the PVK host. The 2 wt. % Re-mopvb-doped PVK device was optimal, which exhibited the best EL performance. The corresponding EL spectrum at RT shown in Fig. 3 is similar to that of the PL in 77 K glasses. This demonstrated that the EL emission originated from a  $^3\text{IL}$  excited state of Re-mopvb in the doped layer, and the isomerization of Re-mopvb did not occur in solid film upon electric excitation.

The bandwidth of EL spectrum of Re-mopvb at RT was broader than that of PL in 77 K glasses, which could be attributed to both the temperature-induced homogeneous broadening of the charge transfer states and inhomogeneous effects of the highly amorphous film.

Why can non-PL Re-mopvb in a solution display EL behavior at RT? It is mainly due to different excitation mechanisms. For PL, excitation energy originated from photon absorption—of which irradiation changed the chemical structure of Re-mopvb—resulting in the nonemissive behavior. But the energy of the EL excitation originated from excitons, upon which the excitation of the chemical structure of Re-mopvb was retained. In addition, the PVK matrix limited the isomerization and the triplet-triplet annihilation. It was believed that the PVK matrix was helpful to restrain the rotation around the double ethylenic bond,<sup>19</sup> hindering the isomerization of Re-mopvb to a certain extent. However, the PL emission of 2 wt % Re-mopvb-doped PVK at RT was very weak. As shown in Fig. 3. This phenomenon can be explained as follows: The dominant purplish-blue emission from PVK suggested that energy transfer from the PVK host to Re-mopvb was inefficient in the PL case, while direct charge recombination on Re-mopvb sites gave rise to bright red emission in the EL case. Another possible reason could be the oxygen-induced quenching effect of the phosphorescence that remarkably decreases PL intensity.<sup>20</sup> However in EL case, the sealed Re-mopvb may effectively prevent quenching effect, bringing in a relatively strong emission.

Figure 4 shows the current density–brightness–voltage characteristics of a 2 wt % Re-mopvb-doped PVK device. Red EL emission of Re-mopvb under 7 V bias was observed, and a maximum brightness of  $121 \text{ cd/cm}^2$  at 11 V and maximum efficiency of  $0.75 \text{ cd/A}$  at 7.5 V were achieved.

Shown in the inset of Fig. 4 is the effect of doping concentration on the current–voltage ( $I$ – $V$ ) characteristics of the EL devices. Generally, PVK and BCP films function as efficient charge-blocking layers for electrons and holes, respectively. By increasing the doping concentration of Re-mopvb from 1 to 4 wt %, the current density monotonously increased at same driving voltage, indicating that the dopant

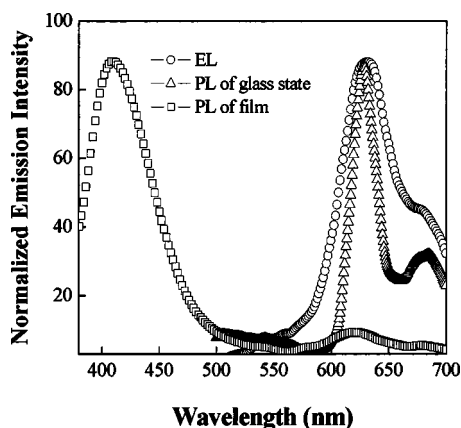


FIG. 3. EL spectra (○); PL spectra of Re-mopvb in glass state (△) and 2 wt % Re-mopvb:PVK blend films (□). Excitation at 330 nm.

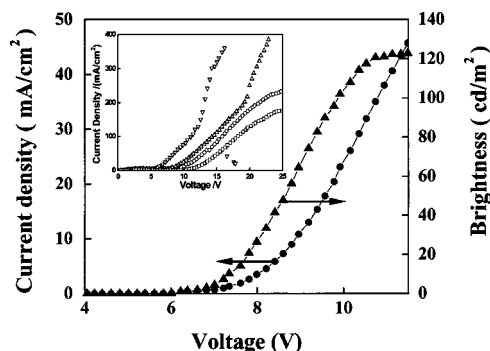


FIG. 4. Current density–brightness–voltage characteristics of a Re-mopvb-doped PVK device. Inset:  $I$ – $V$  curves for different doping concentration of 1% (rectangle), 2% (circle), 3% (up triangle), and 4% (down triangle).

helped the electron injection and transporting in the PVK layer. On the other hand, the lowest unoccupied molecular orbital level of PVK and Re-mopvd was determined to be  $-2.3$  eV and  $-2.9$  eV with respect to the vacuum level, suggesting that our postulation was reasonable. Therefore, direct charge recombination on Re-mopvd sites may dominate in the EL devices, especially in the case of high doping concentration, while the contribution of host-to-guest energy transfer was minor.

In summary, we obtained red electrophosphorescence from a stilbene-containing Re(I) complex at RT, from which bright photophosphorescence can only be observed in 77 K glass. It implies that some materials with poor PL efficiency at the given conditions can also produce good EL performance due to the essential differences between PL and EL excitation models. Our study helps to further an understanding of the EL mechanism. It opens a door to obtain EL materials.

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