PAPER

# New rhenium(1) complexes with substituted diimine ligands for highly efficient phosphorescent devices fabricated by a solution process<sup>†</sup>

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A series of new carbonyl rhenium(1) complexes chelated by a substituted 1,10-phenanthroline ligand with the general formula  $Re(CO)_{3}LCl$ , where L = 2-(2'-methoxyphenyl)-1,10-phenanthroline ( $L_{1}$ ), 2-(4'-methoxyphenyl)-1,10-phenanthroline (L<sub>2</sub>) and 2-(4'-diphenylaminophenyl)-1,10-phenanthroline  $(L_3)$ , have been systemically synthesized. The molecular structure of complex 1 was determined by single crystal X-ray diffraction studies, showing that the complex adopts a distorted octahedral geometry. The electrochemical, photophysical, and thermal properties, as well as the electroluminescent behaviors of three rhenium(I) complexes, were investigated. The solution processable complex 1, 2 or 3 was used as a yellow emitting dopant to fabricate electrophosphorescent devices with a polymer host. The device based on complex 3 exhibits a maximum current efficiency of 12.2 cd A<sup>-1</sup> and a peak brightness in excess of 7300 cd m<sup>-2</sup>, respectively. Even at a high luminance of 5000 cd cm<sup>-2</sup> with current density of 81 mA cm<sup>-2</sup>, the current efficiency of this device remains as high as  $6.4 \text{ cd } A^{-1}$ . These results represent the best values reported for electophosphorescent devices based on solution processable rhenium(I) complexes.

## Introduction

In recent years, heavy metal complexes have been extensively studied as electrophosphorescent materials to fabricate highly efficient organic light-emitting devices (OLEDs) since the original works of Thompson, Förrest and Ma.1,2 The OLEDs based on phosphorescent materials show remarkable enhancement in their electroluminescent (EL) performance due to the use of both singlet and triplet excitons caused by strong spin-orbital coupling in the existence of the heavy metal atoms, and exhibit higher internal quantum efficiency of up to 100% in principle. Iridium(III),<sup>3</sup> platinum(II),<sup>4</sup> and ruthenium(II)<sup>5</sup> complexes have been mainly exploited in OLEDs. Recent research results indicate that rhenium(1) complexes<sup>6,7</sup> also serve as a class of electrophosphorescent materials for OLEDs with features of high room temperature phosphorescence quantum yield, relatively short excited state lifetime and excellent thermal, chemical, and photochemical stability.8 So far, some rhenium(1) complexes with

different ligands have been reported,<sup>6-9</sup> and parts of them have been applied as emitters in OLEDs.<sup>6,7</sup> For example, Li et al. reported efficient devices based on (2,9-dimethyl-1,10-phenathroline)Re(CO)<sub>3</sub>Cl doped into 4,4'-N,N'-dicarbazole-biphenyl (CBP) with a high current efficiency of 7.15 cd  $A^{-1}$ .<sup>6a</sup> Liu *et al.* achieved yellow electoluminescence devices with a maximum current efficiency of 17.6 cd A<sup>-1</sup> and a brightness of 6500 cd m<sup>-2</sup> by doping (3-ethyl-2-(4'-diphenylaminophenyl)imidano[4,5-f] 1,10-phenanthroline)Re(CO)<sub>3</sub>Cl into CBP.<sup>7a</sup> Recently, the groups of Li and Chu7b reported a more efficient OLED based on (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)Re(CO)<sub>3</sub>Br with a maximum EL efficiency and luminance of 21.8 cd  $A^{-1}$  and 8315 cd m<sup>-2</sup>, respectively. Utilizing the vacuum-deposition method, the rhenium(1) complexes based OLEDs show high efficiency and good luminance. However, it is well known that the sublimation process has critical drawbacks including considerable loss of the expensive materials during evaporation, complex manufacturing process and high manufacturing costs. Therefore, solution processed OLEDs are attracting much attention as potential candidates for large area flat panel displays, owing to their simple processing route and low manufacturing cost. Up to now, to the best our knowledge, rhenium(I) complexes based devices made by a solution process were less reported and showed relatively low efficiency and luminescence, which may be attributed to neutral rhenium(I) complexes having poor solubility.<sup>10</sup> In this context, the rational design of new rhenium complexes with good solubility and the exploitation of their electroluminescence properties of solution

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processed OLEDs is also an important project. Hence, we have synthesized three new soluble rhenium(1) complexes and found that highly efficient phosphorescent devices can be fabricated with these complexes by the spin casting solution process. In this paper, we report the synthesis, characterization, electrochemical, photophysical, and thermal properties, as well as EL behaviors, of three new rhenium(1) complexes Re(CO)<sub>3</sub>LCl [L = 2-(2'-methoxyphenyl)-1,10-phenanthroline (1), 2-(4'-methoxyphenyl)-1,10-phenanthroline (2) and 2-(4'-diphenylamino-phenyl)-1,10-phenanthroline (3)].

## **Results and discussion**

## Synthesis and characterization of compounds

Ligands  $L_1-L_3$  were prepared according to a known procedure (Scheme 1).<sup>11</sup> Of them,  $L_3$  is a new compound while ligands  $L_1$ , and  $L_2$  are known compounds. The new ligand  $L_3$  was synthesized by the reaction of dry 1,10-phenanthroline with 4-diphenylaminophenyllithium in moderate yields after oxidative rearomatization. The 4-diphenylaminophenyllithium was prepared by treatment of 4-diphenylamino-bromobenzene with n-BuLi. These ligands were characterized by <sup>1</sup>H NMR spectroscopy along with elemental analysis. Reaction of Re(CO)5Cl with one equivalent of ligands L1-L3 in toluene at refluxing temperature afforded the corresponding complexes 1-3 in high yields (>80%) as pale yellow solids (Scheme 1). Three complexes were all characterized by <sup>1</sup>H NMR spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and elemental analyses, and satisfactory analytic results were obtained. The <sup>1</sup>H NMR spectra of complexes 1-3 show that the resonances of the protons on the phenanthroline aromatic rings shift toward low field compared to the corresponding signals in their free ligands, indicating the formation of the coordination bonds between the ligand and the rhenium(I) center (Fig. S1, ESI<sup>†</sup>).<sup>12</sup> The FT-IR spectra of these complexes show three bands in the 1869-2021 cm<sup>-1</sup> region, which can be attributed to the stretching vibrations of the three carbonyl groups at different positions around the rhenium(1) metal. Complexes 1-3 are moderately soluble in dimethylsulphoxide, dichloromethane (CH2Cl2), N,N-dimethylformamide and tetrahydrofuran, while insoluble in saturated hydrocarbon solvents.

