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Synthesis, electrochemistry and structural characterization of luminescent rhenium(I) monoynyl complexes and their homo- and hetero-metallic binuclear complexes

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Abstract

A series of luminescent rhenium(I) monoynyl complexes, $[Re(N–N)(CO)_3(C\equiv C–R)]$ (N–N = bpy, $^tBu_2bpy$; R = C_6H_5, $C_6H_4–Cl$-4, $C_6H_4–OCH_3$-4, $C_6H_4–C_8H_{17}$-4, $C_6H_4–C_6H_5$, C_8H_{17}, C_4H_3S, $C_4H_2S–C_4H_3S$, C_5H_4N), together with their homo- and hetero-metallic binuclear complexes, $\{Re(N–N)(CO)_3(C\equiv C–C_5H_4N)[M]\}$ (N–N = bpy, $^tBu_2bpy$; [M] = $[Re\{(CF_3)_2$-bpy$\}(CO)_3]ClO_4$, $[Re(NO_2$-phen$)(CO)_3]ClO_4$, $W(CO)_5$) have been synthesized and their electrochemical and photoluminescence behaviors determined. The structural characterization and electronic structures of selected complexes have also been studied. The luminescence origin of the rhenium(I) alkynyl complexes has been assigned as derived states of a $[d\pi(Re) \rightarrow \pi^*(N–N)]$ metal-to-ligand charge transfer (MLCT) origin mixed with a $[\pi(C\equiv CR) \rightarrow \pi^*(N–N)]$ ligand-to-ligand charge transfer (LLCT) character. The assignments are further supported by extended Hückel molecular orbital (EHMO) calculations, which show that the LUMO mainly consists of $\pi^*(N–N)$ character while the HOMO is dominated by the antibonding character of the Re–$C\equiv CR$ moiety resulted from the overlap of the $d\pi(Re)$ and $\pi(C\equiv CR)$ orbitals.
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1. Introduction

In recent years, there has been a rapidly growing interest in the design and synthesis of organometallic complexes containing carbon-rich, rigid and π-conjugated chains due to their potential use as precursors for the syntheses of organometallic polymers [1] and π-conjugated bi- or multi-metallic systems. This class of complexes also exhibit significantly altered physical properties compared with their conjugated organic oligomers and polymers [2]. The preparations of one-dimensional organometallic polymers have also been reported [1,2]. Despite the growing interests and studies in metal alkynyl systems, relatively less attention was

focused on the luminescence behavior of this class of compounds [3–10]. As a continuing research effort on the luminescence studies of d^8 and d^{10} transition-metal alkynyl complexes [11–16], the d^6 metal polypyridine complexes with intriguing metal-to-ligand-charge-transfer (MLCT) excited states have aroused our interests and we have recently explored on the luminescence studies of rhenium(I) alkynyl complexes. Incorporation of the alkynyl framework into the luminescent rhenium(I) diimine system has been achieved and reported by us and the effects on the luminescence behavior upon extension of the sp carbon chain and coordination of d^{10} metal centers onto the alkynyl ligand have also been explored [17].

Since we have developed a rather general synthetic route for the preparation of luminescent rhenium(I) alkynyl diimine complexes, the incorporation of functionalized alkynyl groups into these complexes may

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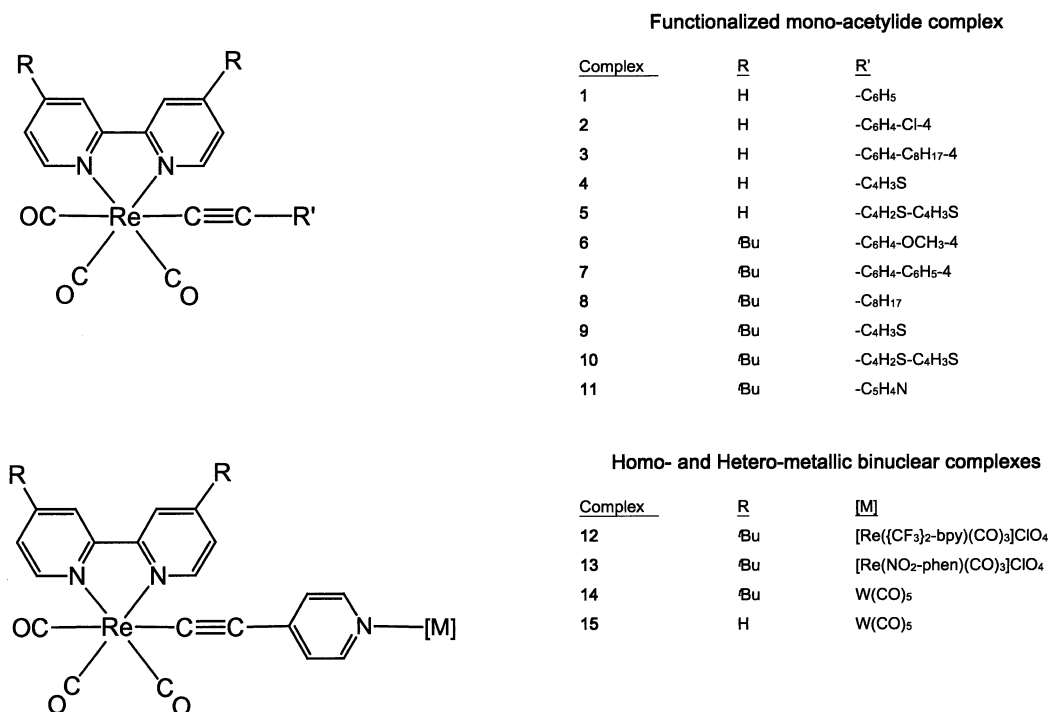*E-mail address:* wwyam@hku.hk (V.W.-W. Yam).

represent an interesting area of research. In this regard, we have identified two major areas. One involves the use of thiophene and bithiophene moieties as the functional unit since oligo- and polythiophenes are currently attracting a great deal of attention due to the fact that the properties of one-dimensional organometallic polymers can be fine-tuned by variation of the fragments of the chain [18]. Another area involves the incorporation of coordinating ligands such as pyridine to the alkynyl unit since this would open up new avenues for the construction of homo- and hetero-binuclear complexes by making use of the rhenium(I) alkynyl complex as the building block. In view of these, a series of rhenium(I) monoynyl complexes containing different diimine ligands and alkynyl groups including thiophene, bithiophene and pyridyl substituents $[Re(N-N)(CO)_3(C \equiv C-R)]$ (N–N = bpy, R = C_6H_5, **1**; C_6H_4-Cl-4, **2**; $C_6H_4-C_8H_{17}$-4, **3**; C_4H_3S, **4**; $C_4H_2-C_4H_3S$, **5**; N–N = $^tBu_2$bpy, R = $C_6H_4-OCH_3$-4, **6**; $C_6H_4-C_6H_5$-4, **7**; C_8H_{17}, **8**; C_4H_3S, **9**; $C_4H_2-C_4H_3S$, **10**; C_5H_4N, **11**) as well as their related homo- and hetero-binuclear complexes $\{Re(N-N)(CO)_3(C \equiv C-C_5H_4N)[M]\}$ (N–N = $^tBu_2$bpy, [M] = $[Re\{(CF_3)_2$-bpy\}(CO)_3]ClO_4$, **12**; $[Re(NO_2$-phen)(CO)_3]ClO_4$, **13**; $[W(CO)_5]$, **14**; N–N = bpy, [M] = $[W(CO)_5]$, **15**) have been synthesized (Scheme 1). Their photophysical and electrochemical properties have been studied. X-ray crystal structure determinations of **1**, **10** and **11** and EHMO study of **10** have also been performed.

2. Experimental

2.1. Materials

Rhenium pentacarbonyl chloride $[Re(CO)_5Cl]$ and tungsten hexacarbonyl $[W(CO)_6]$ were obtained from Strem Chemicals, Inc. 2,2′-Bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine(Me_2bpy), silver trifluoromethanesulfonate (AgOTf), copper(I) chloride (CuCl), 4-*n*-octylphenylacetylene, 4-methoxyphenylacetylene and 1-decyne were obtained from Aldrich Chemical Co. Triethylamine, phenylacetylene and 1-chloro-4-phenylacetylene were purchased from Lancaster Synthesis Ltd. 4,4′-Di-*tert*-butyl-2,2′-bipyridine [19] ($^tBu_2$bpy) and 5,5′-bis(trifluoromethyl)-2,2′-bipyridine [20] $\{(CF_3)_2$-bpy\}$, 2-ethynylthiophene [21] ($HC \equiv CC_4H_3S$), 5-ethynyl-2,2′-bithiophene [22] ($HC \equiv CC_4H_2S-C_4H_3S$) and 4-ethynylpyridine [23] ($pyC \equiv CH$) were prepared according to the literature procedures. $[Re(^tBu_2bpy)(CO)_3Cl]$ [24], $[Re(bpy)(CO)_3Cl]$ [24], $[Re\{(CF_3)_2$-bpy\}(CO)_3(MeCN)]OTf$ [25], $[Re(NO_2$-phen)(CO)_3(MeCN)]OTf$ [25] and $W(CO)_5(pyC \equiv CH)$ [26] were synthesized by slight modification of the reported procedure.

Pyridine was obtained from BDH Chemical Co. Ltd. and was pre-dried over KOH and distilled under an inert atmosphere of nitrogen before use. THF was distilled over sodium benzophenone ketyl before use. CH_2Cl_2 and MeCN were purified and distilled using standard procedures before use. All other reagents were of analytical grade and were used as received.

Functionalized mono-acetylide complex

Complex	R	R'
1	H	$-C_6H_5$
2	H	$-C_6H_4-Cl$-4
3	H	$-C_6H_4-C_8H_{17}$-4
4	H	$-C_4H_3S$
5	H	$-C_4H_2S-C_4H_3S$
6	^tBu	$-C_6H_4-OCH_3$-4
7	^tBu	$-C_6H_4-C_6H_5$-4
8	^tBu	$-C_8H_{17}$
9	^tBu	$-C_4H_3S$
10	^tBu	$-C_4H_2S-C_4H_3S$
11	^tBu	$-C_5H_4N$

Homo- and Hetero-metallic binuclear complexes

Complex	R	[M]
12	^tBu	$[Re(\{CF_3\}_2$-bpy)(CO)_3]ClO_4$
13	^tBu	$[Re(NO_2$-phen)(CO)_3]ClO_4$
14	^tBu	$W(CO)_5$
15	H	$W(CO)_5$

Scheme 1.

