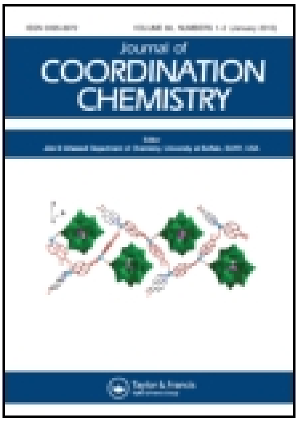

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Syntheses and photoluminescence properties of rhenium(I) complexes based on dipyrido[3,2-a:2′,3′-c]phenazine derivatives with carbazole moiety

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Syntheses and photoluminescence properties of rhenium(I) complexes based on dipyrido[3,2-a:2′,3′-c]phenazine derivatives with carbazole moiety

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Four rhenium(I) complexes **ReL1**–**ReL4** based on dipyrido[3,2-a:2′,3′-c]phenazine (**L1**) and derivatives **L2**-**L4** ligands (**L2**: 10,13-dibromodipyrido[3,2-a:2′,3′-c]phenazine, **L3**: 10-bromo-13-carbazolyl-dipyrido[3,2-a:2′,3′-c]phenazine, **L4**: 10,13-dicarbazolyldipyrido[3,2-a:2′,3′-c]phenazine) were synthesized and characterized. The Re(I) complexes **ReL1**–**ReL4** show photoluminescent emissions at 556, 582, 637 and 662 nm, respectively, assigned to dπ (Re)→π^* (diimine) MLCT phosphorescence in CH_2Cl_2 solution. The carbazole containing complexes **ReL3** and **ReL4**, as compared to **ReL1**, exhibit higher luminescence. These observations imply that modification of diimine rhenium(I) carbonyl complexes with carbazole moiety would lead to efficient phosphorescent properties.

Keywords: Rhenium(I) complex; Dipyrido[3,2-a:2′,3′-c]phenazine; Carbazole; Phosphorescence emission

1. Introduction

Organic light emitting diodes (OLEDs) based on transition metal complexes [1–5] have received considerable attention for high-emission quantum efficiency and rich excited-state behavior. Rhenium complexes [6–11] often exhibit extraordinary luminescent properties and play an important role in the photophysics and photochemistry of transition metal complexes. In particular, the rhenium(I) tricarbonyl complexes *fac*-$Re(CO)_3(L)X$, where L is a bidentate diimine ligand and X is a halogen, have been studied and applied in various areas such as electroluminescent materials in OLED devices [12], solar energy conversion [13] and photocatalytic CO_2 reduction [14, 15].

However, performances of Re(I) complex-based OLEDs are far from practical application in electroluminescence because of serious triplet–triplet annihilation (TTA) of

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the emitters, caused by saturation of the emissive sites, which leads to low efficiency at high current density [16–18]. Many efforts have been focused on both the ligand structure and rigidity of the complexes to tune the excited state properties. Basically, there are two strategies to overcome the above mentioned shortcoming: (i) through the synthesis of novel diimine ligands with different ligand-field (molecular design) [19–21] that would modify the molecular orbital energy levels in the Re(I) complexes and (ii) by addition of functional groups with electron-accepting or -donating properties into the diimine ligands [22–26] in order to avoid the TTA by steric hindrance effect. Accordingly, we synthesized and reported Re(I) complexes with carbazole and oxadiazole moieties showing enhanced luminescence properties [10, 27].

With consideration of these reasons, we synthesized the dipyrido[3,2-a:2′,3′-c]phenazine (**L1**) and derivatives (**L2**: 10,13-dibromodipyrido[3,2-a:2′,3′-c]phenazine, **L3**: 10-bromo-13-carbazolyl-dipyrido[3,2-a:2′,3′-c]phenazine, **L4**: 10,13-dicarbazolyl-dipyrido[3,2-a:2′,3′-c]phenazine) and their corresponding Re(I) complexes **ReL1**–**ReL4**. The appended carbazole moieties widen the absorption profile and act as light-harvesting units, improving the hole-transporting ability and luminescence, preventing crystallization of complexes and increasing the solubility in common organic solvents. All the complexes show good phosphorescent emission.

2. Experimental

2.1. *Materials and measurements*

Rhenium pentacarbonyl chloride and 1,3-dimethyl-3,4,5,6-terahydro-2(1H)-pyrimidinone (DMPU) were bought from Alfa Aesar Co. (China). Carbazole, CuI, 18-Crown-6 and K_2CO_3 were purchased from Yuan Hang Reagent Co. (China). All were used as received. The solvents except toluene were used without purification.