## Crystal structure

The molecular structure of complex 1 was determined by X-ray crystallographic analysis. Samples of the complex suitable for X-ray crystal structure determination were grown from  $CH_2Cl_2$  at room temperature. The ORTEP drawing of the molecular

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Table 1 Selected bond lengths (Å) and bond angles (°) for complex 1

Re(1)-C(1)	1.898(8)	C(2)-Re(1)-C(1)	88.9(3)
Re(1)-C(2)	1.892(7)	C(2)-Re(1)-C(3)	90.6(3)
Re(1) - C(3)	1.921(7)	C(3)-Re(1)-C(1)	87.2(3)
Re(1)-N(2)	2.166(5)	C(2)-Re(1)-N(1)	95.2(3)
Re(1)-N(2)	2.213(5)	C(1)-Re(1)-N(2)	94.2(3)
O(1) - C(1)	1.148(9)	N(2)-Re(1)-N(1)	75.51(19)
O(2) - C(2)	1.154(9)	C(1)-Re(1)-Cl(1)	92.6(3)
O(3)–C(3)	1.156(9)	C(3)-Re(1)-Cl(1)	91.6(2)

**Fig. 1** ORTEP drawing of a crystal of **1** with displacement ellipsolids at the 30% probability level.

C(17)

CIQ

structure of 1 is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The X-ray analysis reveals that complex 1 adopts a distorted octahedron geometry with the metal center coordinated by one chloride atom, three carbonyl ligands and two nitrogen atoms of the ligand  $L_1$ . The bond distances of C(1)-Re, C(2)-Re, and C(3)-Re are 1.898(8), 1.892(7), and 1.921(7), respectively. These values are consistent with the bond lengths found in related octahedral rhenium(I) carbonyl complexes.<sup>13</sup> The average Re–N bond distances are 2.189 Å, which are longer than the ones previously reported for related octahedral rhenium(I) complexes.<sup>7c,14</sup> The C-Re-C bond angles are in the range  $87.2-90.6^{\circ}$ , being close to the ideal  $90^{\circ}$  bond angle for octahedral complexes, while the N-Re-N bond angle is 75.51°. In complex 1, the dihedral angle between the phenyl ring and the phenanthroline plane is 72.2°. In addition, there are abundant weak interactions, such as  $\pi - \pi$  stacking interactions, hydrogen bonding and  $CH\cdots\pi$  interactions, in the packing structure of 1. The hydrogen bonding between a carbonyl oxygen atom in one molecule and a hydrogen atom of the phenanthroline group in an adjacent molecule with an H…O distance of 2.56 Å, and between its chlorine atom and a hydrogen atom of the phenanthroline group in another adjacent molecule with a H…Cl distance of 2.79 Å, can be observed. The hydrogen bonding interactions link the molecules of 1 into one-dimensional chains. Meanwhile, the one-dimensional chains are bound together into two-dimensional sheets by weak  $CH \cdots \pi$  and hydrogen bonds between molecules in adjacent chains with distances of 2.81 A for the CH... $\pi$  interaction and 2.90 Å for the hydrogen bond, respectively (Fig. S2, ESI<sup>†</sup>).



Scheme 1 Synthesis of ligands and their rhenium(1) complexes.

## Photophysical properties

The absorption and emission spectral data along with lifetimes and emission quantum yields for the free ligands  $L_1-L_3$  in both solution and the solid state are summarized in Table S1, ESI, † All free ligands display an intense absorption band with the absorption maxima about 283 nm, which can be attributed to the  $\pi$ - $\pi^*$  electronic transition of the phenanthroline moiety in these ligands. An additional absorption band observed at 382 nm for  $L_3$  may result from a charge transfer from the triphenylamine donor to phenanthroline acceptor. Upon irradiation with an excited light, the free ligands  $L_1-L_3$  emit a blue light in  $CH_2Cl_2$ solution with emission peaks at 460-470 nm, respectively (Fig. 2. and Table S1, ESI<sup> $\dagger$ </sup>). The fluorescence decay lifetime of L<sub>1</sub>-L<sub>3</sub> were found to be in the range from 3.16 to 3.24 ns. In comparison with the ligands  $L_1$  and  $L_2$ ,<sup>11</sup> the emission frequency of  $L_3$  show strong solvent-dependence. For example, the emission  $\lambda_{max}$  of L<sub>3</sub> appears at 435 nm in toluene, 470 nm in CH<sub>2</sub>Cl<sub>2</sub>, and 495 nm in acetonitrile (CH<sub>3</sub>CN), respectively. The emission spectra of  $L_3$  in various solvents and their photos under irradiation of light at 365 nm are shown in Fig. S4 and S5, ESI.† It should also be noted that no significant solvatochromism is observed in the UV-visible absorption spectra of L<sub>3</sub>. The solvent-dependent emission demonstrates the presence of a highly polarized exited state<sup>15</sup> in which the lowest unoccupied molecular orbital (LUMO) level may be dominated by the phenanthroline unit, while the highest occupied molecular orbital (HOMO) can be dominated by the triphenylamine group.<sup>16</sup> L<sub>3</sub> was found to be a very bright emitter in solution, and its quantum yield was determined to be 0.49, 0.40 and 27.7 in toluene, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN respectively, which are higher than the data of other ligands (Table S1, ESI<sup>†</sup>). L<sub>3</sub> in the solid state emits weak fluorescence and its emission peak is red shifted about 23 nm in comparison with emission in CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 2). The red shift phenomenon can be attributed to the  $\pi$ -stacking of the aromatic rings in these molecules in the solid state.

