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Introduction

Bipyridine (bpy) complexes obtained from $Re(CO)_5Cl$ and its derivatives have attracted considerable attention over the years.¹ This is mainly due to the interesting photochemical properties of the Re(I) d⁶ low-spin centre which may show metal-to-ligand-charge-transfer (MLCT) luminescence owing to the presence of the bipyridine group.² This class of complexes exhibits good phosphorescence properties thanks to the strong spin–orbit coupling induced by the Re ion that enhances the singlet–triplet mixing, affording a fairly long-lived excited state and appreciable emission quantum efficiencies, potentially exploitable for applications in organic light-emitting

Synthesis and photoluminescence properties of rhenium(1) complexes based on 2,2':6',2''-terpyridine derivatives with hole-transporting units†

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Based on 2,2':6',2''-terpyridine ligands (L1), five terpyridine derivatives, namely 4'-carbazol-9-yl-2,2': 6',2''-terpyridine (L2), 4'-diphenylamino-2,2':6',2''-terpyridine (L3), 4'-bis(4-*tert*-butylphenyl)amino-2,2':6',2''-terpyridine (L4), 4'-[naphthalen-1-yl-(phenyl)amino]-2,2':6',2''-terpyridine (L5), 4'-[naphthalen-2-yl(phenyl)amino]-2,2':6',2''-terpyridine (L6) and their corresponding Re(I) complexes ReLⁿ(CO)₃Cl (n = 1-6) have been synthesized and characterized by elemental analysis and ¹H NMR spectroscopy. The X-ray crystal structure of ReL3(CO)₃Cl has also been obtained. The luminescence spectra of ReL2(CO)₃Cl-ReL5 (CO)₃Cl, obtained in CH₂Cl₂ solution at room temperature, show strong d π (Re) $\rightarrow \pi^*$ (diimine) MLCT character ($\lambda_{max} \sim 600$ nm) and a small red shift relative to ReL1(CO)₃Cl. This, confirmed by the study of the triplet energy levels of the L1–L6 ligands at low temperature (77 K rigid matrix), indicates that the introduction of electron-donating moieties on the terpyridine unit decreases the triplet levels of the ligands, leading to a reduction of the energy gap between d and π^* orbitals. In the solid state, upon MLCT excitation, all the complexes show an even stronger emission and a blue spectral shift ($\lambda_{max} \sim 550$ nm) compared to those obtained in solution.

diodes (OLEDs)² and in other fields such as solar energy conversion,³ supramolecular chemistry,⁴ catalysis,⁵ and medicinal chemistry.⁶

2,2':6',2"-Terpyridine (terpy) also forms many stable complexes with a variety of transition metal ions, which are useful in catalysis and molecular electronics, as well as in supramolecular chemistry.7 Nevertheless, the reaction product of Re(CO)₅Cl with 2,2':6',2"-terpyridine, made by Juris et al.,⁸ and characterized as fac-Re(σ^2 -terpy)(CO)₃Cl,⁹ was found to be nonluminescent in solution at room temperature. To enhance the application potential of this type of complex, there are several scientific studies describing the possibility of improving the emission performance by insertion of terpy ligand structural modifications.¹⁰ However, the resulting Re(I) complexes have been rarely employed in electroluminescent devices due to triplet-triplet annihilation (TTA) that leads to low efficiency at high current density.^{1d,2} Accordingly, many efforts have been made on both the ligand structure and rigidity of the complexes to enhance the excited state properties. Basically, there are two feasible strategies to overcome the above mentioned shortcoming: (i) the synthesis of novel diimine ligands with different ligand-field (molecular design)¹¹ which would affect the molecular orbital energy in the Re(1) complexes and (ii) the addition of groups with electron-donating or -accepting properties into the diimine ligands^{2a,d,12} to avoid the triplet-triplet

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annihilation thanks to the steric hindrance effect. Accordingly, we have already synthesized Re(I) complexes with carbazole and oxadiazole moieties showing enhanced luminescence properties.¹³

