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Light-emitting multifunctional rhenium (I) and ruthenium (II) 2,2'-bipyridyl complexes with bipolar character

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A series of multifunctional molecules consisting of hole transport, electron transport, and light-emitting moieties were synthesized and fabricated into single-layer organic light-emitting devices. The light-emitting units were based on 2,2'-bipyridine complexes of rhenium and ruthenium. It was found that, due to the bipolar character of the molecules, the charge carrier mobilities, charge injection barrier, and the device performance were improved. The electron carrier mobilities are on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a maximum luminescence of 730 cd/m^2 was observed. © 1999 American Institute of Physics. [S0003-6951(99)04251-5]

The use of transition-metal complexes in inorganic photochemistry has grown rapidly since the 1950s because of both fundamental and practical interests. Tris(2,2'-bipyridine) ruthenium (II) $[\text{Ru}(\text{bpy})_3]^{2+}$ and its derivatives are among the most studied luminescent transition-metal complexes.¹ The complexes are chemically stable with unique redox properties and excited-state activities. The excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ were found to be metal-to-ligand charge transfer (MLCT) in nature. They are promising candidates for photosensitizers, emission sensitizers, and photocatalysts for solar-energy conversion. The excited-state properties such as emission energy, lifetime, and quantum yield can be adjusted by changing the nature of the ligands.

In the development of organic light-emitting diodes for display applications, different types of molecular and polymeric materials have been studied and good progress has been made in the last few years.² However, relatively little attention was paid to transition-metal complexes compared to complexes of main group elements such as tris(8-hydroxyquinoline) (Alq_3). There are several reports on using ruthenium,³ zinc,⁴ and osmium⁵ complexes for electroluminescence (EL) applications. Our research effort has been focused on the design and synthesis of molecular and polymer metal complexes for optoelectronic applications.⁶ Recently, Choong *et al.* reported the fabrication of a light-emitting diode consisting of a bipolar transport layer based on a mixture of Alq_3 and N,N' -diphenyl- N,N' -bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB).⁷ The device performance was improved. In our previous report, we synthesized two trifunctional light-emitting molecules in which the hole carrier, electron carrier, and light-emitting unit are incorporated in one single molecule.⁸ The light-emitting functional groups were based on the ruthenium (II) or rhenium (I) bipyridine complexes. The resulting molecules exhibited bipolar character and improved EL performance. Their electronic absorption and emission behaviors were manifested by the metal complexes. In addition, the luminescence originates from the MLCT triplet excited states. The triplet excitons resulting from charge recombination can be utilized and the quantum

efficiency of the light-emission process could possibly exceed the intrinsic quantum efficiency (25%) by singlet excitons.⁹ Here, we report the charge-transport and light-emitting properties of some derivatives of these multifunctional molecules. It was found that both the metal complex and the structure of the ligands could affect the optoelectronic properties.

The structures of the ligands are shown in Fig. 1. Four ligands which are either symmetrically (1a and 2a) or asymmetrically functionalized (1b and 2b) based on 2,2'-bipyridine-5,5'-diyl were synthesized. Ligands 1a and 1b are trifunctional ligands which contain both triphenylamine (TPA) and aromatic 1,3,4-oxadiazole (OXA) moieties. Ligands 2a and 2b were only functionalized with the OXA unit so that the function of TPA in the charge-transport process could be investigated. The rhenium and ruthenium complexes were synthesized by direct complexation of the

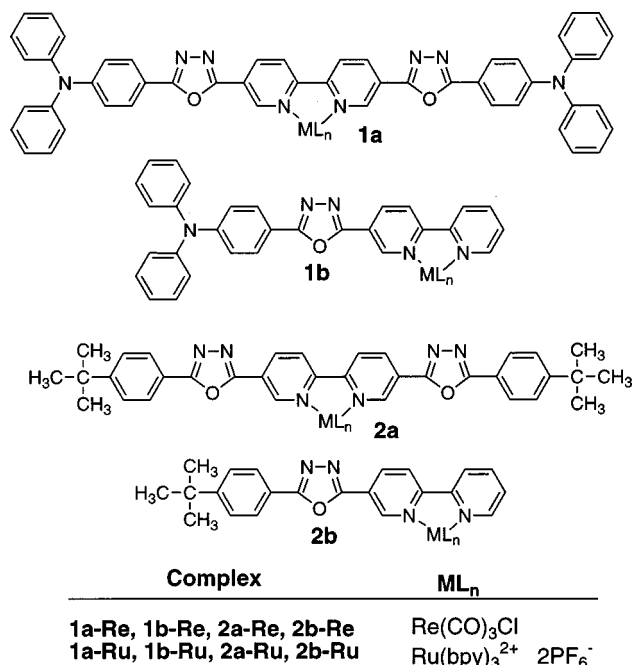


FIG. 1. Chemical structures of the multifunctional light-emitting metal complexes.