IR spectra were taken on a Vector22 Bruker spectrophotometer (400–4000 cm^{-1}) with KBr pellets. ^{1}H NMR spectra were measured on a Bruker AM 500 spectrometer. Elemental analyzes for C, H, and N were performed on an Elementar Vario MICRO analyzer. Absorption and emission spectra were measured on a UV-3100 spectrophotometer and a Hitachi F4600 luminescence spectrophotometer, respectively. Photoluminescence lifetimes were measured with an Edinburgh Instruments FLS920P fluorescence spectrometer. Luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (air-equilibrated and degassed acetonitrile solution of $[Ru(bpy)_3]^{2+}\cdot 2Cl^-$) and the unknown sample according to the equation [28]:

$$\Phi_{unk} = \Phi_{std}\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2$$

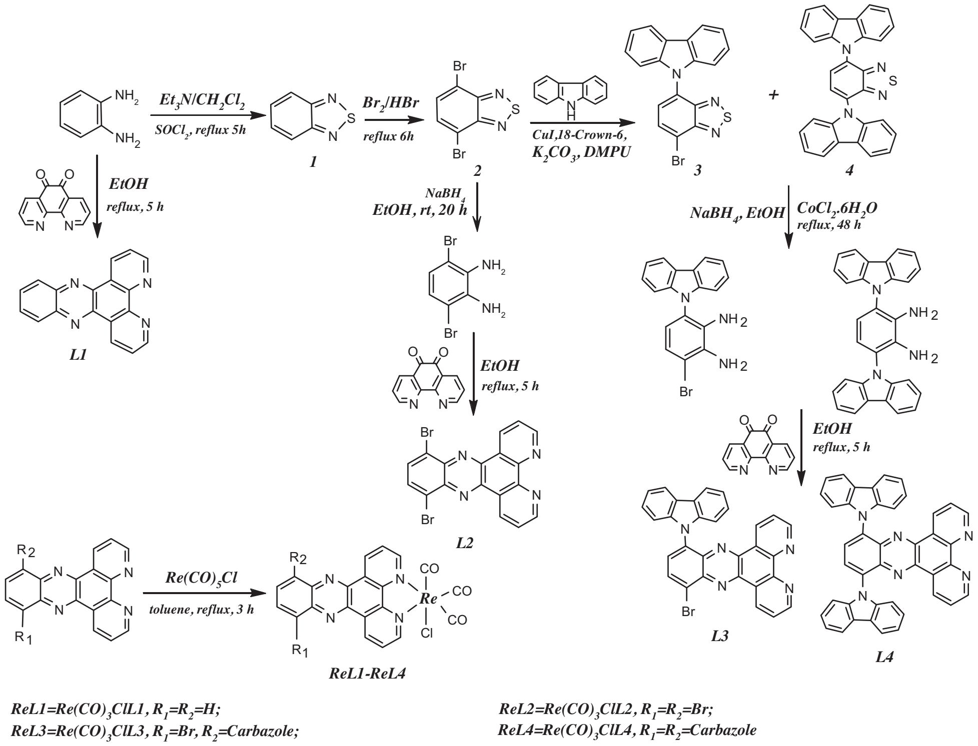
where, Φ_{unk} and Φ_{std} are the luminescence quantum yields of the unknown sample and air-equilibrated acetonitrile solution of $[Ru(bpy)_3]^{2+}\cdot 2Cl^-$, respectively. I_{unk} and I_{std} are the integrated emission intensities of the unknown sample and $[Ru(bpy)_3]^{2+}\cdot 2Cl^-$ solution, respectively. The A_{unk} and A_{std} are the absorbance of the unknown sample and $[Ru(bpy)_3]^{2+}\cdot 2Cl^-$ acetonitrile solution at their excitation wavelengths ($A < 0.1$), respectively. The η_{unk} and η_{std} terms represent the refractive indices of the corresponding solvents (pure solvents were assumed). The Φ_{std} of air-equilibrated and degassed acetonitrile solution of $[Ru(bpy)_3]^{2+}\cdot 2Cl^-$ are 0.018 and 0.094, respectively.