Here we report the synthesis of five 2,2':6',2"-terpyridine derivative ligands with carbazole and diphenylamine derivatives, 4'-carbazol-9-yl-2,2':6',2"-terpyridine (L2), 4'-diphenylamino-2,2':6',2"-terpyridine (L3), 4'-bis(4-tert-butyl-phenyl)amino-2,2':6',2"-terpyridine (L4), 4'-[naphthalen-1-yl(phenyl)amino]-2,2':6',2"-terpyridine (L5), 4'-[naphthalen-2-yl(phenyl)amino]-2,2':6',2"-terpyridine (L6) and their corresponding Re(I) complexes $\operatorname{ReL}^{n}(\operatorname{CO})_{3}\operatorname{Cl}(n = 2-6)$. The ligand L2 has been reported in our former publication¹⁴ and ligands L3-L6 are novel. Similar to that shown previously,⁹⁻¹¹ here only two N atoms are coordinated to the same Re(1) ion despite the three pyridine rings in the 2,2':6',2"-terpyridine derivatives. The choice of appending carbazole and diphenylamine derivatives moieties in $\operatorname{ReL}^{n}(\operatorname{CO})_{3}\operatorname{Cl}(n = 2-6)$ has been dictated by their ability to act as light-harvesting systems, sensitizing and protecting the metal emitting states, together with their intrinsic charge-transporting capability, making such molecules potentially interesting for the fabrication of OLEDs.^{2a-c,12a-c}

Experimental section

Materials

Rhenium pentacarbonyl chloride, 2,2':6',2''-terpyridine (L1), 4-chloro-2,2':6',2''-terpyridine, diphenylamine, bis(4-*tert*-butylphenyl)amine, *N*-phenylnaphthalen-1-amine, *N*-phenylnaphthalen-2-amine 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, K₂CO₃ were purchased from Yuan Hang Reagent Co. and Sinopharm Chemical Reagent Co. (China), respectively. All of them were used as received. The solvents were used without further purification, except for toluene.

Spectroscopy

¹H NMR spectra were measured on a Bruker AM 500 spectrometer. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. Mass spectra were determined with an Autoflex IITM instrument for MALDI-TOF-MS. Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 luminescence spectrophotometer, respectively. The photoluminescence lifetimes were measured with an Edinburgh Instruments FLS920P fluorescence spectrometer. The 77 K phosphorescence spectra were measured by Perkin-Elmer LS-50 spectrofluorometer equipped with a pulsed xenon lamp with variable repetition rate. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (air-equilibrated acetonitrile solution of [Ru-(bpy)₃]²⁺·2Cl⁻) and the unknown sample according to eqn (1):¹⁵

$$\Phi_{\rm unk} = \Phi_{\rm std} \left(\frac{I_{\rm unk}}{I_{\rm std}} \right) \left(\frac{A_{\rm std}}{A_{\rm unk}} \right) \left(\frac{\eta_{\rm unk}}{\eta_{\rm std}} \right)^2 \tag{1}$$

where Φ_{unk} and Φ_{std} are the luminescence quantum yield of the unknown sample and air-equilibrated acetonitrile solution of $[Ru(bpy)_3]^{2+} \cdot 2Cl^-$, respectively. The 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 acetonitrile solution of $[Ru(bpy)_3]^{2+} \cdot 2Cl^-$ has been revealed to be 0.018.¹⁶

Crystallography

The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo Ka radiation (λ = 0.71073 Å) at 291 K. Cell parameters were retrieved using SMART software and refined using SAINT¹⁷ on all observed reflections. Data was collected using a narrowframe method with scan widths of 0.30° in ω and an exposure time of 10 s per frame. The highly redundant data sets were reduced using SAINT¹⁷ and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS¹⁸ supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97.19 The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and leastsquares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso} .

Synthesis

The chemical structures of the materials used in this work and the synthetic routes are depicted in Scheme 1. The ligand L2 was synthesized from 4-chloro-2,2':6',2"-terpyridine and carbazole with our reported procedure.¹⁴ Ligands L3–L6 were synthesized using 4-chloro-2,2':6',2"-terpyridine and diphenylamine



Scheme 1 Synthetic routes for ligands and corresponding Re(I) complexes.

derivatives as the starting materials by a modified Ullmann reaction.²⁰ The Re(1) complexes **ReL**^{*n*}(**CO**)₃**Cl** (n = 1-6) were obtained with a modification of previously published procedures by reacting Re(CO)₅Cl with the appropriate ligand in toluene.^{2,13,21}

General synthesis route for ligands L3-L6

A mixture of diphenylamine or derivatives, 4-chloro-2,2':6',2"terpyridine, potassium *tert*-butoxide and DMPU was put into a reactor, then heated at 205 °C for 12 h under nitrogen. After cooling to room temperature, the mixture was dissolved in dichloromethane, washed with water 3 times, and the solid obtained was purified with column chromatography on SiO₂ using ethyl acetate and petroleum ether (v/v = 1 : 2) as eluent, and then the resulting solid was purified again by recrystallization from an ethyl acetate–petroleum ether solution to yield ligands L3–L6.