The photophysical properties of **1–3** are listed in Table 2. The absorption spectra of three complexes in dilute CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 3a. These spectra display a strong absorption around 280 nm and a broad absorption between 330 and 490 nm. The absorption at high energy is primarily due to the  $\pi$ – $\pi$ \* transition of the phenanthroline moiety in their ligands, and the lower energy absorption band is typically from the spin-allowed



Fig. 2 Absorption and emission spectra of  $L_3$  in solution and solid state.

metal ( $d\pi$ ) to ligand ( $\pi^*$ ) charge transfer (MLCT).<sup>17</sup> The MLCT absorption bands of three complexes are similar to those previously reported for rhenium(1) complexes with similar ligands.<sup>18</sup> Excitations at the  $\pi$ - $\pi$ \* and MLCT absorption frequencies do not lead to the same MLCT emission at room temperature for 1-3, indicating that potential surface crossing from the higher  $\pi - \pi^*$ state to the lower MLCT state is not efficient.<sup>19</sup> The emission spectra of complexes 1-3 show a similar profile in CH<sub>2</sub>Cl<sub>2</sub> with exited wavelength at peak of corresponding MLCT absorption (Fig. 3a). The emission peaks at about 570 nm for these complexes should predominantly be as a result of the <sup>3</sup>MLCT exited state. In the solid state, an emission band at about 550 nm can be observed at room temperature for complexes 1-3 (Fig. 3b). Their maximum emission peaks display pronounced hypsochromic shifts in comparison to the ones observed in CH<sub>2</sub>CI<sub>2</sub>. This phenomenon is typical for phosphorescent emission from the <sup>3</sup>MLCT excited state, which has been observed in other rhenium(I) complexes in the literature.<sup>20,21</sup> The excited state lifetime of 1-3 at 570 nm in CH<sub>2</sub>Cl<sub>2</sub> is listed in Table 3. The values of the lifetime in the range 13-80 ns were determined by exponential decay curve-filling analysis (Fig. S6, ESI<sup>+</sup>). The short excited state lifetime may provide the opportunity to use them for highly efficient OLEDs.

## Electrochemistry

The electrochemical properties of complexes 1-3 were investigated by cyclic voltammetry (CV) measurements and the results are given in Table 2. Three complexes show a reduction reaction with reduction potentials in the range -1.43 V to -1.57 V in CH<sub>3</sub>CN solution, which can be assigned to the redox couple of the phenanthroline ligand. For complexes 1 and 2, an oxidation reaction with a potential of about +1.00 V was observed, which process takes place on a centred metal rhenium(I) associated with the Re(I)/Re(II) redox couple. In contrast to 1 and 2, two oxidation reactions were observed for 3. The first oxidation reaction at the low potential of around +0.65 V could be ascribed to the oxidation of the triphenylamine unit in its ligand, while the second oxidation reaction with a potential of about +1.07 V should be for the Re(I)/Re(II) redox couple. As an example, the CV curves of 2 and 3 are shown in Fig. 4. The HOMO energy levels of complex 3 estimated from its first oxidation potential is -5.36 eV. This data reveals that the introduction of the triphenylamine unit to the ligand lowers the barrier height of these complexes for hole injection, thereby facilitating the transfer of holes.

## Thermal analysis

Thermogravimetric analysis (TGA) was performed on 1–3 to investigate their thermal stability. The thermal decomposition temperatures of these complexes are given in Table 2. All complexes 1–3 show high thermal decomposition temperatures (307–343 °C), which demonstrates their good thermal stability. The TGA traces of three complexes exhibit two thermal decomposition processes. As examples, the first weight loss step starts from 343 °C, and the second weight loss step starts from 436 °C for complex 3 (Fig. S7, ESI†). The first thermal decomposition process might be attributed to the loss of the carbonyl

Table 2 Photophysical, electrochemical, thermal and infrared data for complexes 1-3

Complex	$\lambda_{abs}{}^a$ (nm) $\epsilon \times 10^3 \text{ M}^{-1} \text{cm}^{-1}$	$\lambda_{ex}^{b}$ (nm)	$\lambda_{em}^{c}$ (nm)	$\lambda_{\rm em}^{\ \ d}  ({\rm nm})$	Lifetime (ns)	$E_{\text{onset}}^{\text{ox}} e(\mathbf{v})$	$E_{\text{onset}}^{\text{red}\ e}(\mathbf{v})$	$E_{\rm red}^{f}(\mathbf{v})$	$T_d^g (^\circ C)$	FT-IR (cm <sup>-1</sup> ) CO
1	275(11.3), 394(2.8)	344, 418	570	550	42.82	0.98	-1.58	-1.57	310	1886, 1913, 2020
2	276(27.4), 343(5.1), 390(2.1)	315, 346	571	549	66.74	1.00	-1.58	-1.54	307	1869, 1909, 2021
3	282(17.3), 392(4.7)	382, 431	570	551	79.49	0.65, 1.03	-1.55	-1.43	343	1882, 1913, 2017

<sup>*a*</sup> Maximum absorption wavelength, measured in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>*b*</sup> Maximum excitation wavelength, measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*c*</sup> Maximum emission wavelength, measured in the solid state. <sup>*e*</sup> Estimated by CV using a platinum disk as the working electrode, platinum wire auxiliary electrode, Ag/Ag<sup>+</sup> reference electrode with ferrocene as the internal standard, Bu<sub>4</sub>NBF<sub>4</sub> as supporting electrolyte in CH<sub>3</sub>CN. <sup>*f*</sup> These data were calculated using the  $E_{onset}^{ox}$  and the optical bandgap. <sup>*g*</sup> Thermal decomposition temperature.