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TABLE I. Physical properties and device performance of the light emitting multifunctional rhenium and ruthenium complexes.

Complex	HOMO (eV) ^a	LUMO (eV) ^a	$\lambda_{\text{max,EL}}$ (nm)	V_{on} (V)	η_{ext} (%)	Max. luminance (cd/m ²)	μ_h (10 ⁻⁴ cm ² /V s) ^b	μ_e (10 ⁻⁴ cm ² /V s) ^b
1a-Re	-5.63	-3.53	678	4	0.1	730	4.1	7.1
1a-Ru	-5.53	-3.57	665	5	0.1	650	3.4	5.8
1b-Re	-5.57	-3.28	665	6	0.08	350	2.9	6.1
1b-Ru	-5.70	-3.26	700	5	0.07	130	2.6	4.6
2a-Re	-5.88	-3.55	674	6	0.06	175	3.2	5.8
2a-Ru	-5.78	-3.43	710	5	0.04	160	2.5	4.2
2b-Re	-5.84	-3.31	680	6	0.05	180	2.8	4.9
2b-Ru	-5.73	-3.37	720	7	0.03	190	2.3	3.6

^aEstimated from the electrochemical method.^bUnder an externally applied electric field $E=40$ kV/cm.

corresponding ligands with $\text{Re}(\text{CO})_5\text{Cl}$ and $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (bpy=2,2'-bipyridine), respectively. The synthetic procedures will be published elsewhere.¹⁰

Electronic absorption spectra of the complexes showed an absorption band at the vicinity of 440–480 nm, which is the characteristic absorption due to the MLCT transitions [$d\pi(\text{Re or Ru}) \rightarrow \pi^*(\text{di-imine})$]. The MLCT transition bands for the symmetric complexes (1a-Re/Ru and 2a-Re/Ru) complexes shifted to lower energy compared to those of the asymmetric ones (1b-Re/Ru and 2b-Re/Ru) owing to the longer conjugation length. Therefore, it is possible to tune the band gap and the emission energy by simply changing the conjugation length and substituents on the ligands.

The complexes were doped into different polymer hosts for physical measurements. Polycarbonate (PC) and poly(vinyl alcohol) (PVOH) were chosen as the hosts for the rhenium and ruthenium complexes, respectively, because of the good compatibility between the complexes and hosts. The concentration of the metal complexes in polymer hosts can be as high as 40 wt.% without phase separation. Optical quality films for physical characterizations were prepared by either casting or by spin coating the polymer solution on an indium–tin–oxide (ITO) -coated glass slide.

The charge-carrier mobilities reveal how fast the charges (holes and electrons) transport in the materials, which is an important factor to be considered in the design of light-emitting materials. The drift mobilities of the charge carriers were determined by the time-of-flight experiment using a nitrogen laser ($\lambda = 337.1$ nm; pulse energy = 120 μJ ; pulse width = 3 ns) as the excitation source.¹¹ The carrier mobilities of these complexes are of the order of 10^{-4} cm²V⁻¹s⁻¹ (Table I), and are both electric field and temperature dependent. These values are significantly higher than some polymer films doped with OXA or TPA derivatives.¹² It was found that the electron carrier mobilities of the complexes are generally higher than those of the hole carriers. In addition, those complexes based on ruthenium or with symmetrical ligands also exhibit higher charge-carrier mobilities. From these results, it indicates that both the nature of the metal center and the structure of the ligand can affect the charge-transport properties. Figure 2 shows the plot of field-dependent electron carrier mobilities for different complexes. As the electric field was increased, the carrier mobility decreased. This phenomenon was explained by the presence of off-diagonal disorder in the complexes.¹³ Owing to the fluctuation of the overlap between different hopping

sites, the charge may take indirect paths that contain steps against the direction of the applied field.

The metal complexes were doped into polymer hosts and fabricated into a single-layered device ITO/metal complex: polymer host/Al. A forward bias was applied to the device with the ITO electrode being positive and the Al electrode being negative. The current–luminance–voltage characteristic of the device ITO/1a-Re/Al is shown in Fig. 3. The device exhibits a low turn-on voltage at approximately 4 V. The light emission also follows the current closely, indicating an equally efficient charge injection and transport process for both electrons and holes. The charge injection process can be examined further by studying the energy levels of the devices. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the complexes were estimated by an electrochemical method (Table I). From this simplified model, the symmetrically functionalized complexes (1a-Re/Ru and 2a-Re/Ru) exhibit a lower LUMO energy level, and hence, a lower electron injection barrier. This is probably due to the presence of two electron withdrawing OXA units in the ligand. In addition, both complexes 1a-Re and 2a-Re exhibit a similar electron injection barrier (~ 0.66 eV), but the hole injection barrier for 2a-Re is 0.25 eV higher, indicating that removal of