The brown solid was purified.

4-Diphenylamino-2,2':6',2"-terpyridine (L3). Diphenylamine (0.50 g, 3.0 mmol), 4-chloro-2,2':6',2"-terpyridine (0.22 g, 0.82 mmol), potassium *tert*-butoxide (0.22 g, 2.0 mmol) and DMPU (0.1 mL), L3: 0.16 g (yield: 50%). M.p.: 213–218 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.60 (dd, J = 10.6, 6.1 Hz, 4H), 8.02 (s, 2H), 7.84 (s, 2H), 7.39 (s, 4H), 7.28 (d, J = 8.4 Hz, 6H), 7.22 (s, 2H). MS(ESI): m/z 401.05 [M]⁺. Anal. Calcd for C₂₇H₂₀N₄ (400.4747): C 80.98, H 5.03, N 13.84. Found: C 80.84, H 5.03, N 13.99.

4-Bis(4-*tert***-butylphenyl)amino-2,2':6',2"-terpyridine (I.4).** Bis(4*tert*-butylphenyl)amine (0.88 g, 3.1 mmol), 4-chloro-2,2':6',2"terpyridine (0.20 g, 0.73 mmol), potassium *tert*-butoxide (0.20 g, 1.8 mmol) and DMPU (0.1 mL), **L4**: 0.19 g (yield: 51%). M.p.: 208–213 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.62 (s, 2H), 8.56 (s, 2H), 7.95 (s, 2H), 7.85 (s, 2H), 7.38 (s, 4H), 7.33–7.29 (m, 2H), 7.20 (s, 4H), 1.36 (s, 18H). MS(ESI): *m/z* 513.69 [M]⁺. Anal. Calcd for C₃₅H₃₆N₄ (512.6873): C 81.99, H 7.08, N 10.93. Found: C 81.97, H 7.07, N 10.89.

4-(Naphthalen-1-yl(phenyl)amino)-2,2':6',2"-terpyridine (L5). *N*-Phenylnaphthalen-1-amine (0.89 g, 4.0 mmol), 4-chloro-2,2':6',2"-terpyridine (0.29 g, 1.1 mmol), potassium *tert*-butoxide (0.30 g, 2.7 mmol) and DMPU (0.1 mL), **L5**: 0.17 g (yield: 34%). M.p.: 237–239 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.56 (t, *J* = 7.3 Hz, 4H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.92 (q, *J* = 7.9 Hz, 4H), 7.81 (td, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.54–7.47 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.32 (dt, *J* = 15.7, 7.8 Hz, 4H), 7.26 (dd, *J* = 6.4, 5.1 Hz, 2H), 7.14 (t, *J* = 7.1 Hz, 1H). MS(ESI): *m*/*z* 451.53 [M]⁺. Anal. Calcd for C₃₁H₂₂N₄ (450.5333): C 82.64, H 4.92, N 12.44. Found: C 82.78, H 4.95, N 12.42.

4-[Naphthalen-2-yl(phenyl)amino]-2,2':6',2"-terpyridine (L6). *N*-Phenylnaphthalen-2-amine (0.75 g, 3.4 mmol), 4-chloro-2,2':6',2"-terpyridine (0.25 g, 0.93 mmol), potassium *tert*-butoxide (0.25 g, 2.2 mmol) and DMPU (0.1 mL), **L6**: 0.09 g (yield: 22%). M.p.: 210–212 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.59 (s, 4H), 8.09 (s, 2H), 7.90–7.81 (m, 4H), 7.74–7.69 (m, 1H), 7.65 (s, 1H), 7.44 (d, *J* = 38.5 Hz, 5H), 7.30 (d, *J* = 16.7 Hz, 4H), 7.23 (s, 1H). MS(ESI): *m/z* 451.53. [M]⁺. Anal. Calcd for C₃₁H₂₂N₄

(450.5333): C 82.64, H 4.92, N 12.44. Found: C 82.69, H 5.06, N 12.41.

General synthesis of ReL1(CO)₃Cl–ReL6(CO)₃Cl. Re(CO)₅Cl (0.035 g, 0.10 mmol) was refluxed with an equimolar quantity of appropriate ligand in toluene for 6 h under nitrogen. After the mixture was cooled to RT, the solvent was distilled off. The resulting yellow solid was purified by recrystallization from ethyl acetate and petroleum ether.