Fig. 3 Absorption and emission spectra of complexes 1-3 in  $CH_2Cl_2$  (a) and in the solid state (b).

 Table 3
 Summary of the performance of complexes 1–3 based OLEDs

Complex	Concentration	${\eta_1}^a$	$\eta_2^{\ b}$	$B_{\max}^{c}$	$\eta_3^{d}$
1	0.5	7.10	5.42	3140	3.19
	1.0	10.74	7.08	3074	4.82
2	0.5	8.85	6.79	2742	4.19
	1.0	6.79	5.41	4219	2.91
3	0.25	8.1	7.0	5233	2.83
	0.5	10.8	9.5	6490	4.30
	1.0	12.2	11.4	7308	2.74
	2.0	9.8	8.1	6237	2.48
<sup>a</sup> Maximun	efficiency (cd $A^{-1}$ )	. <sup>b</sup> Efficien	cy at 1000	cd $m^{-2}$ (c	d A <sup>-1</sup> ).

groups and partial decomposition of their ligands, while the second weight loss process is likely to be caused by the loss of their ligands. The good thermal stability of new rhenium(I) complexes is important for application in OLEDs.



Fig. 4 CV curves of complex 2 (a) and 3 (b) measured in  $CH_3CN$  at 0.1 v/s scan rate.

## Electroluminescence

Polymer-based light-emitting diodes with the new rhenium(1) complex 1, 2 or 3 as a dopant were fabricated by the spin casting and their EL performances were investigated. To our knowledge, there are very few reports on EL devices using solution processable rhenium(I) complexes as the emission layer and their EL performances are not expected.<sup>10</sup> The crystal structure of 1 reveals these complexes have a strong aggregation tendency in the solid state. If these rhenium(I) complexes are dispersed as a guest in a polymer host, it can suppress the intermolecular interaction of the dopant and increase the performances of the EL device. The polymer blend PVK-PBD (40 wt%) was selected as the host, for which the emission band overlaps with the absorption bands of these rhenium(I) complexes. PVK is a good hole-transporting material while PBD is an electron-transporting material. Employment of the PVK-PBD mixture host would enhance balance of carriers in the light-emitting layer and thus enhance the emitting efficiency of devices.<sup>22</sup> Indium-tinoxide (ITO) glass and aluminum were used as the anode and cathode, respectively. In addition, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and LiF were used as materials for facilitating the hole and electron injection from the two electrodes, and 2,2',2"-(1,3,5-benzenetriyl) tris[1-phenyl-benzimidazole] (TPBI) was chosen as an electron-transporting material. The structure of the devices are as follows: ITO/PEDOT:PSS (40 nm)/PVK–PBD (40 wt%): x wt% rhenium(i) complex (80 nm)/TPBI (40 nm)/LiF (0.7 nm)/Al (100 nm). The rhenium(i) complex was doped into the host PVK– PBD in the range 0.25–2.0 wt% as the light-emitting layer. The thickness of the doped light-emitting layer is about 80 nm. The TPBI layer and the electrode layers were deposited by a resistive heating method. Atomic force microscopy (AFM) was employed to explore the surface image of light-emitting layer containing rhenium(i) complexes guest and PVK–PBD host. The AFM images reveal similar smooth and uniform topographies, free of pinholes, particle aggregation, or phase separation, with rootmean-square surface roughnesses of about 0.60 nm for these complexes (Fig. S8, ESI†). This suggested that new rhenium(i) complexes good miscibility to the PVK–PBD blend.

The selected performance parameters of the OLEDs based on 1, 2 and 3 are summarized in Table 3. The device performance shows a dependence on the doping concentration, when 1, 2 and 3 were blended with PVK–PBD in a mass ratio of 1.0%, 0.5% and 1.0% respectively, the devices demonstrate the best performances. Fig. 5a presents the current density–brightness–voltage characteristics of the optimized devices. The turn-on voltage, that is the voltage needed to reach 1 cd m<sup>-2</sup>, is 7 V, 7 V and 8 V for optimized devices of 1, 2 and 3, respectively. The maximum luminance of optimized device is 3074, 2742 and 7308 cd m<sup>-2</sup> at a corresponding driving voltage. These values of maximum brightness observed for the EL devices based on new rhenium(1) complexes are higher than the 960 cd m<sup>-2</sup> previously reported for a device based on the [Re<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -diazine)] complex



Fig. 5 Current density-brightness-voltage curves (a) and current efficiency-current density curves (b) of 1 (1.0 wt%), 2 (0.5 wt%) and 3 (1.0 wt%) based devices.

incorporated into PVK polymer with a device structure of ITO/ PEDOT:PSS/PVK:Re<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -diazine)/TPBI/Ba/Al,<sup>10b</sup> and higher than 730 cd m<sup>-2</sup> for a rhenium(1) complex with derivative 2,2'-bipyridine doped in host material of polycarbonate (PC) and the device configuration of ITO/ PVK:Re:PC/Al.<sup>10c</sup> Fig. 5b shows the current efficiency–current density characteristics of the optimized devices and all devices exhibit a slowly decrease in the efficiency with an increase in the current density. These devices based on new rhenium(1) display high efficiency, which is 10.74 cd A<sup>-1</sup> for 1 and 8.85 cd A<sup>-1</sup> for 2, respectively. In particular, a maximum efficiency as high as 12.2 cd A<sup>-1</sup> was obtained from the device doped with 1.0 wt% of 3.