2.2. *Syntheses*

The chemical structures of the materials used in this work and the synthetic routes are depicted in scheme 1. 2,1,3-Benzothiadiazole (**1**), its derivatives (**2**–**4**), 1,10-phenanthroline-5,6-dione, **L1**–**L4** and their corresponding Re(I) complexes were synthesized according to the published literature (figures S1–S12) [29–31].

2.2.1. Synthesis of 10-bromo-13-carbazolyl-dipyrido[3,2-a:2′,3′-c]phenazine (L3) and 10,13-dicarbazolyl-dipyrido[3,2-a:2′,3′-c]phenazine (L4). The solution of precursor **3** or **4** (0.56 mmol), $NaBH_4$ (11.2 mmol) and $CoCl_2 \cdot 6H_2O$ (5.6×10^{-3} mmol) in 30 mL of ethanol was stirred with exclusion of light for 48 h at 70 °C. After cooling, 2.8 mmol 1,10-phenanthroline-5,6-dione in 10 mL ethanol and 5 mL hartshorn were added and the solution was refluxed for 8 h. The solvent was removed under vacuum; the crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (v/v = 1 : 3) as eluant to obtain **L3** and **L4**.

L3: yield: 24%, M.p.: >300 °C. IR (KBr, cm^{-1}): 3010, 1641, 1450, 1081, 802, 738. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 9.622 (d, $J = 9.0$ Hz, 1H), 9.220 (d, $J = 4.0$ Hz, 1H), 9.055 (d, $J = 4.0$ Hz, 1H), 8.492 (d, $J = 9.0$ Hz, 1H), 8.405 (d, $J = 8.5$ Hz, 1H), 8.235 (d, $J = 8.5$ Hz, 2H), 8.154 (d, $J = 7.0$ Hz, 1H), 8.103 (t, $J = 7.5$, 1H), 7.772–7.746 (m, 1H), 7.362–7.333 (m, 2H), 7.307–7.280 (m, 2H). MS matrix-assisted laser desorption/ionization



Scheme 1. The syntheses for **1**–**4**, **L1**–**L4** and **ReL1**–**ReL4**.

time of flight (MALDI-TOF): m/z 526.455 $[M]^+$. Anal. Calcd for $C_{30}H_{16}N_5Br$ (%): C, 68.45; H, 3.06; N, 13.31. Found: C, 67.93; H, 3.64; N, 13.72.

L4: yield: 26%, M.p.: >300 °C. IR (KBr, cm^{-1}): 3047, 1595, 1497, 1448, 1227, 1085, 747. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 9.195 (d, $J = 2.0$ Hz, 2H), 8.554 (d, $J = 4.0$ Hz, 2H), 8.451 (t, $J = 1.0$, 2H), 8.352–8.331 (m, 4H), 7.515–7.491 (m, 2H), 7.438–7.414 (m, 8H), 7.370–7.349 (m, 4H). MS (MALDI-TOF): m/z 613.434 $[M + 1]^+$. Anal. Calcd for $C_{42}H_{24}N_6$ (%): C, 82.33; H, 3.97; N, 13.72. Found: C, 82.17; H, 4.05; N, 13.61.

2.2.2. General synthesis of ReL1–ReL4. $Re(CO)_5Cl$ (0.035 g, 0.10 mmol) was refluxed with equimolar quantities of **L1**–**L4**, respectively, in 30 mL toluene for 6 h under nitrogen. After the mixture was cooled, the crude product was filtered and purified by column chromatography on silica gel using ethyl acetate and petroleum ether (v/v = 1 : 2, together with a small amount of triethylamine) as eluant to give the corresponding Re(I) complexes **ReL1**–**ReL4**.

ReL1 (yield: 71%): IR (KBr, cm^{-1}): 2018, 1920, 1902, 1884, 1489, 1416, 1358, 1077, 822, 771, 727, 471. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 9.897 (dd, 2H), 9.492 (dd, 2H), 8.483 (m, 2H), 8.094 (m, 2H), 8.051 (m, 2H). MS (MALDI-TOF): m/z. 553.238 $[M–Cl]^+$. Anal. Calcd. for $C_{21}H_{10}N_4O_3ClRe$ (%): C, 42.90; H, 1.71; N, 9.53. Found: C, 43.08; H, 1.65; N, 9.42.