2.2. Physical measurements and instrumentation

UV–vis spectra were obtained on a Hewlett–Packard 8452A diode array spectrophotometer. IR spectra as Nujol mulls on a Bio-Rad FTS-7 Fourier-transform infrared spectrophotometer (4000–400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^{1}H-NMR spectra were recorded on a 270 MHz JEOL JNM-GSX270 or a 300 MHz Bruker DPX300 fourier-transform NMR spectrometer. Chemical shifts (δ ppm) were reported relative to tetramethylsilane (Me$_4$Si). Positive ion FAB mass spectra were collected on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed by the Butterworth Laboratories Ltd or on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix model TDS-620A (500 MHz, 2GS/s) digital oscilloscope, and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10-cm^3 round-bottom flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Cyclic voltammetric measurements were performed by using a CH Instrument Inc. model CHI 620 Electroanalytical Analyzer, interfaced to a personal computer. The ferrocenium–ferrocene couple was used as the internal standard in the electrochemical measurements in MeCN (0.1 M ^{n}Bu$_4$NPF$_6$). The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode, with Ag/AgNO$_3$ (0.1 M in MeCN) as the reference electrode and a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported previously [27].

2.3. Syntheses

The rhenium(I) diimine monoynyl complexes were synthesized by either of the two methods.

2.3.1. Method A

A solution of [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl] (0.174 mmol) in THF (10 ml) was treated at -40 °C with a solution of RC≡CLi (0.575 mmol) in THF (10 ml), prepared in situ from RC≡CH and ^{n}BuLi, under an inert atmosphere of nitrogen, followed by stirring at room temperature (r.t.) for 24 h. Water was then added to destroy the unreacted RC≡CLi. The product was extracted with a THF–Et$_2$O mixture, dried over anhydrous magnesium sulfate, and then filtered. The filtrate was reduced in volume and purified by column chromatography on silica gel using CH$_2$Cl$_2$–n-hexane (1:1, v/v) as eluent. Subsequent recrystallization from an acetone–n-hexane mixture gave the desired product.

2.3.2. Method B

A reaction mixture of [Re(CO)$_3$(N–N)Cl] (N–N = ^{t}Bu$_2$bpy, bpy) (0.54 mmol), AgOTf (0.60 mmol), Et$_3$N (0.60 mmol), HC≡CR (0.76 mmol) and THF (100 ml) was allowed to reflux under an inert atmosphere of nitrogen in the dark for 24 h. After cooling to r.t., the dark brown suspension was filtered and the orange–red filtrate was reduced in volume under reduced pressure. The residue was then purified by column chromatography on silica gel using CH$_2$Cl$_2$ as eluent. Subsequent recrystallization from acetone–Et$_2$O afforded the desired product.

2.4. Synthesis of [Re(bpy)(CO)₃(C≡C–C₆H₅)] (1)

This was synthesized according to method B in which HC≡CC$_6$H$_5$ was used. Yield: 85 mg, 30%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 6.80 (d, 2H, aryl H *meta* to ethynyl group), 6.96 (m, 3H, aryl H *ortho* and *para* to ethynyl group), 7.74 (t, 2H, 4- and 4′-pyridyl H's), 8.30 (t, 2H, 5- and 5′-pyridyl H's), 8.70 (d, 2H, 3- and 3′-pyridyl H's), 9.12 (d, 2H, 6- and 6′-pyridyl H's). IR (Nujol mull, cm^{-1}): 2083 ν(C≡C); 2008, 1904, 1885 ν(C≡O). Positive FABMS: ion clusters at m/z 529 [M]$^+$, 500 [M−CO]$^+$. Elemental analyses, Found: C, 47.40; H, 2.31; N, 5.28. Calc. for [Re(bpy)(CO)$_3$(C≡C–C$_6$H$_5$)]: C, 47.78; H, 2.46; N, 5.31%.

2.5. Synthesis of [Re(CO)₃(bpy)(C≡C–C₆H₄–Cl-4)] (2)

This was synthesized by method B in which HC≡C–C$_6$H$_4$–Cl-4 was used. Yield: 91 mg, 30%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 6.78 (d, 2H, aryl H *meta* to ethynyl group), 7.00 (m, 2H, aryl H *ortho* to ethynyl group), 7.74 (t, 2H, 4- and 4′-pyridyl H's), 8.30 (t, 2H, 5- and 5′-pyridyl H's), 8.70 (d, 2H, 3- and 3′-pyridyl H's), 9.12 (d, 2H, 6- and 6′-pyridyl H's). IR (Nujol mull (cm^{-1})): 2092 ν(C≡C); 2005, 1901, 1876 ν(C≡O). Positive FABMS: ion clusters at m/z 562 [M]$^+$, 534 [M−CO]$^+$. Elemental analyses, Found: C, 44.54; H, 1.86; N, 4.65. Calc. for [Re(bpy)(CO)$_3$(C≡C–C$_6$H$_4$–Cl-4)]: C, 44.86; H, 2.14; N, 4.98%.

2.6. Synthesis of [Re(bpy)(CO)$_3$(C≡C−C$_6$H$_4$−C$_8$H$_{17}$-4)] (3)

This was synthesized by method B in which HC≡C−C$_6$H$_4$−C$_8$H$_{17}$-4 was used. Yield: 104 mg, 30%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 0.84 (t, 3H, −CH$_3$−), 1.24 (m, 10H, −CH$_2$−), 1.46 (m, 2H, −CH$_2$−), 2.42 (t, 2H, −CH$_2$−), 6.70 (d, 2H, aryl H *meta* to ethynyl group), 6.82 (m, 2H, aryl H *ortho* to ethynyl group), 7.74 (t, 2H, 4- and 4′-pyridyl H's), 8.30 (t, 2H, 5- and 5′-pyridyl H's), 8.70 (d, 2H, 3- and 3′-pyridyl H's), 9.12 (d, 2H, 6- and 6′-pyridyl H's). IR (Nujol mull (cm^{-1})): 2083 v(C≡C); 2005, 1916, 1890 v(C≡O). Positive FABMS: ion clusters at m/z 640 [M]$^+$, 612 [M−CO]$^+$. Elemental analyses, Found: C, 54.34; H, 4.41; N, 4.28. Calc. for [Re(bpy)(CO)$_3$(C≡C−C$_6$H$_4$−C$_8$H$_{17}$-4)]: C, 54.44; H, 4.54; N, 4.38%.

2.7. Synthesis of [Re(bpy)(CO)$_3$(C≡C−C$_4$H$_3$S)] (4)

This was synthesized according to method B in which HC≡C−C$_4$H$_3$S was used. It was purified by column chromatography on silica gel using CH$_2$Cl$_2$−petroleum ether (boiling point (b.p.) 40–60 °C) (4:1 v/v) as eluent. Subsequent recrystallization from CH$_2$Cl$_2$−n-hexane gave orange crystals of **4**. Yield: 63 mg, 55%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si), 6.70 (dd, 1H, J = 1.2 and 5.2 Hz, 5-thiophene H), 7.70 (t, 2H, J = 6.1 Hz, 4- and 4′-pyridyl H's), 8.20 (t, 2H, J = 7.8 Hz, 5- and 5′-pyridyl H's), 8.60 (d, 2H, J = 8.1 Hz, 3- and 3′-pyridyl H's), 9.10 (d, 2H, J = 5.2 Hz, 6- and 6′-pyridyl H's). IR (Nujol mull on KBr disc, v (cm^{-1})): 2080 v(C≡C); 2006, 1912, 1888 v(C≡O). Positive FABMS: ion clusters at m/z 534 [M]$^+$, 460 [M−(C≡C−C$_4$H$_3$S)]$^+$. Elemental analyses Found: C, 42.00; H, 2.01; N, 4.76. Calc. for [Re(bpy)(CO)$_3$(C≡C−C$_4$H$_3$S)]·1/2H$_2$O: C, 42.06; H, 1.78; N, 4.68%.

2.8. Synthesis of [Re(bpy)(CO)$_3$(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)] (5)

The procedure was similar to that of **4**, except HC≡C−C$_4$H$_2$S−C$_4$H$_3$S was used instead. Yield: 40 mg, 30%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 6.20 (d, 1H, J = 3.7 Hz, 4-bithiophene H), 6.70 (d, 1H, J = 3.7 Hz, 3-bithiophene H), 6.80 (dd, 1H, J = 3.6 and 5.1 Hz, 4′-bithiophene H), 6.90 (dd, 1H, J = 1.1 and 3.6 Hz, 3′-bithiophene H), 7.10 (dd, 1H, J = 1.1 and 5.1 Hz, 5′-bithiophene H), 7.70 (t, 2H, J = 6.1 Hz, 4- and 4′-pyridyl H's), 8.20 (t, 2H, J = 7.8 Hz, 5- and 5′-pyridyl H's), 8.60 (d, 2H, J = 8.1 Hz, 3- and 3′-pyridyl H's), 9.10 (d, 2H, J = 5.2 Hz, 6- and 6′-pyridyl H's). IR (Nujol mull on KBr disc, v (cm^{-1})): 2100 v(C≡C); 2014, 1915, 1890 v(C≡O). Positive FABMS: ion clusters at m/z 616 [M]$^+$, 588 [M−CO]$^+$, 427 [M−(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)]$^+$. Elemental analyses Found: C, 44.81; H, 4.71;

N, 4.55. Calc. for [Re(bpy)(CO)$_3$(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)]: C, 45.01; H, 4.62; N, 4.54%.

2.9. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_6$H$_4$−OCH$_3$-4)] (6)

This was synthesized according to method A in which 4-methoxyphenylacetylene was used. Yield: 55 mg, 47%. ^{1}H-NMR (270 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.4 (s, 18H, ^{t}Bu), 3.65 (3H, s, −OCH$_3$ group), 6.54, 6.58 (4H, 2d, phenyl H), 7.77–7.76 (2H, dd, 5- and 5′-pyridyl H's), 8.70–8.71 (2H, d, 3- and 3′-pyridyl H's), 8.98–9.00 (2H, dd, 6- and 6′-pyridyl H's). IR (Nujol mull (cm^{-1})): 2085 v(C≡C); 1996, 1901, 1878 v(C≡O). Positive FABMS: ion clusters at m/z 670 [M]$^+$, 539 [M−C≡C−C$_6$H$_4$−OCH$_3$-4]$^+$.