The value of maximum current efficiency observed for the EL devices studied in this paper was enhanced about 6-fold compared to the best previously reported value (2.1 cd A<sup>-1</sup>).<sup>10d</sup> For these devices, the current efficiencies at the benchmark luminance of 100 cd m<sup>-2</sup> are close to their maximum efficiencies. When the luminance reaches to 1000 cd  $m^{-2}$ , the 1.0 wt % of 3 doped device still exhibits a maximum current efficiency of 11.4 cd  $A^{-1}$ . Even at a much higher luminance of 5000 cd  $m^{-2}$  with current density of 81 mA cm<sup>-2</sup>, the current efficiency of this device remains as high as  $6.4 \text{ cd } A^{-1}$ , which is higher than half of the peak value. The slow decrease in current efficiency with increasing the current density has been attributed to the fact that the saturation of the phosphorescence sites under these conditions is not severe<sup>6c</sup> due to the short triplet lifetime of the lightemitting material.23 Nevertheless, the performances of these devices are greatly improved in comparison with the previously reported results from OLEDs fabricated by solution processable rhenium(1) complexes.<sup>9</sup> It seems that the introduction of the methoxyphenyl or the diphenylaminophenyl group on the 1,10phenanthroline skeleton can decrease molecular interaction of rhenium complexes, and restrain the effect of triplet-triplet annihilation. In particular, the triphenylamine moiety in 3 can also improve the hole injection ability of this complex. In addition, efficient exciton formation on the rhenium(I) molecules by direct electron and hole capturing is also responsible for the excellent performances. Generally, this can be estimated from the analysis of the PL and EL spectra of PVK films with different concentrations of 3 and energy levels of emitting and transporting materials.

To test the efficiency of Förster energy transfer, PVK-PBD films containing different concentrations of 3 were prepared and their PL spectra were determined with an excitation radiation of 325 nm. The normalized PL spectra of these films are shown in Fig. 6a. There are two emission peaks in these PL spectra: the one centred at ~425 nm is from the PVK-PBD host; the other peak with lower energy is a result from 3. The emission at 425 nm decreases significantly with the increasing in doping concentration of 3, and disappears at doping concentrations of 3 higher than 2.0 wt%. The decrease in the host emission and the simultaneous increase in the emission of 3 are consistent with Förster energy transfer from the PVK-PBD host to 3.<sup>24</sup> Fig. 6b shows the corresponding EL spectra obtained with the devices made from the same solutions. The emission of the host disappears at doping concentrations of 3 higher than 0.5 wt%. The host EL emission is completely converted into the emission of 3 at lower doping concentration than that observed for the PL emission, suggesting that the molecules of 3 act as recombination centers. The EL



**Fig. 6** PL spectra (a) and EL spectra (b) of **3** with different concentrations in PVK–PBD (40 wt%) films.

emission spectra dominated by 3 have a central wavelength at 560 nm and the maximum emission peaks do not vary with the change in doping concentration (Fig. 6b).

The HOMO and LUMO energies of PVK, PBD, TPBI and **3** were estimated by CV measurements. By comparing the HOMO energies of **3** (-5.36 eV) and PVK (-5.55 eV), it is evident that the guest molecule of **3** would be a hole trap with a depth of *ca*. 0.19 eV (Fig. S9, ESI†). On the other hand, the LUMO energy of **3** (-3.16 eV) is lower than the ones of TPBI (-2.70 eV) and PBD (-2.54 eV), which indicate that **3** would also be a good electron trap. So the holes and electrons in the emissive layer can be trapped directly by molecules of **3**. Fig. S10, ESI,† shows the current–voltage (*I–V*) characteristics of devices with different doping concentrations of **3**. The turn-on voltage increases with the increase in the doping concentration of **3**, which is clear evidence for charge trapping in the doped system.<sup>24a</sup>

# Conclusions

In summary, three new rhenium(1) complexes with substituted diimine ligands were synthesized, characterized and their photophysical and electroluminescent properties have been studied. Crystal structure analysis reveals rhenium(1) complexes adopt distorted octahedron geometry and have a strong aggregation tendency in the solid state. These rhenium(1) complexes exhibit bright yellow luminescence with relatively short triplet lifetime. The high-efficiency polymer-based electrophosphorescent lightemitting devices have been fabricated using rhenium(1) complexes as dopant and PVK–PBD as host. In particular, **3** doped devices exhibited a maximum current efficiency up to 12.2 cd  $A^{-1}$ , and a peak brightness as high as 7308 cd  $m^{-2}$ . Even at

a high luminance of 5000 cd m<sup>-2</sup>, the high current efficiency of 6.4 cd  $A^{-1}$  can be maintained. To the best our knowledge, these performances are the best reported for devices by spin casting technology employing solution rhenium(I) complexes as the emission layer. We suggest that short triplet lifetime, enhanced charge injection, and efficient charge capturing are responsible for the excellent performances of devices fabricated with solution processable complexes as the luminescent layer.

# **Experimental section**

#### **General information**

All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene and diethyl ether were dried by refluxing over sodium and benzophenone and distilled under nitrogen prior to use. Solvents used in luminescent and electrochemical studies were anhydrous and of spectroscopic grade. CH<sub>3</sub>CN, Bu<sub>4</sub>NBF<sub>4</sub>, PVK, PBD, TPBI, PEDOT:PSS, 1,10-phenanthroline and "BuLi were purchased from Aldrich and used as received. The FT-IR spectra were acquired using a Magna560 spectrophotometer. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. The elemental analysis was performed on a Perkin-Elmer 2400 analyzer. UV-vis absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence measurements were carried out on an RF-5301PC. Room-temperature luminescence quantum yields were measured at a single excitation wavelength (360 nm) referenced to quinine sulfate in sulfuric acid aqueous solution ( $\Phi = 0.546$ ). The quantum yields were calculated using known procedures.<sup>25</sup> Time-resolved fluorescence measurements were performed by the time-correlated single photon counting (TCSPC) system under right-angle sample geometry. A 379 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 20MHz) were used to excite the sample. The emission was detected by a photomultiplier tube (Hamamatsu H5783p) and a TCSPC board (Becker&Hickel SPC-130). The instrument response function (IRF) is about 220 ps. All measurements were done at room temperature (22 °C). TGA was performed on  $\sim 2$  mg of 1–3 using a Perking-Elmer thermal analyzer in air. The samples were dried under vacuum at 60 °C before being heated to 600 °C at a heating rate of 10.0 °C min-1. Electrochemical measurements were performed with a BAS 100W bioanalytical system, using a platinum disk ( $\varphi = 3$ mm) as the working electrode, a platinum wire as the auxiliary electrode, and a porous glass wick Ag/Ag<sup>+</sup> as the reference electrode with ferrocenium-ferrocene (Fc<sup>+</sup>/Fc) as the internal standard. CV studies of 1-3, PBD, TPBI and PVK were carried out at a scan rate of 100 mV s<sup>-1</sup> in CH<sub>3</sub>CN containing, 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> as the supporting electrolyte. From the onset, the anodic peak potential for the oxidation process,  $E_{onset}^{ox}$ , and the onset cathodic peak potential for the reduction process,  $E_{onset}^{red}$ , and the HOMO and LUMO energy levels of compound were estimated according to the following formula:  $E_{\text{HOMO}} = -4.71 - 4.71$  $E_{\text{onset}}^{\text{ox}}$  and  $E_{\text{LUMO}} = -4.71 - E_{\text{onset}}^{\text{red}}$ .