ReL2 (yield: 75%): IR (KBr, cm^{-1}): 2024, 1920, 1889, 1641, 1485, 1099, 824, 730, 477. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 9.943 (dd, 2H), 9.537 (dd, 2H), 8.284 (s, 2H), 8.106 (m, 2H). MS (MALDI-TOF): m/z. 711.086 $[M–Cl]^+$. Anal. Calcd for $C_{21}H_8N_4O_3ClRe$ (%): C, 33.82; H, 1.08; N, 7.51. Found: C, 33.67; H, 1.53; N, 7.42.

ReL3 (yield: 69%): IR (KBr, cm^{-1}): 2020, 1890, 1640, 1448, 1260, 1091, 800, 472. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 9.910 (d, $J = 6.5$ Hz, 1H), 9.498 (d, $J = 5.5$ Hz, 1H), 9.320 (d, $J = 7.0$ Hz, 1H), 9.645 (d, $J = 9.5$ Hz, 2H), 8.351 (d, $J = 8.5$ Hz, 1H), 8.304 (t, $J = 8.0$ Hz, $J = 5.0$ Hz, 2H), 8.080–8.054 (m, 1H), 7.668–7.642 (m, 1H), 7.398–7.315 (m, 4H), 7.710 (d, $J = 7.5$ Hz, 1H), 7.096 (d, $J = 8.5$ Hz, 1H). MS (MALDI-TOF): m/z.718.128 $[M–Br–Cl]^+$. Anal. Calcd for $C_{33}H_{16}N_5O_3ClBrRe$ (%): C, 47.60; H, 1.94; N, 8.41. Found: C, 74.32; H, 2.33; N, 8.66.

ReL4 (yield: 67%): IR (KBr, cm^{-1}): 2020, 1889, 1624, 1496, 1447, 1093, 799, 750, 724, 464. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 3.326 (dd, 2H), 8.675 (dd, 2H), 8.566 (s, 2H), 8.354 (t, $J = 5.0$ Hz, 4H), 7.693–7.666 (m, 2H), 7.453–7.373 (m, 8H), 7.275 (d, $J = 8.0$ Hz, 4H). MS (MALDI-TOF): m/z. 883.158 $[M–Cl]^+$. Anal. Calcd. for $C_{45}H_{24}N_6O_3ClRe$ (%): C, 54.93; H, 2.63; N, 9.15. Found: C, 54.82; H, 2.91; N, 9.02.

3. Results and discussion

3.1. *Synthesis*

Dipyrido[3,2-a:2′,3′-c]phenazine (**L1**) can be synthesized from reaction of *o*-phenylenediamine and 1,10-phenanthroline-5,6-dione in good yield. To synthesize **L2**, it is necessary to prepare 3,6-dibromo-o-phenylenediamine from 4,7-dibromobenzothiadiazole with $NaBH_4$ as a reducing agent first. To prepare **L3** and **L4**, $CoCl_2 \cdot 6H_2O$ is used as the catalyst together with the reducing agent $NaBH_4$ to get the diamine intermediates 3-bromo-6-carbazoly-o-phenylenediamine and 3,6-dicarbazoly-o-phenylenediamine. Because it is difficult to purify the intermediate products, we used the “one pan” method to synthesize **L3** and **L4** where excess 1,10-phenanthroline-5,6-dione was added to the above mixture and the solution was refluxed for 8 h. Probably due to high conjugation by carbazole decreasing the reaction activity, yields for preparation of **L3** and **L4** are not high (around 25%).

3.2. *Optical property*

UV–vis absorption spectra of **L1**–**L4** and **ReL1**–**ReL4** in CH_2Cl_2 solutions with the same concentration ($1 \times 10^{-4}\,mol\,L^{-1}$) are shown in figure 1. Compared with **L1**, absorption of **L2** red shifts with similar shape. For **L3** and **L4**, complicated peaks were observed due to introduction of carbazole moieties. On comparison with the absorption spectra of **L1**, **L2** and the results of our former studies [10, 27], peaks at 258, 290 and 335 nm belong to the π–π^* transition of carbazole. Absorption spectra of the Re(I) complexes exhibit bathochromic shift compared to the corresponding ligands at ca. 220–390 nm with extinction coefficients of $10^4\,mol\,L\,cm^{-1}$, which can be assigned to spin-allowed intraligand ($\pi \rightarrow \pi^*$) transitions. Introduction of carbazole improves the absorption and molar extinction coefficient among these complexes. From previous studies on related rhenium(I) systems [6–27], [32, 33], at low energy bands (>390 nm) there should be metal to ligand charge-transfer $d\pi$ (Re)$\rightarrow\pi^*$ (diimine) (MLCT) absorptions, but in our complexes the MLCT absorptions are very weak.