2.10. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_6$H$_4$−C$_6$H$_5$-4)] (7)

This was synthesized according to method A in which ethynylbiphenyl was used to give orange crystals of **7**. Yield: 57 mg, 46%. ^{1}H-NMR (270 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.4 (s, 18H, ^{t}Bu), 6.86–7.56 (9H, m, biphenyl H), 7.77–7.76 (2H, dd, 5- and 5′-pyridyl H's), 8.70–8.71 (2H, d, 3- and 3′-pyridyl H's), 8.98–9.00 (2H, dd, 6- and 6′-pyridyl H's). IR (Nujol mull (cm^{-1})): 2094 v(C≡C); 2015, 1912, 1898 v(C≡O). Positive FABMS: ion clusters at m/z: 747 [M]$^+$, 539 [M−C≡C−C$_6$H$_4$−C$_6$H$_5$-4]$^+$.

2.11. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_8$H$_{17}$)] (8)

This was synthesized according to method A in which 1-decyne was used to give orange crystals of **8**. Yield: 53 mg, 45%. ^{1}H-NMR (270 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 0.9 (3H, t, −Me), 1.0–1.4 (12H, m, −CH$_2$−), 1.4 (18H, s, ^{t}Bu), 1.75 (2H, t, −CH$_2$C≡C−), 7.78–7.80 (2H, dd, 5- and 5′-pyridyl H's), 8.79–8.81 (2H, d, 3- and 3′-pyridyl H's), 8.98–9.00 (2H, d, 6- and 6′-pyridyl H's). IR (Nujol mull (cm^{-1})): 2012 v(C≡C); 2001, 1909, 1874 v(C≡O). Positive FABMS: ion clusters at m/z 678 [M]$^+$, 539 [M−C≡C−C$_8$H$_{17}$]$^+$.

2.12. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_4$H$_3$S)] (9)

The procedure was similar to that of **4**, except [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl] was used as a precursor. Yield: 65 mg, 59%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.40 (s, 18H, ^{t}Bu), 6.30 (dd, 1H, J = 1.2 and 3.5 Hz, 3-thiophene H), 6.50 (dd, 1H, J = 3.5 and 5.2 Hz, 4-thiophene H), 6.70 (dd, 1H, J = 1.2 and 5.2 Hz, 5-thiophene H), 7.70 (dd, 2H, J = 1.8 and 5.8 Hz, 5- and 5′-pyridyl H's), 8.60 (d, 2H, J = 1.8 Hz, 3-

and 3′-pyridyl H's), 8.90 (d, 2H, $J = 5.8$ Hz, 6- and 6′-pyridyl H's). IR (Nujol mull on KBr disc, v (cm^{-1})): 2078 v(C≡C); 2006, 1908, 1883 v(C≡O). Positive FABMS: ion clusters at m/z 646 [M]$^+$, 618 [M−CO]$^+$, 539 [M−(C≡C−C$_4$H$_3$S)]$^+$. Elemental analyses Found: C, 50.15; H, 4.18; N, 4.33. Calc. for [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_4$H$_3$S)]: C, 50.33; H, 4.19; N, 4.36%.

2.13. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)] (10)

The procedure was similar to that of **5**, except [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl] was used as a precursor. Yield: 50 mg, 40%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.40 (s, 18H, ^{t}Bu), 6.30 (d, 1H, $J =$ 3.7 Hz, 4-bithiophene H), 6.70 (d, 1H, $J = 3.7$ Hz, 3-bithiophene H), 6.80 (dd, 1H, $J = 3.6$ and 5.1 Hz, 4′-bithiophene H), 6.90 (dd, 1H, $J = 1.1$ and 3.6 Hz, 3′-bithiophene H), 7.20 (dd, 1H, $J = 1.1$ and 5.1 Hz, 5′-bithiophene H), 7.70 (dd, 2H, $J = 1.8$ and 5.8 Hz, 5- and 5′-pyridyl H's), 8.60 (d, 2H, $J = 1.8$ Hz, 3- and 3′-pyridyl H's), 8.90 (d, 2H, $J = 5.8$ Hz, 6- and 6′-pyridyl H's). IR (Nujol mull on KBr disc, v (cm^{-1})): 2096 v(C≡C); 2010, 1910, 1888 v(C≡O). Positive FABMS: ion clusters at m/z 728 [M]$^+$, 700 [M−CO]$^+$, 539 [M−(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)]$^+$. Elemental analyses Found: C, 49.01; H, 3.89; N, 3.63. Calc. for [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)]·1/2CH$_2$Cl$_2$: C, 48.79; H, 3.87; N, 3.54%.

2.14. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)] (11)

This was synthesized according to method A in which 4-ethynylpyridine was used. It was purified by column chromatography on silica gel using Et$_2$O as eluent. Subsequent recrystallization by slow evaporation of an acetone solution of the complex gave orange crystals of **11**. Yield: 45 mg, 40%. ^{1}H-NMR (270 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.4 (18H, s, ^{t}Bu), 6.70 (2H, broad, pyridyl H $meta$ to N), 7.77–7.79 (2H, dd, 5- and 5′-pyridyl H's), 8.19 (2H, broad, pyridyl H $ortho$ to N), 8.73–8.74 (2H, d, 3- and 3′-pyridyl H's), 9.00–9.02 (2H, dd, 6- and 6′-pyridyl H's). IR (Nujol mull (cm^{-1})): 2096 v(C≡C); 2003, 1917, 1892 v(C≡O). Positive FABMS: ion clusters at m/z 641 [M]$^+$, 539 [M−C≡C−C$_5$H$_4$N]$^+$.

2.15. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)Re{(CF$_3$)$_2$-bpy}(CO)$_3$]ClO$_4$ (12)

The complex was prepared by a method similar to that of other related rhenium(I) tricarbonyl diimine pyridine systems [25]. [Re{(CF$_3$)$_2$-bpy}(CO)$_3$(MeCN)]OTf (100 mg, 0.13 mmol) was dissolved in THF, and one equivalent of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)] (83 mg, 0.13 mmol) was added to it and the

mixture was heated to reflux under an inert atmosphere of nitrogen for 12 h to give a bright yellow solution. After evaporation of the solution to dryness, the yellow solid mass was redissolved in minimum amount of methanol, and a saturated methanolic solution of LiClO$_4$ was added to precipitate the product as its perchlorate salt. The solid was further recrystallized by slow diffusion of Et$_2$O vapor into a MeCN solution in the dark to give yellow crystals of **12**. Yield: 118 mg, 70%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.4 (18H, s, ^{t}Bu), 6.62–6.65 (2H, dd, pyridyl H $meta$ to N), 7.75–7.77 (2H, dd, 5,5′-H of ^{t}Bu$_2$bpy), 8.14–8.17 (2H, dd, pyridyl H $ortho$ to N), 8.71–8.72 (2H, d, 3,3′-H of ^{t}Bu$_2$bpy), 8.85–8.88 (2H, 2d, 4,4′-H of (CF$_3$)$_2$-bpy), 8.95–8.97 (2H, d, 6,6′-H of ^{t}Bu$_2$bpy), 9.09–9.12 (2H, d, 3,3′-H of (CF$_3$)$_2$-bpy), 9.77 (2H, s, 6,6′-H of (CF$_3$)$_2$-bpy). IR (Nujol mull (cm^{-1})): 2105 v(C≡C); 2035, 1999, 1937, 1929, 1908, 1898 v(C≡O). Positive FABMS: ion clusters at m/z 1203 [M]$^+$, 563 [M−Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)]$^+$, 539 [M−Re{(CF$_3$)$_2$-bpy}(CO)$_3$(C≡C−C$_5$H$_4$N)]$^+$.

2.16. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)Re(NO$_2$-phen)(CO)$_3$]ClO$_4$ (13)

The synthesis was similar to **12**, except [Re(NO$_2$-phen)(CO)$_3$(MeCN)]OTf was used instead of [Re{(CF$_3$)$_2$-bpy}(CO)$_3$(MeCN)]OTf. Yield 94 mg, 60%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.4 (18H, s, ^{t}Bu), 6.52–6.55 (2H, d, pyridyl H $meta$ to N), 7.70–7.72 (2H, d, pyridyl N $ortho$ to N), 8.09–8.01 (2H, d, 5,5′-H of ^{t}Bu$_2$bpy), 8.40–8.48 (2H, m, 3,8-H of NO$_2$-phen), 8.66–8.67 (2H, d, 3,3′-H of ^{t}Bu$_2$bpy), 8.89–8.91 (2H, dd, 6,6′-H of ^{t}Bu$_2$bpy), 9.27–9.31 (2H, s+d, 's' for the 6-H and 'd' for the 4-H of NO$_2$-phen), 9.42–9.45 (1H, d, 7-H of NO$_2$-phen), 9.93–9.98 (2H, td, 2,9-H of NO$_2$-phen). IR (Nujol mull (cm^{-1})): 2100 v(C≡C); 2010, 1998, 1942, 1928, 1917, 1909 v(C≡O). Positive FABMS: ion clusters at m/z 1135 [M]$^+$, 539 [M−Re(NO$_2$-phen)(CO)$_3$(C≡C−C$_5$H$_4$N)]$^+$.