ReL1(CO)₃**Cl.** Yield: 61%. M.p.: 265–267 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.13 (d, J = 4.9 Hz, 1H), 8.85 (d, J = 4.1 Hz, 1H), 8.29 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.17 (t, J = 7.9 Hz, 1H), 8.10 (t, J = 7.8 Hz, 1H), 7.95 (d, J = 5.9 Hz, 2H), 7.80 (d, J = 7.5 Hz, 1H), 7.55 (dd, J = 13.2, 6.5 Hz, 2H). MS (MALDI-TOF): m/z 476.451 [M⁺]. Anal. Calcd for ReC₁₈H₁₁N₃O₃Cl (538.9581): C 40.11, H 2.06, N 7.80. Found: C 40.03, H 2.08, N 7.88.

ReL2(CO)₃**Cl.** Yield: 41%. M.p.: 263–266 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.15 (s, 1H), 8.89 (s, 1H), 8.47 (s, 1H), 8.21 (s, 1H), 8.11 (d, *J* = 32.0 Hz, 6H), 7.74 (s, 2H), 7.59 (s, 2H), 7.52 (s, 2H), 7.41 (s, 2H). MS (MALDI-TOF): *m/z* 641.961 [M⁺]. Anal. Calcd for ReC₃₀H₁₈N₄O₃Cl (668.6961): C 51.17, H 2.58, N 7.96. Found: C 51.12, H 2.60, N 7.99.

ReL3(CO)₃**Cl.** Yield: 68%. M.p.: 272–275 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.06 (s, 1H), 8.75 (s, 1H), 7.91 (d, *J* = 38.5 Hz, 3H), 7.75 (s, 1H), 7.49 (s, 7H), 7.35 (s, 6H), 7.01 (s, 1H). MS (MALDI-TOF): *m*/*z* 643.638 [M⁺]. Anal. Calcd for ReC₃₀H₂₀N₄O₃Cl (706.1647): C 51.03, H 2.85, N 7.93. Found: C 50.99, H 2.87, N 7.98.

ReL4(CO)₃**Cl.** Yield: 31%. M.p.: >300 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.07 (d, J = 5.1 Hz, 1H), 8.76 (d, J = 4.5 Hz, 1H), 7.95 (t, J = 7.4 Hz, 1H), 7.86 (t, J = 7.1 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.54–7.40 (m, 7H), 7.24 (t, J = 11.3 Hz, 4H), 6.98 (d, J = 2.3 Hz, 1H), 1.37 (s, 18H). MS (MALDI-TOF): m/z 755.753 [M⁺]. Anal. Calcd for ReC₃₈H₃₆N₄O₃Cl (818.3773): C 55.77, H 4.43, N 6.85. Found: C 55.72, H 4.46, N 6.89.

ReL5(CO)₃**Cl.** Yield: 37%. M.p.: 215–218 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.04 (d, J = 4.6 Hz, 1H), 8.72 (dd, J = 14.3, 4.1 Hz, 1H), 7.98 (td, J = 16.8, 8.1 Hz, 4H), 7.83 (td, J = 11.8, 4.9 Hz, 2H), 7.75 (t, J = 8.4 Hz, 1H), 7.64–7.53 (m, 5H), 7.43 (dd, J = 15.7, 4.9 Hz, 8H). MS (MALDI-TOF): m/z 693.110 [M⁺]. Anal. Calcd for ReC₃₄H₂₂N₄O₃Cl (756.2233): C 54.00, H 2.93, N 7.41. Found: C 53.97, H 2.95, N 7.44.

ReL6(CO)₃**Cl.** Yield: 45%. M.p.: 214–217 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.07 (d, J = 5.0 Hz, 1H), 8.73 (d, J = 4.3 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.91 (s, 2H), 7.86–7.77 (m, 4H), 7.73 (d, J = 8.1 Hz, 1H), 7.56 (dd, J = 11.1, 6.5 Hz, 4H), 7.51–7.47 (m, 2H), 7.45–7.36 (m, 6H). MS (MALDI-TOF): m/z693.331 [M⁺]. Anal. Calcd for ReC₃₄H₂₂N₄O₃Cl (756.2233): C 54.00, H 2.93, N 7.41. Found: C 53.98, H 2.94, N 7.46.