Figure 2 shows the photoluminescence spectra of the ligands and complexes in CH_2Cl_2 solutions at room temperature. For **L1**, the maximum is 502 nm which is bluish-green color. When the two bromines were introduced, the emission of **L2** red shifts to yellowish-green ($\lambda_{max} = 560$ nm). From the former report [24], the energy of the π^* orbital is lowered by the electron-withdrawing moiety and heightened by introduction of an electron-donating moiety. For **L3** and **L4**, the emissions also red shift to 594 and 617 nm, respectively, due to delocalization of π-electrons in the carbazole ring system through the electron-donating carbazole.

Excited at the $\pi \rightarrow \pi^*$ absorption, **ReL1**–**ReL4** show broad bands centered at ca. 556, 582, 637 and 662 nm (figure 2(b)) assigned to $d\pi(Re) \rightarrow \pi*$ (diimine) MLCT phosphorescence [32], respectively. Heavy metal would provide efficient spin-orbit coupling facilitating intersystem crossing and thereby enhance the orbital crossing in the singlet–triplet forbidden transition [32]. Thus, strong phosphorescence can be observed. Compared with the emission

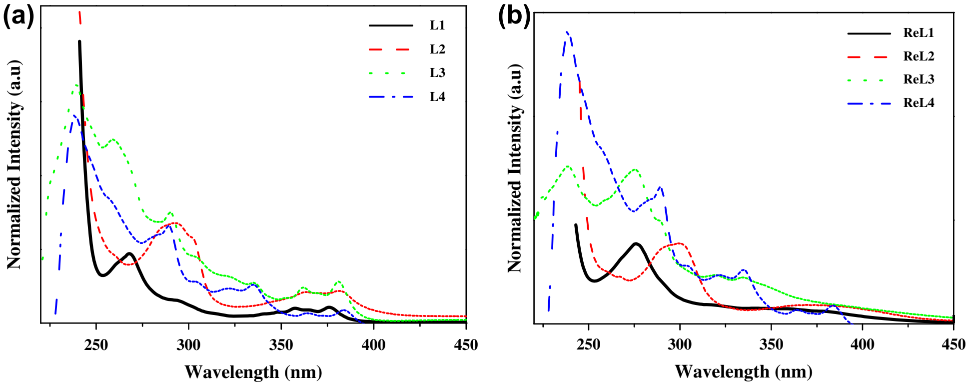


Figure 1. UV–vis absorption spectra of **L1**–**L4** (a) and **ReL1**–**ReL4** (b) in CH_2Cl_2 solution ($1 \times 10^{-4}\,mol\,L^{-1}$) at room temperature.

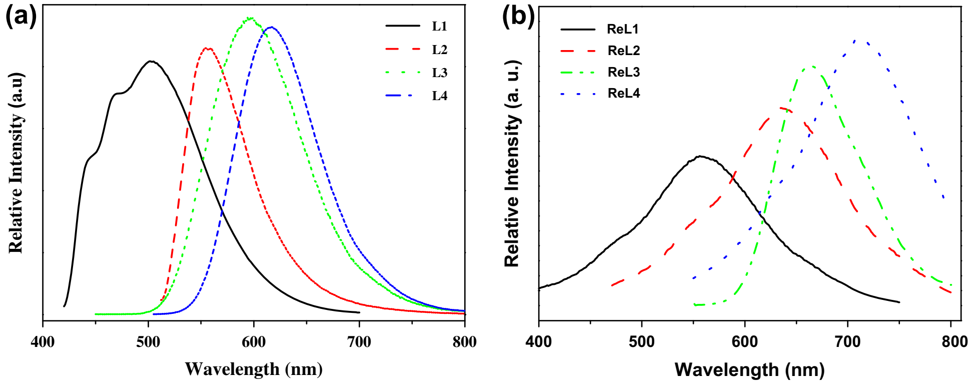


Figure 2. Emission spectra of **L1**–**L4** (a) and **ReL1**–**ReL4** (b) in CH_2Cl_2 solution ($1 \times 10^{-4}\,mol\,L^{-1}$) at room temperature.

bands in **ReL1**, the maximum MLCT emission bands red shift in **ReL2**–**ReL4**, implying that the ligand substituents affect the MLCT emission energies of the complexes. The emissions of **ReL3** and **ReL4** show obvious red shift because of the high conjugation caused by the carbazole.