2.17. Synthesis of [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)W(CO)$_5$] (14)

A mixture of [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl] (100 mg, 0.17 mmol), Et$_3$N (52 mg, 0.51 mmol), AgOTf (48 mg, 0.19 mmol) and W(CO)$_5$(NC$_5$H$_4$C≡CH) (111 mg, 0.26 mmol) in THF (70 ml) was allowed to reflux under an inert atmosphere of nitrogen in the dark for 24 h. After cooling to r.t., the dark brown suspension was filtered and the orange filtrate was reduced in volume under reduced pressure. The residue was then purified by column chromatography on silica gel using Et$_2$O−petroleum ether (b.p. 40–60 °C) (1:1 v/v) as eluent. Subsequent recrystallization from CH$_2$Cl$_2$−n-hexane gave orange crystals of **14**. Yield: 30 mg, 18%. ^{1}H-

NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 1.40 (s, 18H, ^{t}Bu), 6.50 (d, 2H, $J = 6.0$ Hz, pyridyl H *meta* to N), 7.60 (d, 2H, $J = 6.0$ Hz, pyridyl H *ortho* to N), 7.70 (dd, 2H, $J = 1.8$ and 5.8 Hz, 5- and 5′-pyridyl H's), 8.60 (d, 2H, $J = 1.8$ Hz, 3- and 3′-pyridyl H's), 8.90 (d, 2H, $J = 5.8$ Hz, 6- and 6′-pyridyl H's). IR (Nujol mull on KBr disc, ν (cm^{-1})): 2107 ν(C≡C); 2072, 2000, 1979, 1952, 1933, 1900, 1883, 1860 ν(C≡O). Positive FABMS: ion clusters at m/z 965 [M]$^+$, 909 [M − 2CO]$^+$, 539 [M − W(CO)$_5$(NC$_5$H$_4$C≡C)]$^+$. Elemental analyses Found: C, 41.01; H, 2.90; N, 4.35. Calc. for [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)W(CO)$_5$]: C, 40.83; H, 3.04; N, 4.17%.

2.18. Synthesis of [Re(bpy)(CO)$_3$(C≡C− C$_5$H$_4$N)W(CO)$_5$] (15)

The procedure was similar to that described for the preparation of **14**, except [Re(bpy)(CO)$_3$Cl] (79 mg, 0.17 mmol) was used in place of [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl] to give orange crystals of **15**. Yield: 28 mg, 14%. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K, relative to Me$_4$Si): δ 6.50 (d, 2H, $J = 6.0$ Hz, pyridyl H *meta* to N), 7.60 (d, 2H, $J = 6.0$ Hz, pyridyl H *ortho* to N), 7.70 (t, 2H, $J = 6.3$ Hz, 4- and 4′-pyridyl H's), 8.20 (t, 2H, $J = 7.8$ Hz, 5- and 5′-pyridyl H's), 8.70 (d, 2H, $J = 8.1$ Hz, 3- and 3′-pyridyl H's), 9.10 (d, 2H, $J = 5.0$ Hz, 6- and 6′-pyridyl H's). IR (Nujol mull on KBr disc, ν (cm^{-1})): 2110 ν(C≡C); 2065, 2000, 1986, 1958, 1922, 1890, 1883, 1866 ν(C≡O). Positive FABMS: ion clusters at m/z 852 [M]$^+$, 824 [M − 2CO]$^+$, 427 [M − W(CO)$_5$(NC$_5$H$_4$C≡C)]$^+$. Elemental analyses Found: C, 35.21; H, 1.41; N, 3.19. Calc. for [Re(bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)W(CO)$_5$]: C, 35.27; H, 1.60; N, 2.99%.

3. Results and discussion

3.1. Syntheses

The synthesis of luminescent rhenium(I)–bipyridyl type alkynyl complexes, [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡CR)], was firstly reported by employing the reaction of alkynyllithium (LiC≡CR) (R = alkyl, aryl group) with [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl] in diethyl ether (method A) [17a,17b,17c]. Despite the fact that a series of target complexes with various alkynyl groups have been prepared, this method only applies to the use of starting precursor complexes, such as [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl], which are soluble in diethyl ether. No desired products could be obtained under similar reaction conditions for the synthesis of the related unsubstituted 2,2′-bipyridyl analogues. An alternative method was developed to prepare the related analogues [Re(bpy)(CO)$_3$(C≡CR)] by refluxing the suspension of [Re(bpy)(CO)$_3$Cl], AgOTf, HC≡CR and Et$_3$N in THF (method B). All

the complexes were purified by column chromatography on silica gel using CH$_2$Cl$_2$−n-hexane as eluent in both methods.

The synthesis of homo-metallic binuclear complexes **12** and **13** has been achieved by utilization of the 'metalloligand' approach through the use of the starting precursor complex, [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡C−C$_5$H$_4$N)] (**11**), in which the uncoordinated pyridyl nitrogen could serve as the coordination site for a second rhenium metal center. Typical for the preparation of the related cationic luminescent rhenium(I) complexes, [Re-(diimine)(CO)$_3$(C$_5$H$_4$N)]$^+$, complexes **12** and **13** were obtained by the reaction of **11** with [Re({CF$_3$}$_2$-bpy)(CO)$_3$(MeCN)]ClO$_4$ and [Re(NO$_2$-phen)(CO)$_3$-(MeCN)]ClO$_4$, respectively, in THF under reflux condition. In the preparation of mixed-metal rhenium–tungsten complexes **14** and **15**, [W(CO)$_5$(C$_5$H$_4$N−C≡CH)], which serve as the 'metalloligand', was then reacted with the corresponding [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl] and [Re(bpy)(CO)$_3$Cl] under the reaction conditions as described in Section 2.3.2.

3.2. Structural characterization

The perspective drawings of **1**, **10** and **11** are depicted in Figs. 1–3. The crystallographic data are given in Table 1, while their selected bond lenghts and bond angles are collected in Table 2. In general, the coordination geometries of the complexes are distorted octahedral with three carbonyl ligands arranged in a *facial* fashion. As commonly observed in other Re(I) tricarbonyl diimine systems [17], the N−Re−N bond angles [**1**, 74.4(2)°; **10**, 73.6(2)°; **11**, 73.5(2) and 74.1(2)°] are found to be less than 90° as required by the bite distance exerted by the steric demand of the chelating bipyridine ligand. The Re−C−C units show a linear arrangement [**1**, 176.4(6)°; **10**, 175.2(8)°; **11**, 177.3(7) and 178.2(7)°] as expected for the sp hydridization of C≡C bond in the alkynyl moiety. The C≡C bond lengths [**1**, 1.199(9) Å; **10**, 1.20(1) Å; **11**, 1.196(10) and 1.195(10) Å] are typical of terminal σ-bonded metal−alkynyl bonds. [17] In complex **10,** the C−S bond lengths are 1.69(1)− 1.756(10) Å, similar to those commonly found in thiophene systems.[28] The C−C bond distances of the thiophene ring linked directly to the ethynyl unit vary from 1.32(1) to 1.40(1) Å, which are slightly shorter than the distance of 1.44(1) to 1.47(2) Å of the second thiophene ring. The two thiophene rings display a *trans* arrangement in order to minimize the steric repulsion between the lone pairs on each of the sulfur atoms. This has also been commonly observed in free bithiophene ligands and organometallic bithiophene complexes [28].
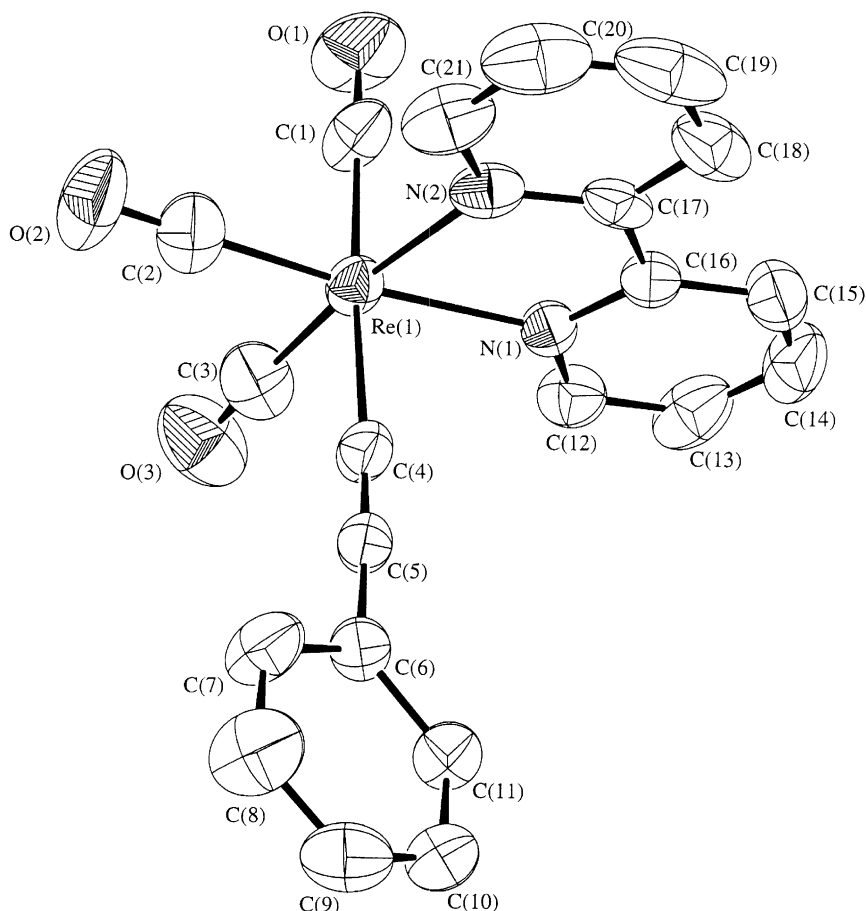
Fig. 1. The perspective drawing of **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