Results and discussion

Crystallography

The crystals of $ReL1(CO)_3Cl$ and $ReL3(CO)_3Cl$ were obtained from the CH_2Cl_2/CH_3OH and CH_2Cl_2/C_2H_5OH solution



Fig. 1 Top: ORTEP view of complex ReL3(CO)₃Cl with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level. Down: The molecular packing of ReL3(CO)₃Cl.

respectively. By single-crystal X-ray diffraction method, their structures were analysed. The crystal structure of **ReL1(CO)₃Cl** is similar to those reported with and without solvent (CCDC No.: 666615).^{9,22} For **ReL3(CO)₃Cl**, the relative ORTEP diagrams and the molecular packing are shown in Fig. 1, the crystal data and selected bond distances, angles are presented in Table 1.

In ReL3(CO)₃Cl, the rhenium atoms are in a distorted octahedral coordination environment with three carbonyl ligands in a fac arrangement, two N atoms from two pyridine rings of the ligand and a chlorine atom. Solvent molecules are found in complexes ReL1(CO)₃Cl (one CH₃OH) and ReL3(CO)₃Cl (one C₂H₅OH). In complex ReL3(CO)₃Cl, the distances of Re-C are 1.884(9)-1.922(10) Å, the average Re-N bond distance is 2.197(6) Å. The bond angles between adjacent CO carbon atoms are 85.2(3)-90.1(4)°, which is close to 90°, indicating that CO ligands are linearly coordinated, while the N-Re-N angle is 74.9(2). The dihedral angle between the free pyridine ring and the coordinated ones is 54.3°, and that between the two coordinated pyridine rings is 14.2°. From the molecular packing of ReL3(CO)₃Cl (Fig. 1, down), there are strong π - π interactions between benzene and pyridine rings of adjacent complexes with the centroid-to-centroid separation of 3.774 Å.

Photophysical properties

The absorption spectra of Re(1) complexes in dichloromethane solution $(1 \times 10^{-5} \text{ mol } \text{L}^{-1})$ at room temperature are depicted in Fig. 2. All of them display intense absorption bands in the

Table 1 Crystallographic data, selected bond lengths (Å) and angles (°) for ReL3(CO)₃Cl

		_		
Dol 2	(\mathbf{CO})		CU	OLI
RCLO	UU	ROL	$U_2\Pi_5$	ОП

Crystallographic data		Bond lengths (Å) and angles (°)			
Formula	C ₃₂ H ₂₆ N ₄ O ₄ ClRe	Re(1)-C(28)	1.922(10)		
$F_{\rm W}$	1458.37	Re(1) - C(29)	1.884(9)		
$T(\mathbf{K})$	293(2)	Re(1)-C(30)	1.894(9)		
Wavelength (Å)	0.71073	Re(1)-N(1)	2.185(6)		
Crystal system	Monoclinic	Re(1)-N(2)	2.209(6)		
Space group	P2(1)/c	Re(1)-Cl(1)	2.481(2)		
a (Å)	7.0443(14)	C(29)-Re(1)-C(30)	86.0(4)		
b (Å)	26.056(5)	C(29)-Re(1)-C(28)	90.1(4)		
c (Å)	17.159(3) A	C(30)-Re(1)-C(28)	85.2(3)		
α (°)	90.00	C28 Re1 N1	175.1(3)		
$\beta(\hat{o})$	107.024(7)	C(29)-Re(1)-N(1)	93.7(3)		
γ (°)	90.00	C30 Re1 N1	98.0(3)		
$V(Å^3)$	3011.5(10)	C28 Re1 N2	101.7(3)		
Z	2	C29 Re1 N2	97.3(3)		
$\rho_{\rm calcd} ({\rm g}{\rm cm}^{-3})$	1.608	C30 Re1 N2	172.3(3)		
μ (Mo K α) (mm ⁻¹)	4.163	C(28)-Re(1)-Cl(1)	91.8(2)		
F (000)	1428	C(29) - Re(1) - Cl(1)	178.2(3)		
Range of transm	2.48 - 25.00	C(30) - Re(1) - Cl(1)	94.4(3)		
factors (°)					
Reflns collected	13 536	N(1)-Re(1)-Cl(1)	84.44(17)		
Unique	5311	N(2)-Re(1)-Cl(1)	82.14(16)		
GOF on F^2	1.031	N(1)-Re(1)-N(2)	74.9(2)		
$R_1^a, WR_2^b [I > 2\sigma(I)]$	0.0497, 0.1275				
R_1^a , w R_2^b (all data)	0.0592, 0.1331				
CCDC No.	826740				

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma F_{o}|$. ${}^{b}wR_{2} = [\Sigma w (F_{o}{}^{2} - F_{c}{}^{2})^{2}/\Sigma w (F_{o}{}^{2})]^{1/2}$.