Intensity of the MLCT emission and the quantum efficiency (Φ) of the corresponding Re(I) complexes are also enhanced after introduction of carbazole, similar to that observed in electronic absorption spectroscopy. Improvement of absorbance and luminescence intensities of the samples by the presence of carbazole is due to the broad and strong absorption bands of carbazole from 220 to 350 nm, in favor of energy absorption and energy transfer from carbazole units to dipyrido[3,2-a:2′,3′-c]phenazine. Similar results were found in similar carbazole containing rhenium and ruthenium complexes [10, 27, 34, 35]. These results confirm that antenna substitutes can increase the light harvesting efficiency of Re(I) complexes. Due to varying ligand field strength caused by the substituents for the present cases, thermally accessible d–d levels could provide a different nonradiative path for disposal of the excitation energy in the Re(I) complexes reported here. This behavior is well known for derivatives of $[Ru(bipy)_3]^{2+}$ in which the ligand-field strength around the metal is reduced by steric distortions [36] and it has recently been demonstrated for a series of Re(I)-tricarbonyl-diimine complexes [37] although a range of other nonradiative decay pathways are in principle available [37, 38]. These observations also imply that modification of some diimine rhenium(I) carbonyl complexes with suitable hole-transporting moieties would lead to better phosphorescence performances. In addition, from quantum efficiency data of the corresponding Re(I) complexes in air-equilibrated and degassed solutions oxygen can decrease the efficiency greatly.

As already reported for Ir(III) complexes, the phosphorescence lifetime is a key factor in TTA in OLEDs operation [39]. The excited state lifetimes (τ) of Re(I) complexes, measured in CH_2Cl_2 solution and solid state at room temperature support the hypothesis of MLCT character of the emitting states. As indicated in figures S13–S16 and table 1, the lifetime decays are monoexponential or two-exponential in the range of sub-microsecond scale. Re(I) carbonyl complexes that show multiexponential decay kinetics are known confirming the existence of two light-emission excited states with comparable energies [32, 39, 40]. By using the equations $\Phi = \Phi_{ISC}\{k_r/(k_r + k_{nr})\}$ and $\tau_p = (k_r + k_{nr})^{-1}$, it is possible to calculate the radiative (k_r) and nonradiative (k_{nr}) decay rates from Φ and τ_1,

Table 1. Absorption and photoluminescence data of **ReL1**–**ReL4** at room temperature.

Compound	Medium	Absorption (λ, nm)	λ, nm[b]	Emission Φ (air/degassed) (%)[c]	Lifetime τ (χ^2)[d], μs	k_r[e] 10^3
ReL1	CH_2Cl_2	276	556	0.11/0.36	1.82 (0.98)	0.60
	Solid	[a]	552	[a]	1.51, 15.69 (0.99)	[a]
ReL2	CH_2Cl_2	299	582	0.17/0.57	1.59, 13.98 (0.99)	1.07
	Solid	[a]	581	[a]	1.52, 13.13 (0.99)	[a]
ReL3	CH_2Cl_2	239, 275	637	0.20/0.68	1.68, 17.74 (0.99)	1.19
	Solid	[a]	633	[a]	2.23 (0.98)	[a]
ReL4	CH_2Cl_2	238, 289, 335, 384	662	0.26/0.84	1.92, 15.52 (0.99)	1.35
	Solid	[a]	673	[a]	1.72, 11.63 (1.00)	[a]

[a] Not measured.

[b] The emission spectra are corrected.

[c] Calculated by $\Phi_s = \Phi_{std}(I_s A_{std} \eta_s^2)/(I_{std} A_s \eta_{std}^2)$ using air-equilibrated ($\Phi_{std} = 1.8\%$ or degassed ($\Phi_{std} = 9.4\%$ $[Ru(bpy)_3]^{2+}$ $2Cl^-$ acetonitrile solution as a standard sample; the error in this method is estimated to be approximately 10% of the measured value.

[d] The lifetime decays were measured in air and in the lifetime analysis, the χ^2 parameter indicates the discrepancy between the observed and the expected values for a certain fitting model. In principle, a $\chi^2 = 1$ is the best-fit for the given data and error bars.