3.3. Electrochemistry

Similar to other rhenium(I) diimine complexes [25,29], both reduction and oxidation couples have been observed in the cyclic voltammongrams upon reductive and oxidative scan, respectively, in complexes **1–15**. Their electrochemical data are summarized in Table 3. For the mononuclear complexes **1–11**, one quasi-reversible reduction couple has been observed at ca. −1.43 to −1.60 V versus SCE, and is tentatively assigned as ligand-centered reduction of the bipyridyl ligand. The reduction potential for complexes **6–11** with $^tBu_2bpy$ ligand occurs at ca. −1.50 to −1.60 V, which is found to be more negative than that for **1–5** with bpy ligand which occurs at ca. −1.43 to −1.48 V. This is in line with the attachment of the electron-donating *tert*-butyl substituents on the bipyridine ligand, which would render the bipyridine ligand more electron-rich and poorer π-accepting, thus decreases its ease of reduction. The first oxidation waves of **1–11**, which occur at +0.82 to +1.07 V, are tentatively assigned as Re(I)/Re(II) oxidation. The observation that the complexes [Re(bpy)(CO)$_3$(C≡CR)] show a less positive potential

for their first oxidation wave than the chloro counter-part, [Re(bpy)(CO)$_3$Cl] (+1.38 V vs. SCE) [25c] is consistent with the better σ-donating ability of the alkynyl than the chloro group, which would render the rhenium(I) metal center more electron rich, and hence increases its ease of oxidation. The bithiophene-substituted complexes, [Re(N−N)(CO)$_3$(C≡C−C$_4$H$_2$S−C$_4$H$_3$S)] (**5** and **10**) (ca. +0.82 V) show a less positive potential than the corresponding monothiophene-substituted complexes, [Re(N−N)(CO)$_3$(C≡C−C$_4$H$_3$S)] (**4** and **9**) (ca. +0.92 V); consistent with the higher π-electron-donating ability of C≡C−C$_4$H$_2$S−C$_4$H$_3$S than that of C≡C−C$_4$H$_3$S, rendering the rhenium(I) center more electron-rich and hence increases its ease of oxidation. In addition to the first oxidation wave at ca. +0.80 to +0.90 V versus SCE, the rhenium(I) complexes with 2-ethynyl-2,2′-bithiophene ligand, **5** and **10**, show two irreversible oxidation waves at ca. +1.15 and +1.35 V versus SCE while the rhenium(I) complexes containing 2-ethynylthiophene ligand, **4** and **9**, show only one irreversible oxidation wave in the range of +1.24 to +1.30 V versus SCE. Fig. 4 depicts the cyclic voltammograms showing the reduction and oxi-
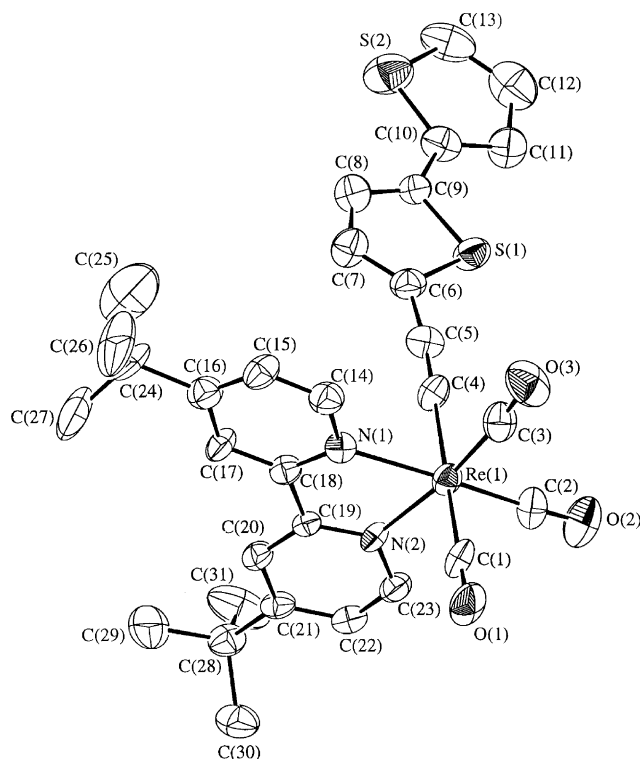
Fig. 2. The perspective drawing of **10** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

dation of **4**. These oxidation waves are assigned as thiophene-based oxidations. Similar observations were reported in other organometallic oligothienylacetylide complexes [28b].

For the homo-metallic binnclear complexes **12** and **13**, far more complicated cyclic voltammograms are obtained. For complex **12**, two quasi-reversible oxidation couples at $+1.19$ and $+1.85$ V versus SCE are observed. With reference to other related alkynyl complexes as well as its mono-rhenium counterparts **11** and $[Re\{(CF_3)_2\text{-}bpy\}(CO)_3(C_5H_4N)]ClO_4$, the first oxidation couple is tentatively assigned as a Re(I)/Re(II) oxidation of the rhenium center that is coordinated to $^tBu_2bpy$ and the alkynyl ligand [29]. The slightly more positive potentials of $+1.19$ V in **12** and $+1.23$ V in **13** than $+1.07$ V in **11** can be rationalized by the coordination of a positively charged $[Re\{(CF_3)_2\text{-}bpy\}(CO)_3]$ and $[Re(NO_2\text{-}phen)(CO)_3]$ unit, respectively, to the pyridine ends in **12** and **13**, which would result in a reduced ease of oxidation, both from the reduced donating ability of the 4-ethynylpyridine ligand upon coordination of a second Re(I) center as well as the increased positive charge on the complex. The second oxidation couple at ca. $+1.85$ V in **12** and $+1.80$ V in **13** are tentatively assigned as the Re(I)/Re(II) oxidation of the respective $[Re\{(CF_3)_2\text{-}bpy\}(CO)_3(NC_5H_4C\equiv C-)]$ and $[Re(NO_2\text{-}phen)(CO)_3(NC_5H_4C\equiv C-)]$ unit as they

matched well with that observed in their counterparts $[Re\{(CF_3)_2\text{-}bpy\}(CO)_3(C_5H_4N)]ClO_4$ and $[Re(NO_2\text{-}phen)(CO)_3(C_5H_4N)]ClO_4$. On the other hand, the first three quasi-reversible reduction couples in complex **12**, which occurred at -0.73, -0.88 and -1.18 V versus SCE are believed to originate from the $[Re\{(CF_3)_2\text{-}bpy\}(CO)_3(NC_5H_4C\equiv C-)]$ unit, as their values are comparable to that of $[Re\{(CF_3)_2\text{-}bpy\}(CO)_3(C_5H_4N)]ClO_4$. The fourth quasi-reversible reduction couple at -1.53 V versus SCE is believed to be $^tBu_2bpy$ ligand-centered reduction, as similar reduction is observed in the analogous complex **11** at -1.55 V. Upon scanning to more negative potential, two additional irreversible reduction waves are observed at -1.97 and -2.20 V. No attempts have been made to assign these two waves which occur at such negative potentials, as decomposition might have occurred as reflected by the disappearance of the anodic peaks of the waves at -0.73, -0.88 and -1.18 V after scanning to -2.40 V. Similarly, for complex **13**, the quasi-reversible reduction couples at -0.58 and -1.16 V are assigned as reduction of the $[Re(NO_2\text{-}phen)(CO)_3(NC_5H_4C\equiv C-)]$ unit while the wave at -1.52 V is assigned as $^tBu_2bpy$ ligand-centered reduction.

For the heterodinuclear 4-ethynylpyridine bridged complexes, $[Re(N-N)(CO)_3(C\equiv C-C_5H_4N)W(CO)_5]$ (**14** and **15**), the cyclic voltammograms display two irreversible oxidation waves at ca. $+1.09$ to $+1.34$ V and a quasi-reversible reduction couple at ca. -1.40 to -1.48 V versus SCE. The first oxidation wave which occurs at ca. $+1.10$ V versus SCE has tentatively been assigned as a Re(I)/Re(II) oxidation, while the second oxidation wave which occurs at ca. $+1.30$ V versus SCE is tentatively assigned as a tungsten-centered oxidation, commonly observed in the electrochemical studies of other related tungsten-containing complexes [30]. The quasi-reversible reduction couple is tentatively assigned as a bipyridyl ligand-centered reduction. The observation that $[Re(^tBu_2bpy)(CO)_3(C\equiv C-C_5H_4N)W(CO)_5]$ (**14**) (-1.48 V vs. SCE) show a more negative reduction potential than that of the corresponding analogue, $[Re(bpy)(CO)_3(C\equiv C-C_5H_4N)W(CO)_5]$ (**15**) (-1.40 V vs. SCE) is similarly attributed to the poorer π-accepting ability of the $^tBu_2bpy$ ligand.

3.4. Electronic absorption and emission spectroscopies

In general, the electronic absorption spectra of rhenium(I) diimine alkynyl complexes show intense high-energy absorption bands at ca. 256–338 nm and low-energy absorption bands at ca. 400 nm with extinction coefficients of the order of 10^3 dm^3 mol^{-1} cm^{-1}. The photophysical data for **1**–**15** together with two related complexes are shown in Table 4. The high-energy absorption bands, which are also found in the free bpy–$^tBu_2bpy$ and alkynyl ligands, are assigned as
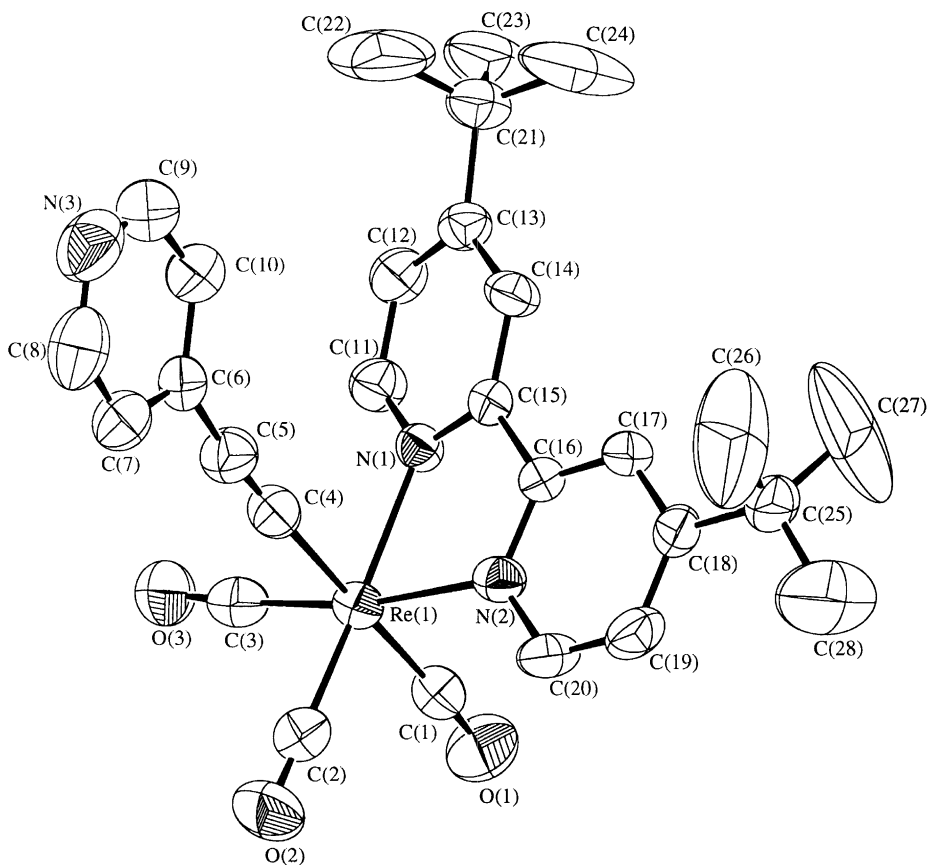
Fig. 3. The perspective drawing of **11** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