Fig. 2 UV-vis absorption spectra of Re(i) complexes in CH_2Cl_2 solution (1 \times $10^{-5}\,mol\;L^{-1})$ at room temperature.

220–330 nm spectral range (extinction coefficients of the order of 10⁴ M⁻¹ cm⁻¹) that can be assigned to the spin-allowed intraligand ($\pi \rightarrow \pi^*$) transitions (IL) as suggested by the comparison with the absorption bands of the free ligands **L1–L6** (Fig. S1, ESI[†]) as well as those of the closely related metal complexes.² By contrast, the broad bands at lower energy in the 330–480 nm region are attributed to the d π (Re) $\rightarrow \pi^*$ (diimine) metal-to-ligand charge-transfer (MLCT) transitions. Notably, the weaker MLCT absorption of **ReL1(CO)₃Cl** (without substituent on the terpyridine unit) relative to **ReL^{***n***}(CO)₃Cl** (*n* = 2–6)



Fig. 3 (a) Excitation and emission spectra of the Re(i) complexes in CH_2Cl_2 solution $(1 \times 10^{-4} \text{ mol } L^{-1})$ and (b) normalized emission spectra of the Re(i) complexes in solid state at room temperature (the pictures of complexes **ReL2** (CO)₃Cl and **ReL4(CO)₃Cl** under 365 nm UV-light excitation were inserted).

indicates that the introduction of carbazole and diphenylamine groups improves the MLCT character of this class of complexes.^{13,23}

The excitation spectra of Re(1) complexes in solution, measured at room temperature by monitoring the corresponding emission maxima (Fig. 3a, left), exhibit two peaks, namely $\pi \to \pi^*$ (at ~370 nm) and MLCT (at ~445 nm).^{2c,j} They differ from the corresponding absorption profiles mainly for the intensity ratio between the LC and MLCT bands since the UV region (<300 nm) is known to be critical for the multiplier response. For ReLⁿ(CO)₃Cl (n = 2-5), the MLCT band becomes dominant after the introduction of hole-transporting units because of the strong spin–orbit coupling imposed by the heavy Re(1) ion that allows the upper excited state to relax into the spin forbidden MLCT state with consequent light emission.

By exciting either $\pi \to \pi^*$ or MLCT absorption bands, the emission spectra of ReL^{*n*}(CO)₃Cl (n = 2-5) (the emission of

ReL6(CO)₃**Cl** in solution is too weak to be measured under these conditions) and that of the reference **ReL1(CO)**₃**Cl** show broad bands centred at *ca.* 530–610 nm, respectively, (Fig. 3a, Table 2) assigned to $d\pi$ (Re) $\rightarrow \pi^*$ (diimine) MLCT phosphorescence. The highest emission intensity obtained by exciting the MLCT states directly, indicates that the orbital overlap between the higher $\pi \rightarrow \pi^*$ and the lower MLCT states is very efficient, and the major contribution of the observed emission is from the latter one.^{2e,j,23a,24}

From Table 2, it has also to be noted that compared to the reference sample ReL1(CO)₃Cl, the introduction of carbazole (ReL2(CO)₃Cl), diphenylamine (ReL3(CO)₃Cl), bis(4-tert-butylphenyl)amine (ReL4(CO)₃Cl), and N-phenyl-naphthalen-1-amine (ReL5(CO)₃Cl) units enhanced the luminescence performances and the quantum efficiency $(\Phi_{\rm p})$ of the corresponding Re(1) complexes since the hole-transporting moieties favour the energy transfer process from the substituents to the central terpyridine as already found in similar carbazole containing rhenium and ruthenium complexes.^{13,25} These results confirm that antenna substitutes can be profitably used to increase the light harvesting efficiency of the Re(I) complexes. In addition, due to the various ligand-field strength caused by the substitutes for the present cases, thermally accessible d-d MC levels could provide different non-radiative 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 distortions²⁶ and it has recently been demonstrated for a series of Re(1)-tricarbonyl-diimine complexes²⁵ although a range of other non-radiative decay pathways are in principle available.^{27,28} For instance, from Fig. 3(a) and Table 2 it can be observed that ReL4(CO)₃Cl (with (4-tertbutylphenyl)amine) shows the strongest emission intensity of the series, followed by ReL5(CO)₃Cl (N-phenyl-naphthalen-1-amine) and ReL3(CO)₃Cl (diphenylamine), respectively. Their emission performances largely exceeded that of the reference sample ReL1(CO)₃Cl. Surprisingly, for ReL6(CO)₃Cl (N-phenylnaphthalen-2-amine), structurally very similar to ReL5(CO)₃Cl, only a weak luminescence has been detected under the same conditions.