[e] Radiative rate constant calculated from $k_r = \Phi/\tau$, where τ is τ_1.

where the intersystem-crossing yield (Φ_{ISC}) is typically assumed to be unitary (1.0) for metal phosphors with strong heavy-atom effect. All the complexes have quite similar k_{nr} values, while **ReL4** has a k_r higher than those of other complexes.

4. Conclusion

Based on dipyrido[3,2-a:2′,3′-c]phenazine (**L1**), some derivatives (**L2**: 10,13-dibromodipyrido[3,2-a:2′,3′-c]phenazine, **L3**: 10-bromo-13-carbazolyl-dipyrido[3,2a:2′,3′c]phenazine, **L4**: 10,13-dicarbazolyl-dipyrido[3,2-a:2′,3′-c]phenazine) and their corresponding Re(I) complexes **ReL1**–**ReL4** were synthesized. All Re(I) complexes show photoluminescent emissions in CH_2Cl_2 solution assigned to dπ (Re) →π^* (diimine) MLCT phosphorescence. **ReL3** and **ReL4** show higher luminescence intensity than ReL1 and ReL2, due to the carbazole. These observations imply that modification of some of the diimine rhenium(I) carbonyl complexes with carbazole would lead to better phosphorescence. By comparison of our materials with carbazole containing Re(I) complexes with good electroluminescent properties, we believe that due to a better carrier-injection and carrier-transportation balance, they are potential phosphorescence emitters for improvement of OLEDs' performance.

Acknowledgments

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References

[1] Y.J. Su, H.L. Huang, C.L. Li, C.H. Chien, Y.T. Tao, P.T. Chou, S. Datta, R.S. Liu. *Adv. Mater.*, **15**, 884 (2003).

[2] B.W. D'Andrade, S.R. Forrest, A.B. Chwang. *Appl. Phys. Lett.*, **83**, 3858 (2003).

[3] W. Zhu, M. Zhu, Y. Ke, L. Su, M. Yuan, Y. Cao. *Thin Solid Films*, **446**, 128 (2004).

[4] Q.S. Zhang, Q.G. Zhou, Y.X. Cheng, L.X. Wang, D.G. Ma, X.B. Jing, F.S. Wang. *Adv. Mater.*, **16**, 432 (2004).

[5] D.F. Qiu, J. Wu, Z.Y. Xie, Y.X. Cheng, L.X. Wang. *J. Organomet. Chem.*, **694**, 737 (2009).

[6] D.R. Striplin, G.A. Crosby. *Coord. Chem. Rev.*, **211**, 163 (2001).

[7] A. Vogler, H. Kunkely. *Coord. Chem. Rev.*, **200–202**, 991 (2000).

[8] A.S. Polo, M.K. Itokazu, K.M. Frin, A.O.T. Patrocínio, N.Y.M. Iha. *Coord. Chem. Rev.*, **250**, 1669 (2006).

[9] S. Sato, T. Morimoto, O. Ishitani. *Inorg. Chem.*, **46**, 9051 (2007).

[10] H.Y. Li, J. Wu, X.H. Zhou, L.C. Kang, D.P. Li, Y. Sui, Y.H. Zhou, Y.X. Zheng, J.L. Zuo, X.Z. You. *Dalton Trans*., 10563 (2009).

[11] A. Boulay, A. Seridi, C. Zedde, S. Ladeira, C. Picard, L. Maron, E. Benoist. *Eur. J. Inorg. Chem.*, **5058**, (2010).

[12] Y. Li, Y. Liu, J. Guo, F. Wu, W. Tian, B. Li, Y. Wang. *Synth. Met.*, **118**, 175 (2001).

[13] A.S. Polo, M.K. Itokazu, N.Y.M. Iha. *Coord. Chem. Rev.*, **248**, 1343 (2004).

[14] F.P.A. Johnson, M.W. George, F. Hartl, J.J. Turner. *Organometallics*, **15**, 3374 (1996).

[15] F. Cecchet, M. Alebbi, C.A. Bignozzi, F. Paolucci. *Inorg. Chim. Acta*, **359**, 3871 (2006).

[16] V.W.W. Yam, B. Li, Y. Yang, B.W.K. Chu, K.M.C. Wong, K.K. Cheung. *Eur. J. Inorg. Chem.*, **25**, 4035 (2003).

[17] K.Z. Wang, L. Huang, L.H. Gao, L.P. Jin, C.H. Huang. *Inorg. Chem.*, **41**, 3353 (2002).