## **Device fabrication**

ITO-coated glass with a sheet resistance of  $<50^{\circ}\Omega \square^{-1}$  was used as substrate. The substrate was pre-patterned by photolithography to form the pattern of devices in size of 4 mm<sup>2</sup>. Pre-treatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. Spin-coating with solutions containing rhenium(1) complexes (0.5–2.0 wt%) in polymer host (PVK–PBD, 40 wt%) (10 mg ml<sup>-1</sup>) in chloroform on ITO substrate gives the active layer with a thickness of 80 nm. The TPBI, LiF and Al was deposited by thermo-evaporation. The luminance of devices was recorded on a PR650 spectrometer. Current–voltage and light intensity measurements were carried out at room temperature and ambient conditions.

## X-ray structure determinations of 1

Single crystals of 1 suitable for X-ray structural analysis were obtained from CH<sub>2</sub>Cl<sub>2</sub>. Diffraction data were collected at 293 K on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) for two complexes. Details of the crystal data, data collection and structure refinements are summarized in Table 4. The structure was solved by direct methods<sup>26</sup> and refined by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL<sup>27</sup> crystallographic software package.

#### Synthesis

Synthesis of L<sub>3</sub>. A solution of "BuLi (7.57 ml, 12.12 mmol) in hexane was added to a solution of 4-bromotriphenylamine (3.93 g, 12.12 mmol) in Et<sub>2</sub>O (15 mL) under a nitrogen atmosphere at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was added dropwise to an ice-cooled solution of 1,10-phenanthroline

Table 4	Crystal da	ta and structura	al refinement	details for	complex 1
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	1			
Formula	C <sub>22</sub> H <sub>14</sub> ClN <sub>2</sub> O <sub>4</sub> Re			
Fw	592.00			
Temp. (K)	293(2)			
Wavelength (Å)	0.71073			
Crystal system	Triclinic			
Space group	P-1			
a (Å)	9.808(2)			
b (Å)	11.209(2)			
c (Å)	12.043(2)			
$\alpha$ (°)	79.92(3)			
$\beta$ (°)	87.34(3)			
$\gamma$ (°)	65.46(3)			
$V(A^3)$	1185.2(4)			
Z	2			
$d_{\rm c} ({\rm Mg}\ {\rm m}^{-3)}$	1.897			
F(000)	568			
Crystal size (mm)	$0.25\times0.23\times0.21$			
$\theta$ range for data collection	3.07° to 24.71°			
limiting indices	$-12 \le h \le 11$			
	$-14 \le k \le 14$			
	$-15 \le l \le 15$			
data/restraints/parameters	4033/0/284			
goodness-of-fit on $F^2$	1.088			
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1^a = 0.0344$			
	$WR_2^{\ b} = 0.0927$			
<sup><i>a</i></sup> $R_1 = \sum   F_o  -  F_c   / \sum  F_o $ . <sup><i>b</i></sup> $wR_2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$ .				

(2.18 g, 12.12 mmol) degassed Et<sub>2</sub>O (20 mL), and a wine-red solution was obtained immediately. The resultant mixture was refluxed for 12 h and cooled in an ice bath, then deionized water (30 mL) was added to hydrolyze the products. The yellow organic phase was separated and stirred with MnO<sub>2</sub> for 48 h, then filtered and dried with MgSO4. The solid was obtained upon concentration of the solution, and chromatography on silica gel with dichloromethane as the eluent afforded a light vellow powder. Yield: 55%. Anal. Calcd for C<sub>30</sub>H<sub>21</sub>N<sub>3</sub> (423.51): C, 85.08; H, 5.00; N, 9.92. Found: C, 85.22; H, 4.83; N, 9.95. 1 H NMR (300 MHz, CDCl<sub>3</sub>, 293 K):  $\delta$  7.06 (t, J = 4.5 Hz, 2H), 7.17 (b, J = 4.8 Hz, 4H), 7.22 (b, J = 5.1 Hz, 2H), 7.29 (t, J = 2.1 Hz, 4H), 7.67 (s, 1H), 7.77 (b, J = 5.4 Hz, 1H), 7.83 (b, J = 5.4 Hz, 1H), 8.07 (b, J = 5.1 Hz, 1H), 8.28 (b, J = 5.1 Hz, 4H), 9.27 (s, 1H) ppm. <sup>13</sup> C NMR (75 MHz, CDCl<sub>3</sub>, 293 K): δ 120.1, 122.9, 123.2, 124.9, 125.4, 125.9, 126.8, 127.3, 128.8, 129.1, 129.4, 133.3, 136.6, 136.8, 145.7, 147.6, 149.3, 149.8, 157.5 ppm.