By contrast, in solid state all the complexes show strong phosphorescent emission centred at ca. 532-562 nm (Fig. 3b) under MLCT excitation. Compared to the solution samples, they are blue shifted showing the rigidochromic effect that was first proposed by Wrighton and Morse.²⁹ Similar rigidiochromism has been reported in the related Re(1) diimine system by measuring the photoluminescence in a frozen glass at 77 K.³⁰ By comparing our results with some work based on iridium complexes,³¹ the stronger emission in solid than that in solution may be attributed to the excimeric interactions between the benzene and pyridine of adjacent complexes in solid state (Fig. 1, down). The strong π - π interactions elongate the overall π -conjugation degree. As a result, the triplet energy level of the charge transfer state from Re(I) to the interacting ligands is reduced and the ligands participate in the excited state in the solid state. In addition, the rotation of the free benzene groups

Table 2 Absorption and photoluminescence data of Re(I) complexes at room temperature

			n i i b	Emission ^b		T'C . d	1.6	, f	
Complex	Medium	Absorption [λ (nm) (ε (10 ³ M ⁻¹ cm ⁻¹))]	Excitation ² λ (nm)	λ (nm)	$\Phi_{ m P}\left(\% ight)$	Lifetime", $\tau_{\rm P}$ $\mu s (\chi^2)$	$\frac{\kappa_{\rm r}}{10^3} {\rm s}^{-1}$	${}^{\kappa_{ m nr}}_{ m 10^5}{ m s}^{-1}$	HOMO/LUMO eV
ReL1(CO) ₃ Cl	CH_2Cl_2 Solid	220(19.3), 295(13.6), 378(2.6)	442 365	509 562	0.3 <i>a</i>	2.02(0.989) 1.95(0.983)	1.5_{a}	4.94 a	-4.93/-2.06
ReL2(CO) ₃ Cl	CH_2Cl_2 Solid	224(62.3), 277(25.9), 397(9.3)	459 365	578 551	0.3 a	1.37 (0.988) 1.66 (0.987)	$_{a}^{2.2}$	7.28 a	-5.72/-2.95
ReL3(CO) ₃ Cl	CH_2Cl_2 Solid	$a^{219(31.4)}, 282(25.3), 380(8.0)$	444 367	600 554	0.6 <i>a</i>	2.50 (0.992) 1.97 (0.987)	$^{2.4}_{a}$	3.98 a	-5.76/-2.91
ReL4(CO) ₃ Cl	CH_2Cl_2 Solid	220(36.6), 256(29.4), 383(8.6)	454 367	593 532	1.3 a	1.44(0.987) 1.87(0.987)	9.0 <i>a</i>	6.85 a	-5.63/-2.80
ReL5(CO) ₃ Cl	CH_2Cl_2 Solid	220(45.5), 279(26.8), 378(6.9)	442 365	601 546	0.9 <i>a</i>	1.33(0.985) 3.04(0.972)	6.8 <i>a</i>	7.45 a	-5.73/-2.77
ReL6(CO) ₃ Cl	CH_2Cl_2 Solid	219(34.6), 255(20.9), 384(5.2) a	450 365	c 551	с а	$\begin{array}{c} (0.989) \\ 1.53 (0.989) \\ 2.94 (0.993) \end{array}$	с а	c a	-5.75/-2.86

^{*a*} Not measured. ^{*b*} The excitation and emission spectra are corrected. ^{*c*} Not detected because of the weakness of the signal. ^{*d*} 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 $k_r = \Phi_p/\tau_p$. ^{*f*} Nonradiative rate constant calculated from $k_{rr} = 1/\tau_p - k_r$.

was also limited. Therefore, strong emissions of the solid samples were observed. High luminescence in immobilized states is more beneficial because the OLEDs are based on the solid state applications.