[18] B. Li, M. Li, Z. Hong, W. Li, T. Yu, H. Wei. *Appl. Phys. Lett.*, **85**, 4786 (2004).

[19] Y. Li, Y. Wang, Y. Zhang, Y. Wu. *Synth. Met.*, **99**, 257 (1999).

[20] F. Li, G. Cheng, Y. Zhao, J. Feng, S. Liu, M. Zhang, Y. Ma, J. Shen. *Appl. Phys. Lett.*, **83**, 4716 (2003).

[21] G. David, P.J. Walsh, K.C. Gordon. *Chem. Phys. Lett.*, **383**, 292 (2004).

[22] C. Fu, M. Li, Z. Su, Z. Hong, W. Li, B. Li. *Appl. Phys. Lett.*, **88**, 093507 (2006).

[23] F. Li, M. Zhang, G. Cheng, J. Feng, Y. Zhao, Y. Ma, S. Liu, J. Shen. *Appl. Phys. Lett.*, **84**, 148 (2004).

[24] X. Gong, P.K. Ng, W.K. Chan. *Adv. Mater.*, **10**, 1337 (1998).

[25] F. Li, M. Zhang, J. Feng, G. Cheng, Z. Wu, Y. Ma, S. Liu. *Appl. Phys. Lett.*, **83**, 365 (2003).

[26] W.K. Chan, P.K. Ng, X. Gong, S. Hou. *Appl. Phys. Lett.*, **75**, 3920 (1999).

[27] J. Wu, H.Y. Li, L.C. Kang, D.P. Li, H.R. Li, X.H. Zhou, Y. Sui, Y.X. Zheng, J.L. Zuo, X.Z. You. J. *Photochem. Photobiol., A*, **211**, 135 (2010).

[28] D.P. Rillema, D.G. Taghdiri, D.S. Jones, C.D. Keller, L.A. Worl, T.J. Meyer, H.A. Levy. *Inorg. Chem.*, **26**, 578 (1987).

[29] Y.M. Tao, H.Y. Li, Q.L. Xu, Y.C. Zhu, L.C. Kang, Y.X. Zheng, J.L. Zuo, X.Z. You. *Synth. Met.*, **161**, 718 (2011).

[30] F.S. Mancilha, B.A.D. Neto, A.S. Lopes, P.F. Moreira, Jr., F.H. Quina, R.S. Goncalves, J. Dupont. *Eur. J. Org. Chem.*, **4924**, (2006).

[31] O. Schiemann, P. Cekan, D. Margraf, T.F. Prisner, S.T. Sigurdsson. *Angew. Chem. Int. Ed.*, **48**, 3292 (2009).

[32] S. Ranjan, S.-Y. Lin, K.-C. Hwang, Y. Chi, W.-L. Ching, C.-S. Liu, Y.-T. Tao, C.-H. Chien, S.-M. Peng, G.-H. Lee. *Inorg. Chem.*, **42**, 1248 (2003).

[33] X.M. Liu, H. Xia, W. Gao, Q.L. Wu, X. Fan, Y. Mu, C.S. Ma. *J. Mater. Chem.*, **22**, 3485 (2012).

[34] X.H. Li, J. Gui, H. Yang, W.J. Wu, F.Y. Li, H. Tian, C.H. Huang. *Inorg. Chim. Acta*, **361**, 2835 (2008).

[35] J. Wu, H.Y. Li, L.C. Kang, D.P. Li, Q.L. Xu, Y.C. Zhu, Y.M. Tao, Y.X. Zheng, J.L. Zuo, X.Z. You. *J. Organomet. Chem.*, **695**, 2048 (2010).

[36] A.M. Barthram, M.D. Ward, A. Gessi, N. Armaroli, L. Flamigni, F. Barigelletti. *New J. Chem.*, **22**, 913 (1998).

[37] K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I.P. Clark, M.W. George, F.P.A. Johnson, J.J. Turner. *J. Am. Chem. Soc.*, **124**, 11448 (2002).

[38] L.A. Worl, R. Duesing, P. Chen, L.D. Ciana, T.J. Meyer. *Dalton Trans*., 849 (1991).

[39] J.R. Shaw, R.H. Schmehl. *J. Am. Chem. Soc.*, **113**, 389 (1991).

[40] L. Wallace, D.P. Rillema. *Inorg. Chem.*, **32**, 3836 (1993).