Synthesis of 1. L<sub>1</sub> (80.1 mg, 0.28 mmol) and Re(CO)<sub>5</sub>Cl (100 mg, 0.27 mmol) were refluxed in 15 mL of toluene for 10 h. After the mixture was cooled to room temperature, the solvent was removed in a water bath under reduced pressure. The resulting yellow solid was purified by silica gel column chromatography with acetic acid ethyl ester and dichloromethane. Yield: 0.13 g (85%). <sup>1</sup> H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 293 K):  $\delta$  3.76 (s, 3H, OC*H*<sub>3</sub>), 7.19 (t, *J* = 3 Hz, 1H), 7.27 (d, *J* = 6 Hz, 1H), 7.37 (d, *J* = 3 Hz, 1H), 7.60 (t, *J* = 6 Hz, 1H), 8.05 (d, *J* = 3 Hz, 1H), 8.11 (t, *J* = 3 Hz, 1H), 8.96–9.00 (m, 2H), 9.45 (d, 1H) ppm. Anal. Calcd for C<sub>22</sub>H<sub>14</sub>CIN<sub>2</sub>O<sub>4</sub>Re (592.02): C, 44.63; H, 2.38; N, 4.73; Found: C, 44.58; H, 2.46; N, 4.65. IR (KBr): *v* 1886, 1913, 2020 cm<sup>-1</sup>.

**Synthesis of 2.** The procedure is similar to that of **1**. <sup>1</sup> H NMR (300 MHz, DMSO- $d_6$ , 293 K):  $\delta$  3.88 (s, 3H, OCH<sub>3</sub>), 7.19 (d, J = 6 Hz, 2H), 7.66–7.68 (m, 2H), 8.10 (d, J = 3 Hz, 1H), 8.16 (d, J = 6 Hz, 1H), 8.36 (d, J = 6 Hz, 2H), 8.97 (d, J = 6 Hz, 1H), 9.00 (d, J = 6 Hz, 1H), 9.47 (s, 1H) ppm. Anal. Calcd for C<sub>22</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>4</sub>Re (592.02): C, 44.63; H, 2.38; N, 4.73; Found: C, 44.57; H, 2.40; N, 4.77. IR (KBr):  $\nu$  1869, 1909, 2021 cm<sup>-1</sup>.

**Synthesis of 3.** The procedure is similar to that of **1**. <sup>1</sup> H NMR (300 MHz, DMSO- $d_6$ , 293 K):  $\delta$  7.14–7.19 (m, 8H), 7.40 (t, J = 6Hz, 4H), 7.57–7.65 (m, 2H), 8.11 (dd, J = 3 Hz, 1H), 8.19 (d, J = 6 Hz, 1H), 8.35 (dd, J = 3 Hz, 2H), 8.97 (d, J = 3 Hz, 1H), 8.99 (d, J = 6 Hz, 1H), 9.47 (d, J = 3 Hz, 1H) ppm. Anal. Calcd for C<sub>33</sub>H<sub>21</sub>ClN<sub>3</sub>O<sub>3</sub>Re (729.20): C, 54.35; H, 2.90; N, 5.76; Found: C, 54.43; H, 2.76; N, 5.71. IR (KBr):  $\nu$  1882, 1913, 2017 cm<sup>-1</sup>.

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#### Notes and references

- (a) M. A. Baldo, D. F. O'Brian, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151; (b) M. A. Baldo, M. E. Thompson and S. R. Forrest, *Pure Appl. Chem.*, 1999, **71**, 2095.
- 2 Y. G. Ma, H. Y. Zhang, J. C. Shen and C. M. Che, Synth. Met., 1998, 94, 245.

- 3 (a) H. Sasabe, J. Takamatsu, T. Motoyama, S. Watanabe, G. Wagenblast, N. Langer, O. Molt, E. Fuchs, C. Lennartz and J. Kido, *Adv. Mater.*, 2010, **22**, 5003; (b) M. Bandini, M. Bianchi, G. Valenti, F. Piccinelli, F. Paolucci, M. Monari, A. Umani-Ronchi and M. Marcaccio, *Inorg. Chem.*, 2010, **49**, 1439.
- 4 (a) S. C. F. Kui, I. H. T. Sham, C. C. C. Cheung, C. W. Ma, B. Q. Yan, N. Y. Zhu, C. M. Che and W. F. Fu, *Chem.-Eur. J.*, 2007, **13**, 417; (b) Y. Unger, D. Meyer, O. Molt, C. Schildknecht, I. Munster, G. Wagenblast and T. Strassner, *Angew. Chem., Int. Ed.*, 2010, **49**, 10214.
- 5 (a) H. Xia, Y. Y. Zhu, D. Lu, M. Li, C. B. Zhang, B. Yang and Y. G. Ma, J. Phys. Chem. B, 2006, 110, 17784; (b) H. Xia, M. Li, D. Lu, C. B. Zhang, W. J. Xie, X. D. Liu, B. Yang and Y. G. Ma, Adv. Funct. Mater., 2007, 17, 1757; (c) H. Xia, C. B. Zhang, S. Qiu, P. Lu, J. Y. Zhang and Y. G. Ma, Appl. Phys. Lett., 2004, 84, 290; (d) J. H. Yang and K. C. Gordon, Chem. Phys. Lett., 2004, 385, 481.
- 6 (a) F. Li, M. Zhang, G. Cheng, J. Feng, Y. Zhao, Y. G. Ma, S. Y. Liu and J. C. Shen, *Appl. Phys. Lett.*, 2004, **84**, 148; (b) N. J. Lundin, A. G. Blackman, K. C. Gordon and D. L. Officer, *Angew. Chem.*, *Int. Ed.*, 2006, **45**, 2582; (c) G. Che, Z. Su, W. Li, B. Chu, M. Li, Z. Hu and Z. Zhang, *Appl. Phys. Lett.*, 2006, **89**, 103511.
- 7 (a) C. B. Liu, J. Li, B. Li, Z. R. Hong, F. F. Zhao, S. Y. Liu and W. L. Li, *Appl. Phys. Lett.*, 2006, **89**, 243511; (b) X. Li, D. Y. Zhang, W. L. Li, B. Chu, L. L. Han, J. Z. Zhu, Z. S. Su, D. F. Bi, D. Wang, D. F. Yang and Y. R. Chen, *Appl. Phys. Lett.*, 2008, **92**, 083302; (c) Z. J. Si, J. Li, B. Li, F. F. Zhao, S. Y. Liu and W. L. Li, *Inorg. Chem.*, 2007, **46**, 6155.
- 8 A. J. Lees, Coord. Chem. Rev., 1998, 177, 3.
- 9 (a) M. V. Werrett, D. Chartrand, J. D. Gale, G. S. Hanan, J. G. Maclellan, M. Massi, S. Muzzioli, P. Raiteri, B. W. Skelton, M. Silberstein and S. Stagni, *Inorg. Chem.*, 2011, **50**, 1229; (b) J. M. Villegas, S. R. Stoyanov, W. Huang and D. P. Rillema, *Dalton Trans.*, 2005, 1042; (c) R. Horvath, C. A. Otter, K. C. Gordon, A. M. Brodie and E. W. Ainscough, *Inorg. Chem.*, 2010, **49**, 4073; (d) M. G. Fraser, A. G. Blackman, G. I. S. Irwin, C. P. Easton and K. C. Gordon, *Inorg. Chem.*, 2010, **49**, 5180.
- (a) Y. Y. Lu, C. C. Ju, D. Guo, Z. B. Deng and K. Z. Wang, J. Phys. Chem. C, 2007, 111, 5211; (b) M. Mauro, E. Q. Procopio, Y. H. Sun, C. H. Chien, D. Donghi, M. Panigati, P. Mercandelli, P. Mussini, G. D'Alfonso and L. De Cola, Adv. Funct. Mater., 2009, 19, 2607; (c) W. K. Chan, P. K. Ng, X. Gong and S. J. Hou, Appl. Phys. Lett., 1999, 75, 3920; (d) Y. P. Wang, W. F. Xie, B. Li and W. L. Li, Chin. Phys. Lett., 2007, 18, 1501; (e) G. David, P. J. Walsh and K. C. Gordon, Chem. Phys. Lett., 2004, 383, 292.
- 11 (a) X. M. Liu, X. Y. Mu, H. Xia, L. Ye, W. Gao, H. Y. Wang and Y. Mu, *Eur. J. Inorg. Chem.*, 2006, 4317; (b) X. M. Liu, H. Xia, W. Gao, B. Gao and Y. Mu, *J. Coord. Chem.*, 2009, **62**, 400.