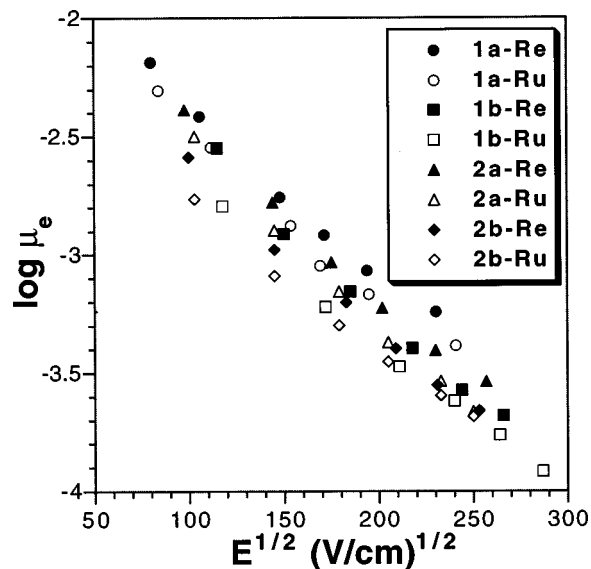


FIG. 2. Plot of electron carrier mobilities as a function of applied electric field for different metal complexes at $T=298$ K.

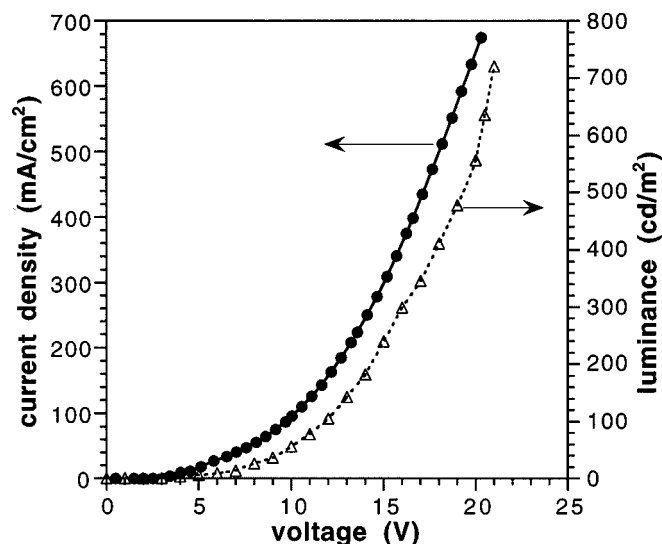


FIG. 3. Plot of current–voltage and intensity–voltage characteristics for the device ITO/1a-Re:PC/ITO.

the electron-rich TPA units results in a higher hole injection barrier.

Figure 4 shows the EL spectra of the devices fabricated from the rhenium complexes. They all exhibit similar emis-

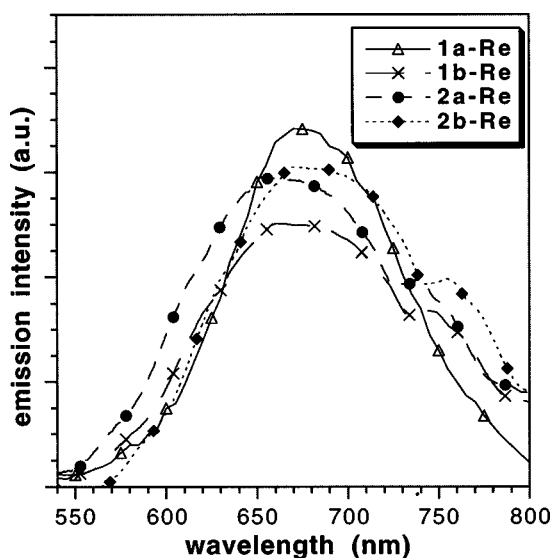


FIG. 4. Electroluminescence spectra of different single-layer devices based on the rhenium complexes.

sion bands centered at ~ 670 nm regardless of the structure of the ligand. These emission bands originate from the MLCT states $\pi^*(\text{bpy}) \rightarrow d\pi$ (Re or Ru) resulting from the recombination of holes and electrons along the conjugated systems. The ruthenium complexes exhibit similar emission properties. It was found that devices fabricated from 1a-Re and 1a-Ru demonstrated the best performance among all the complexes (Table I), indicating that the bipolar character of the ligand is important to the EL performance. The maximum luminance of devices ITO/1a-Re:PC/Al and ITO/1a-Ru:PVOH/Al were 730 and 650 cd/m^2 , respectively. The external quantum efficiencies of the devices were estimated to be 0.1%.

In conclusion, different multifunctional complexes based on rhenium and ruthenium were fabricated into light-emitting devices. It was found that those bipolar metal complexes could facilitate both the charge injection and transport processes and exhibited better device performance. The electronic properties of the complexes can be tuned by modifying the structure of the corresponding ligand.

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