$\pi \to \pi^*$ transitions of bpy–^{t}Bu$_2$bpy and the alkynyl ligands while the low-energy absorption bands are tentatively assigned as the $d\pi(Re) \to \pi^*$(diimine) metal-to-ligand charge transfer (MLCT) transition, probably mixed with some $\pi(C \equiv C) \to \pi^*$(diimine) ligand-to-ligand charge transfer (LLCT) character. This MLCT absorption band is at lower energy than that observed in the related precursor complex [Re(N–N)(CO)$_3$Cl]. It is suggested that the $d\pi(Re)$ orbital in the alkynyl complex is higher-lying in energy as a result of the stronger σ-donating ability of the alkynyl ligand than the chloro counterpart. The 338–372 nm bands which are present in the oligothienyl substituted alkynyl complexes [Re(N–N)(CO)$_3$(C≡C–C$_4$H$_3$S)] and [Re(N–N)(CO)$_3$-(C≡C–C$_4$H$_2$S–C$_4$H$_3$S)] (**4**, **5**, **9** and **10**), are ascribed to the thiophene-based $\pi \to \pi^*$ transitions of the C≡C–C$_4$H$_3$S and C≡C–C$_4$H$_2$S–C$_4$H$_3$S moieties. These bands are absent in the electronic absorption spectra of oligothienyl ligand-free analogues and the extinction coefficients of these thiophene-based $\pi \to \pi^*$ transitions are in the range expected for such transitions [17,24,25]. Fig. 5 depicts the electronic absorption spectra of **4** and **5** in THF solution at room temperature. The red shift in absorption energies from ca. 340 nm in the monothiophene complexes to ca. 370 nm in the bithiophene counterparts with an increase in the extent of π-

conjugation of the oligothienyl ligand is supportive of such an assignment. The trend is also supported by similar observations in the related ruthenium oligothienylacetylide complexes [28b]. As there is a red shift in the π–π^* transition energy upon an increase in the thiophene units in the oligothienyl ligands, the MLCT absorption band at ca. 410–420 nm is suggested to be masked by the intense π–π^* transition energies in the bithiophene-substituted complexes, [Re(N–N)(CO)$_3$(C≡C–C$_4$H$_2$S–C$_4$H$_3$S)] (**5** and **10**). The higher MLCT absorption energies in **9** than that of **4** is consistent with the higher π^* orbital energies of ^{t}Bu$_2$bpy as a result of its poorer π-accepting abilities derived from the presence of the more electron-rich *tert*-butyl substituent on the bipyridine ligand.

For the 4-ethynylpyridine bridged homo-metallic binuclear complexes **12** and **13** and the hetero- binuclear complexes **14** and **15**, a strong absorption band at ca. 350 and 370 nm, respectively, is observed, with extinction coefficients in the order of 10^4 dm^{3}mol^{-1} cm^{-1}, which are much larger than that of the mononuclear counterparts. It is suggested that the absorption band in complexes **12–15** might possess some charge-transfer character between the two metal centers, involving a charge transfer from the donor [Re(^{t}Bu$_2$bpy)(CO)$_3$] or [Re(bpy)(CO)$_3$] unit to the acceptor [Re{(CF$_3$)$_2$-
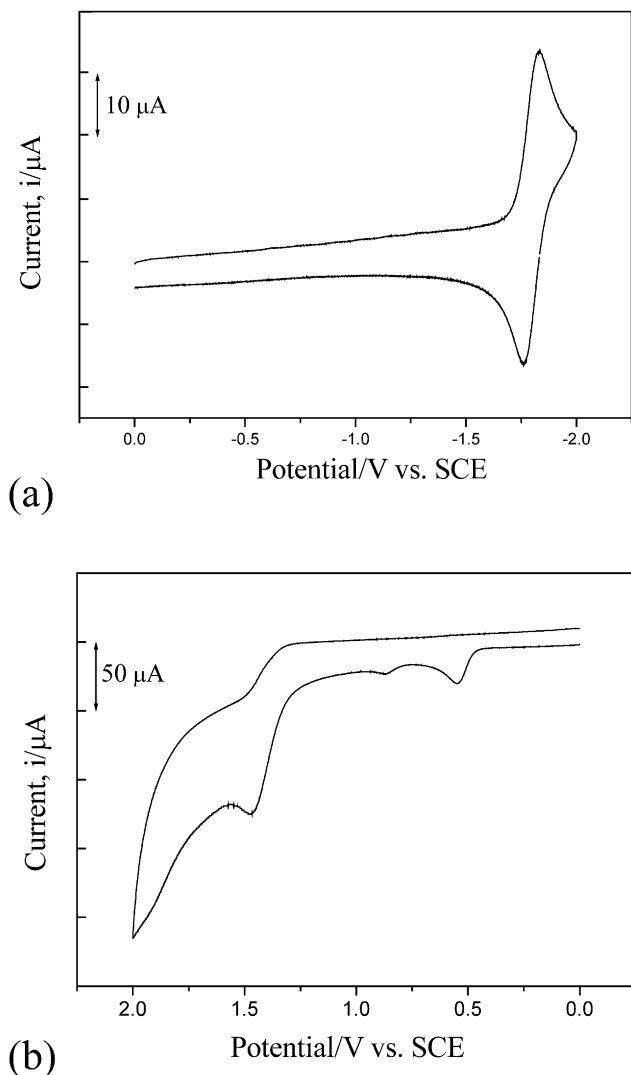
(a)

(b)

Fig. 4. Cyclic voltammogram showing (a) the oxidation and (b) reduction of [Re(CO)$_3$(bpy)(C≡C–C$_4$H$_3$S)] (4) in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$).

bpy}(CO)$_3$], [Re(NO$_2$-phen)(CO)$_3$] or [W(CO)$_5$] moiety. By comparing complexes **12–14** with their mononuclear counterpart **11**, the bridged complexes **12–14** are found to absorb at higher energies than **11**. This could be rationalized by the fact that the 4-ethynylpyridine ligand upon coordinating to two metal centers would be less electron rich and hence rendered the Re dπ orbitals lower-lying in energy, leading to a larger MLCT transition energy. An alternative rationale for the increased MLCT absorption energy is that the electron-donating ability of the 4-ethynylpyridine is lowered as the electron-withdrawing substituent, [Re{(CF$_3$)$_2$-bpy}(CO)$_3$], [Re(NO$_2$-phen)(CO)$_3$] or W(CO)$_5$, is attached to the 4-ethynylpyridine. This would also lead to the increase in the MLCT transition energy.

Upon excitation at λ > 350 nm, the rhenium(I) diimine alkynyl complexes exhibit a long-lived orange–red emission in the solid state and in fluid solution. The origin of the emission has been ascribed to a ^{3}MLCT dπ(Re)→π*(N–N) excited state, similar to that of the other luminescent rhenium(I) diimine systems reported [17,24,25]. In accordance with the trend in MLCT absorption energies, the lower emission energy in the rhenium(I) alkynyl complexes compared with their chloro analogues is ascribed to the better σ-donor ability of the alkynyl moiety which would render the rhenium center more electron rich and hence lower the MLCT emission energy. For the complexes with the same diimine ligand, a dependence of the emission energy on the nature of the alkynyl ligands has been observed. The shift in the emission energy correlates well with the σ- and π-donating ability of the alkynyl ligand, with emission energies in the order: **5 > 4 > 2 > 1 > 3** and **10 > 9 > 8 > 7 > 6 ≈ 11** in the solid state. Fig. 6 shows the solid-state emission spectra of **1–4** at room temperature. The monothiophene-substituted complexes, **4** and **9**, are found to emit at higher energies than their bithiophene-substituted counterparts, **5** and **10**. The observation of a red shift in emission energy upon increasing the number of thiophene units is consistent with the better π-electron-donating ability of C≡C–C$_4$H$_2$S–C$_4$H$_3$S than C≡C–C$_4$H$_3$S, which renders the Re dπ orbital more electron-rich, and raises the Re dπ orbital energy. Complexes **9** and **10** with ^{t}Bu$_2$bpy ligand show higher emission energies than their respective analogues **4** and **5** with bpy ligand, again consistent with the presence of electron-releasing *tert*-butyl groups on the ^{t}Bu$_2$bpy ligand, which renders the π* orbital energy of ^{t}Bu$_2$bpy higher-lying than bpy.

For the 4-ethynylpyridine-bridged donor–acceptor dirhenium(I) complexes **12** and **13**, relatively weak emissions are observed in fluid solution. It is envisaged that with this class of donor–acceptor system, once the molecule is excited, its excited state energy would be transferred from the donor portion of the molecule, [Re(^{t}Bu$_2$bpy)(CO)$_3$] to its acceptor side, [Re{(CF$_3$)$_2$-bpy}(CO)$_3$] and [Re(NO$_2$-phen)(CO)$_3$]. However, in view of their weakly emissive behavior and the close resemblance of the emission energies of both the donor and acceptor parts of the complexes as reflected from the emission data of their mononuclear precursors, no attempts have been made to assign the emission unambiguously. The hetero-metallic complex **14**, on the other hand, is found to emit at a higher emission energy than that of its mononuclear counterpart, **11** both in acetone and in the solid state at 298 K. This is consistent with the decrease in the π-electron-donating ability of the 4-ethynylpyridine ligand upon coordination of the electron-withdrawing W(CO)$_5$ moiety, which resulted in the lowering of Re dπ orbital energy and hence an increase in the MLCT emission energy. The higher MLCT emission energy in **14** than **15** is again consistent with the higher π* orbital energy of the ^{t}Bu$_2$bpy ligand than bpy.