- 12 M. Zhang, P. Lu, X. M. Wang, H. Xia, W. Zhang, B. Yang, L. L. Liu, L. Yang, M. Yang, Y. G. Ma, J. K. Feng and D. J. Wang, *Thin Solid Films*, 2005, **477**, 193.
- 13 (a) D. L. Reger, R. P. Watson, M. D. Smith and P. J. Pellechia, Organometallics, 2006, 25, 743; (b) N. M. Shavaleev, A. Barbieri, Z. R. Bell, M. D. Ward and F. Barigelletti, New J. Chem., 2004, 28, 398; (c) D. L. Reger, R. P. Watson and M. D. Smith, J. Organomet. Chem., 2007, 692, 3094.
- 14 (a) Q. H. Wei, G. Q. Yin, L. Y. Zhang and Z. N. Chen, *Inorg. Chem.*, 2006, **45**, 10371; (b) F. Kennedy, N. M. Shavaleev, T. Koullourou, Z. R. Bell, J. C. Jeffery, S. Faulkner and M. D. Ward, *Dalton Trans.*, 2007, 1492.
- 15 (a) W. L. Jia, M. J. Moran, Y. Y. Yuan, Z. H. Lu and S. N. Wang, J. Mater. Chem., 2005, 15, 3326; (b) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi and K. Tamao, Angew. Chem., Int. Ed., 2003, 42, 2036.
- 16 Z. Y. Ge, T. Hayakawa, S. Ando, M. Ueda, T. Akiike, H. Miyamoto, T. Kajita and M. Kakimoto, *Org. Lett.*, 2008, 10, 421.
- 17 K. K. W. Lo, J. S. Y. Lau, V. W. Y. Fong and N. Y. Zhu, Organometallics, 2004, 23, 1098.
- 18 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 and G. H. Lee, *Inorg. Chem.*, 2003, **42**, 1248.
- 19 L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1990, 29, 4335.
- 20 M. M. Richter, J. D. Debad, D. R. Striplin, G. A. Crosby and A. J. Bard, *Anal. Chem.*, 1996, **68**, 4370.
- 21 (a) V. W. W. Yam, K. Z. Wang, C. R. Wang, Y. Yang and K. K. Cheung, *Organometallics*, 1998, **17**, 2440; (b) S. Das and B. K. Panda, *Polyhedron*, 2006, **25**, 2289.
- 22 X. Gong, M. R. Robinson, J. C. Qstrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2002, 14, 581.
- 23 (a) A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino and K. Ueno, J. Am. Chem. Soc., 2003, 125, 12971; (b) X. Li, D. Zhang, H. Chi, G. Xiao, Y. Dong, S. Wu, Z. Su, Z. Zhang, P. Lei, Z. Hu and W. Li, Appl. Phys. Lett., 2010, 97, 263303.
- 24 (a) R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **83**, 3818; (b) H. Xia, C. B. Zhang, X. D. Liu, S. Qiu, P. Lu, F. Z. Shen, J. Y. Zhang and Y. G. Ma, *J. Phys. Chem. B*, 2004, **108**, 3185.
- 25 K. Ye, J. Wang, H. Sun, Y. Liu, Z. Mu, F. Li, S. Jiang, J. Zhang, Y. Wang and C. M. Che, J. Phys. Chem. B, 2004, 109, 8008.
- 26 SHELXTL; PC Siemens Analytical X-ray Instruments: Madison WI, 1993.
- 27 G. M. Sheldrick, SHELXTL Structure Determination Programs, Version 5.0; PC Siemens Analytical Systems: Madison, WI, 1994.