The phosphorescence lifetime is a key factor in the TTA in the OLEDs operation.³² The excited state lifetimes ($\tau_{\rm P}$) of Re(I) complexes, measured in CH₂Cl₂ solution and solid state at room temperature, support the hypothesis of the MLCT character of the emitting states. As indicated in Table 2, Fig. S1 and S2,[†] all the lifetime decays are monoexponential in the range of sub-microsecond scale $(1.33 - 3.04 \ \mu s)$ and can be assigned to MLCT states.^{19,32–34} By using the equations $\Phi_{\rm P}$ = $\Phi_{\rm ISC}\{k_{\rm r}/(k_{\rm r}+k_{\rm nr})\}$ and $\tau_{\rm p}=(k_{\rm r}+k_{\rm nr})^{-1}$, it is possible to calculate the radiative (k_r) and nonradiative (k_{nr}) decay rates from $\Phi_{\rm P}$ and $\tau_{\rm P}$, where the intersystem-crossing yield ($\Phi_{\rm ISC}$) 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(CO)₃Cl has a k_r sensibly higher than those of other complexes, which is comparable with the emission intensity and quantum efficiency.

As discussed before, the reason for the emission red shift in solution of $\text{ReL}^n(\text{CO})_3\text{Cl}$ (n = 2–5), relative to $\text{ReL1(CO})_3\text{Cl}$ can be attributed to the effect of the substituents on the MLCT emission energy. To get a better insight on the observed behaviour, the triplet energy of the ligands L1–L6 has been determined from the phosphorescence spectra at 77 K in CH₂Cl₂ rigid matrix. The estimated values from Fig. 4 for L1–L6 are 24 090, 21 050, 20 100, 21 950, 19 400 and 19 850 cm⁻¹, respectively. These results, further suggest that the insertion of electron-donating moieties decreases the ligand energy levels resulting in a lowering of the energy gap between d and π^* orbitals that reflects the luminescence behaviour of the corresponding Re(1) complexes.

Electrochemical property

Cyclic voltammograms of L1–L6 and those of $ReL2(CO)_3Cl$ – ReL6(CO)₃Cl (5×10⁻⁴ M) in CH₂Cl₂ solutions of (Bu₄N)PF₆



Fig. 4 Normalized phosphorescence spectra of the ligands at 77 K in CH_2Cl_2 rigid matrix. Applied delay: 100 μ s, λ_{ex} = 300 nm.

(0.1 M) using ferrocene as the internal standard at a sweep rate of 0.1 V s⁻¹ are shown in Fig. 3S and 4S.[†] All the free ligands have chemical irreversible monoelectron reduction at negative potentials. On the oxidation side, L1 has a single reversible oxidation at -1.30 V, while L2-L6 have reversible oxidations at more positive potentials (-1.19 to -0.87 V). The oxidation potential decreases according to the electron-donating ability sequence of the substituents of terpyridine ligands. All complexes (Fig. $S5^{\dagger}$) show a couple of irreversible anodic waves vs. SCE associated with a Re(I)-based oxidation process (Re^I/Re^{II}) and a couple of quasi-reversible cathodic waves vs. SCE associated with a ligand-based reduction process [ReICl(CO)₃(L)]/ $[ReICl(CO)_3(L^{\cdot})]^{-}$.³⁵ On the basis of the potentials of the oxidation and reduction couples of the Re(I) complexes, the HOMO/LUMO energy levels of ReL2(CO)₃Cl-ReL6(CO)₃Cl were estimated (Table 2), respectively, with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level).³⁶ Since the six complexes have the same central ion structure, the reduction potential has been affected slightly.

The oxidation potential of the complexes decreases with the similar sequence of the ligands contained.

Conclusions

By introduction of the hole-transporting carbazole and diphenylamine derivatives, we have successfully synthesized five new ligands based on 2,2':6',2"-terpyridine and their corresponding Re(I) complexes. The complexes ReL3(CO)₃Cl-ReL5-(CO)₃Cl show $d\pi$ (Re) $\rightarrow \pi^*$ (diimine) MLCT phosphorescence around 533-611 nm and quantum efficiency higher than those of ReL1(CO)₃Cl without hole-transporting moiety, and the (4-tert-butylphenyl)amine containing complex has the strongest emission intensity of the series, followed by ReL5(CO)₃Cl (N-phenyl-naphthalen-1-amine) and ReL3(CO)₃Cl (diphenylamine), respectively. The long lifetime decay from the MLCT state indicates that the potential surface crossing from the π - π^* to the MLCT states in the complexes is efficient. These observations imply that the modification of some of the diimine rhenium(1) carbonyl complexes with suitable hole-transporting moieties would lead to better phosphorescence performances.

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