Table 1
Crystallographic data for complexes **1**, **10** and **11**

Complex	**1**	**10**	**11**
Empirical formula	[ReC$_{21}$H$_{13}$N$_2$O$_3$]·1/2[(CH$_3$)$_2$CO]	[(ReC$_{31}$H$_{29}$N$_2$O$_3$S$_2$)·CH$_2$Cl$_2$]	[ReO$_3$N$_2$C$_{28}$H$_{28}$]
Formula weight	556.59	812.84	640.75
Temperature (K)	301	301	301
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbcn* (No. 60)	*P*2$_1$/*n* (No.14)	*P*2$_1$/*n* (No.14)
a (Å)	18.104(3)	10.695(2)	20.405(5)
b (Å)	11.266(1)	12.217(2)	12.186(3)
c (Å)	20.429(2)	26.198(3)	23.312(4)
α (°)	90	90	90
β (°)	90	96.26(2)	112.85(1)
γ (°)	90	90	90
V (Å^3)	4166(1)	3402.6(9)	5352(2)
Z	8	2	8
D$_{calc}$ (g cm^{-3})	1.774	1.587	1.590
μ(Mo–K$_\alpha$) (cm^{-1})	58.63	38.86	45.74
F(000)	2144	1608	2528
Crystal size (mm)	0.35 × 0.20 × 0.15	0.35 × 0.10 × 0.07	0.20 × 0.10 × 0.35
Collection range (°)	2θ_{max} = 48	2θ_{max} = 50.9	2θ_{max} = 45
Index ranges	*h*: 0–20; *k*: 0–12; *l*: −23 to 0	*h*: 0–12; *k*: 0–13; *l*: −31 to 31	*h*: 0–21; *k*: 0–13; *l*: −22 to 22
Independent reflections	3690	5855	7389
Reflections used in refinement	2345	4461	4924
Number of parameters	263	379	631
R	0.027 [a]	0.052 [b]	0.027 [c]
wR	0.032	0.072	0.030
Goodness-of-fit on *F*^{2}	1.61	2.22	1.14
Largest difference peak and hole (e Å^{-3})	+0.83, −0.50	+0.72, −2.02	+0.44, −0.45

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.015F_o^2)^2]$ with $I > 3\sigma(I)$.
[b] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.035F_o^2)^2]$ with $I > 3\sigma(I)$.
[c] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) = (0.017F_o^2)^2]$ with $I > 3\sigma(I)$.

3.5. Molecular orbital calculation

Molecular orbital studies using extended Hückel molecular orbital (EHMO) theory on a selected rhenium(I) diimine alkynyl complex **10** have been performed. The calculated molecular orbital energies, percentage composition and the HOMO–LUMO energy gap are shown in Table 5. Fig. 7 shows the CACAO plots of the HOMO and LUMO. EHMO study shows that the LUMO mainly consists of π*(^{t}Bu$_2$bpy) character while the HOMO is mainly dominated by the antibonding character of the Re–C≡C–C$_4$H$_2$S–C$_4$H$_3$S moiety resulted from the overlap of the dπ(Re) and π(C≡C–C$_4$H$_2$S–C$_4$H$_3$S) orbitals, which is supportive of a mixed dπ(Re) → π*(^{t}Bu$_2$bpy) MLCT/π(C≡C–C$_4$H$_2$S–C$_4$H$_3$S) → π*(^{t}Bu$_2$bpy) LLCT character for the electronic transition.

4. Conclusions

A number of luminescent mononuclear rhenium(I) alkynyl complexes, together with some binuclear com-

plexes, have been synthesized and some of them have been structurally characterized. Low-energy absorption bands at ca. 400 nm, attributable to the dπ(Re) → π*(N–N) MLCT transition probably with some mixing of a some π(C≡C) → π*(N–N) LLCT character, have been observed in the electronic absorption spectra. All of the complexes display intense orange–red emission at ca. 600 nm upon excitation at $\lambda > 350$ nm, assigned as ^{3}MLCT emissions. Semi-empirical EHMO and electrochemical studies provide further support for the spectral assignments.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 200101–200103 for complexes **1**, **10** and **11**, respectively. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**, **10** and **11**

Compound **1**

Bond length

Re(1)–N(1)	2.181(5)	Re(1)–N(2)	2.182(6)
Re(1)–C(1)	1.955(8)	Re(1)–C(2)	1.918(8)
Re(1)–C(3)	1.904(9)	Re(1)–C(4)	2.151(7)
C(4)–C(5)	1.199(9)		

Bond angles

N(1)–Re(1)–C(2)	173.1(3)	N(2)–Re(1)–C(3)	173.4(3)
C(1)–Re(1)–C(4)	176.3(3)	Re(1)–C(4)–C(5)	176.4(6)
C(4)–C(5)–C(6)	176.3(7)	N(1)–Re(1)–N(2)	74.4(2)

Compound **10**

Re(1)–N(1)	2.177(7)	Re(1)–N(2)	2.188(6)
Re(1)–C(1)	1.955(9)	Re(1)–C(2)	1.917(10)
Re(1)–C(3)	1.914(9)	Re(1)–C(4)	2.144(8)
C(4)–C(5)	1.20(1)	C(8)–C(9)	1.38(1)
N(1)–Re(1)–C(2)	167.9(3)	N(2)–Re(1)–C(3)	172.3(3)
C(1)–Re(1)–C(4)	179.2(3)	Re(1)–C(4)–C(5)	175.2(8)
C(4)–C(5)–C(6)	175.7(10)	N(1)–Re(1)–N(2)	73.6(2)

Compound **11**

Re(1)–N(1)	2.175(5)	Re(1)–N(2)	2.184(6)
Re(1)–C(1)	1.948(9)	Re(1)–C(2)	1.914(9)
Re(1)–C(3)	1.891(9)	Re(1)–C(4)	2.121(8)
C(4)–C(5)	1.196(10)	Re(1)–N(4)	2.178(6)
Re(1)–N(5)	2.179(6)	Re(2)–C(29)	1.957(9)
Re(2)–C(30)	1.913(9)	Re(2)–C(31)	1.903(9)
Re(2)–C(32)	2.126(8)	C(32)–C(33)	1.195(10)
N(1)–Re(1)–C(2)	170.1(3)	N(2)–Re(1)–C(3)	169.7(3)
C(1)–Re(1)–C(4)	177.5(3)	Re(1)–C(4)–C(5)	177.3(7)
N(1)–Re(1)–N(2)	73.5(2)	N(4)–Re(2)–C(30)	171.9(3)
N(5)–Re(2)–C(31)	169.8(3)	C(29)–Re(2)–C(32)	178.5(3)
Re(2)–C(32)–C(33)	178.2(7)	N(4)–Re(2)–N(5)	74.1(2)

Table 3
Electrochemical data for **1**–**15** and the related complexes in acetonitrile (0.1 mol dm^{-3} ^{n}BuNPF$_6$) at 298 K [a]

Complex	Oxidation [b] E_{pa} (V) vs. SCE	Reduction [c] $E_{1/2}$ (V) vs. SCE (ΔE_p (mV))
1	+0.99, +1.78	−1.47 (70)
2	+1.02, +1.78	−1.45 (80)
3	+0.94, +1.78	−1.46 (70)
4	+0.92, +1.24, +1.79	−1.43(71)
5	+0.82, +1.14, +1.34, +1.82	−1.48(84)
6	+0.88, +1.33, +1.76	−1.60 (70)
7	+0.97, +1.40, +1.90	−1.54 (60)
8	+0.97, +1.75	−1.60 (58)
9	+0.91, +1.30, +1.76	−1.51 (75)
10	+0.82, +1.16, +1.36, +1.79	−1.50 (75)
11	+1.07, +1.25, +1.74	−1.55 (69)
12	+1.19, +1.85	−0.73 (88), −0.88 (80), −1.18 (67), −1.53 (75), −1.97 [d], −2.20 [d]
13	+1.23, +1.80	−0.58 (71), −1.16 (79), −1.52 (86), −1.76 [d], −2.19 [d], −2.40 [d]
14	+1.09, +1.34	−1.48 (84)
15	+1.09, +1.32	−1.40 (79)
[Re{(CF$_3$)$_2$-bpy}(CO)$_3$(C$_5$H$_4$N)]ClO$_4$ [e]	+1.84	−0.69 (63), −0.91 (168), −1.19 (117), −1.20 (101)
[Re(NO$_2$-phen)(CO)$_3$(C$_5$H$_4$N)]ClO$_4$ [e]	+1.80	−0.56 (64), −1.01 (163), −1.60, −1.73 [d], −1.85 [d]

[a] Working electrode: glassy carbon; ΔE_p of F_c^+/F_c ranges from 61 to 64 mV; scan rate: 100 mV s^{-1}.

[b] E_{pa}, anodic peak potential.

[c] $E_{1/2} = \dfrac{Epa + Epc}{2}$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively. $\Delta E_p = |E_{pa} - E_{pc}|$.

[d] Cathodic peak potential for irreversible wave.

[e] Ref. [31].

Table 4
Photophysical spectral data for **1**–**15**

Complex	Medium (T (K))	Absorption λ_{abs} (nm) (ε (dm^3 mol^{-1} cm^{-1}))	Emission λ_{em} (nm) (τ_o (μs))
1	Solid (298)		585 (0.19)
	Solid (77)		570
	CH$_2$Cl$_2$ (298)	286 (37 250), 298sh (30 160), 326sh (10 430), 420 (3240)	654 (< 0.01)
2	Solid (298)		580 (0.20)
	Solid (77)		565
	CH$_2$Cl$_2$ (298)	284 (39 880), 298sh (35 380), 324sh (13 330), 420 (2710)	650 (< 0.01)
3	Solid (298)		597 (0.27)
	Solid (77)		588
	CH$_2$Cl$_2$ (298)	278 (36 120), 298sh (29 200), 328sh (9570), 424 (2430)	668 (< 0.01)
4	Solid (298)		573 (< 0.1)
	Solid (77)		580 (10.35, 1.77) [a]
	THF (298)	246 (27 220), 296 (35 920), 338sh (11 570), 420 (3110)	640 (< 0.1)
	Glass (77) [b]		575 (6.99, 0.61) [a]
5	Solid (298)		560 (< 0.1)
	Solid (77)		548 (0.52)
	THF (298)	246 (29 740), 300 (23 030), 370 (30 480), 390sh (24 320)	649 (< 0.1)
	Glass (77) [b]		520 (3.51, 0.39) [a]
6	Solid (298)		600 (0.15)
	Solid (77)		585
	THF (298)	338sh (6620), 420 (2290)	720 (< 0.1)
7	Solid (298)		590 (0.27)
	Solid (77)		572
	THF (298)	310 (36 680), 338 (25 850), 406 (2780)	680 (< 0.1)
	Me$_2$CO	396sh (2860)	680 (< 0.1)
8	Solid (298)		580 (0.13)
	Solid (77)		570
	THF (298)	256 (17 965), 292 (19 225), 336sh (2510), 424 (2540)	690 (< 0.1)
9	Solid (298)		585 (< 0.1)
	Solid (77)		570 (0.91, 0.10) [a]
	THF (298)	242 (31 010), 294 (40 790), 338sh (11 400), 412 (3180)	625 (< 0.1)
	Glass (77) [b]		551 (7.16, 0.88) [a]
10	Solid (298)		550 (< 0.1)
	Solid (77)		530 (0.84, 0.12) [a]
	THF (298)	242 (48 140), 298 (33 540), 372 (43 250), 390sh (35 020)	640 (< 0.1)
	Glass (77) [b]		520 (3.14, 0.19) [a]
11	Solid (298)		600 (0.23)
	Solid (77)		580
	Me$_2$CO (298)	384 (3620)	670 (< 0.1)
12	CH$_2$Cl$_2$	364 (43 000)	Not measured
	Me$_2$CO (298)	352 (41 000)	650 (< 0.1)
13	CH$_2$Cl$_2$ (298)	272 (12 235), 296sh (8810), 362 (7070)	670 (< 0.1)
	Me$_2$CO (298)	352 (22 300)	640 (< 0.1)
14	Solid (298)		555 (< 0.1)
	Solid (77)		545 (3.14, 0.27) [a]
	THF (298)	252 (64 040), 296 (48 570), 362 (38 450), 390sh (25 060)	610 (< 0.1)
	Me$_2$CO (298)	358 (25 640), 380sh (20 430)	615 (< 0.1)
	Glass (77) [b]		527 (5.94, 1.57) [a]
15	Solid (298)		564 (< 0.1)
	Solid (77)		552 (2.60, 0.19) [a]
	THF (298)	244 (58 900), 298 (42 770), 372 (39 560), 394sh (26 710)	620 (< 0.1)
	Glass (77) [b]		526 (5.66, 0.80) [a]
[Re{(CF$_3$)$_2$-bpy}(CO)$_3$(C$_5$H$_4$N)]ClO$_4$ [c]	Me$_2$CO (298)	382 (3030)	680 (< 0.1)
[Re(NO$_2$-phen)(CO)$_3$(C$_5$H$_4$N)]ClO$_4$ [c]	Me$_2$CO (298)	360sh (4550)	630 (1.20)

[a] Double exponential decay.
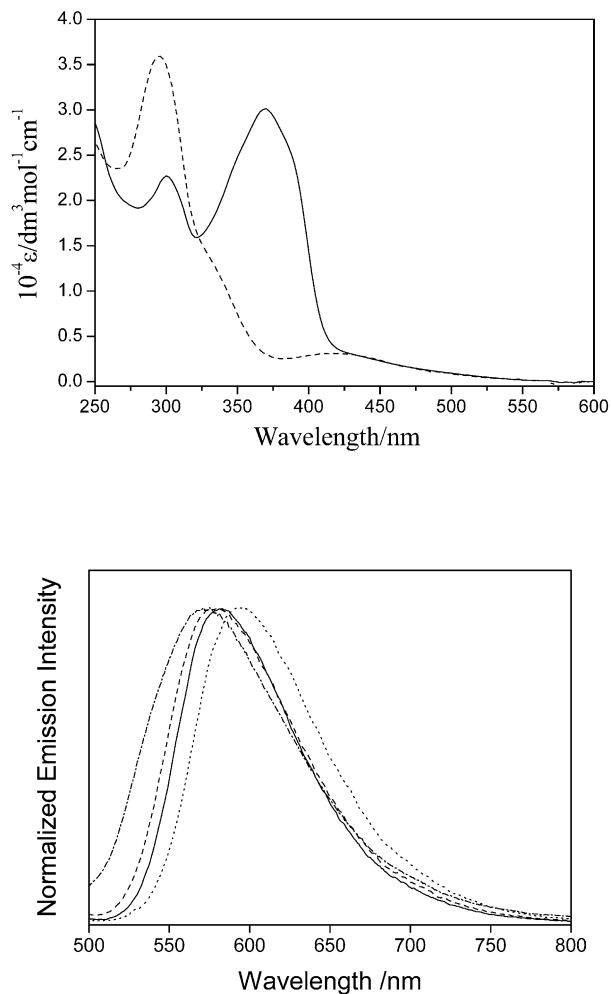[b] EtOH–MeOH (4:1 v/v).
[c] Ref. [31].

Fig. 6. Solid-state emission spectra of **1** (—), **2** (---), **3** (···) and **4** (– ·–) at 298 K.
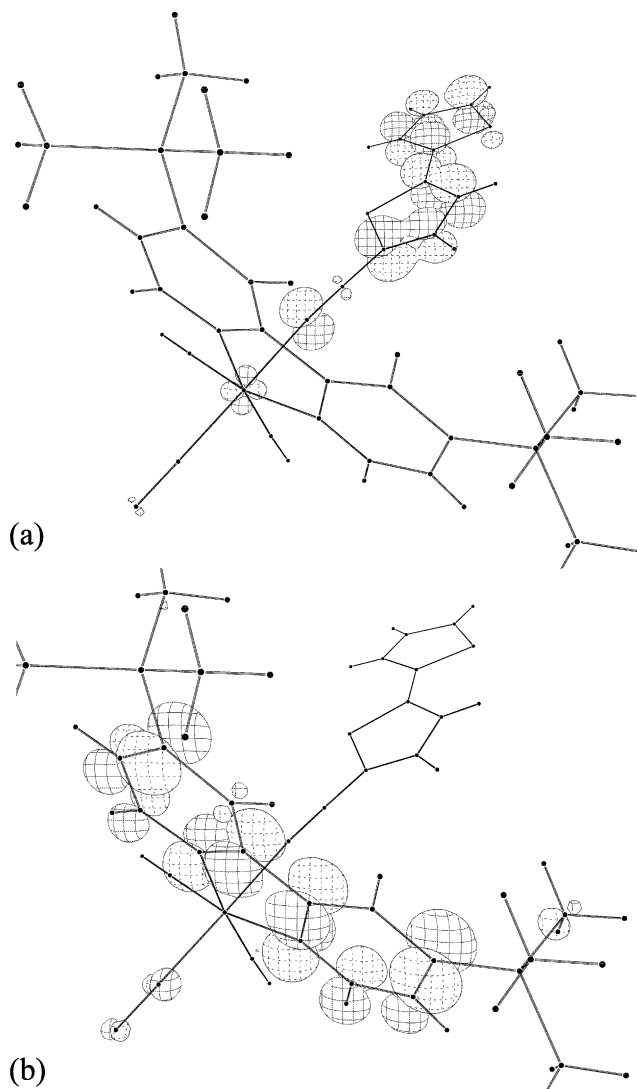

(a)

(b)

Fig. 7. CACAO plots of (a) HOMO and (b) LUMO of **10**.

Table 5
Calculated molecular orbital energies and transition energies

Number	Level (eV)	Composition (%)				HOMO–LUMO energy gap ΔE_{gap} (eV)
		Re	C≡CC$_4$H$_2$S–C$_4$H$_3$S	3CO	$^tBu_2$bpy	
103	−8.876	a	16	1	77	1.964
102	−8.956	1	68	14	13	(100 → 101)
101 (LUMO)	−9.447	a	a	2	94	
100 (HOMO)	−11.411	1	94	a	a	
99	−12.282	8	3	a	76	
98	−12.374	15	65	8	11	

a Percentage composition of less than 0.5%.

References

[1] I. Manners, Angew. Chem. Int. Ed. Engl. 35 (1994) 1602.

[2] (a) H.E. Katz, J. Mater. Chem. 7 (1997) 369;
(b) G. Horowitz, D. Fichou, X.Z. Peng, Z.G. Xu, F. Garnier, Solid State Commun. 72 (1987) 381;
(c) G. Horowitz, X.Z. Peng, D. Fichou, F. Garnier, J. Appl. Phys. 67 (1990) 528;
(d) F. Garnier, G. Horowitz, X.Z. Peng, D. Fichou, Adv. Mater. 2 (1990) 592;
(e) P. Ostoja, S. Guerri, M. Impronta, P. Zabberoni, R. Danieli, S. Rossini, C. Taliani, R. Zammoni, Adv. Mater. Opt. Electron. 1 (1992) 127;
(f) P. Ostoja, S. Guerri, S. Rossini, M. Servidori, C. Taliani, R. Zamboni, Synth. Met. 54 (1993) 447.

[3] P. Nguyen, P. Gómez-Elipe, I. Manners, Chem. Rev. 99 (1999) 1515 (and references there).

[4] (a) J. Stahl, J.C. Bohling, E.B. Bauer, T.B. Peters, W. Mohr, J.M. Martín-Alvarez, F. Hampel, J.A. Gladysz, Angew. Chem. Int. Ed. 41 (2002) 1871;
(b) R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. 1222 (2000) 810;
(c) S.B. Falloon, S. Szafert, A.M. Arif, J.A. Gladysz, Chem. Eur. J. 4 (1998) 1033.

[5] (a) F. Paul, J.Y. Mevellec, C. Lapinte, J. Chem. Soc. Dalton Trans. (2002) 1783.;
(b) F. Paul, W.E. Meyer, L. Toupet, H. Jiao, J. Gladysz, C. Lapinte, J. Am. Chem. Soc. 122 (2000) 9405;
(c) T. Weyland, K. Costuas, L. Toupet, J.F. Halet, C. Lapinte, Organometallics 19 (2000) 4228;
(d) F. Paul, C. Lapinte, Coord. Chem. Rev. 178–180 (1998) 431.

[6] (a) M.I. Bruce, B.C. Hall, B.W. Skelton, M.E. Smith, A.H. White, J. Chem. Soc. Dalton Trans. (2002) 995.;
(b) M.I. Bruce, K. Costuas, J.F. Halet, B.C. Hall, P.J. Low, B.K. Nicholson, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (2002) 383.;
(c) P.J. Low, M.I. Bruce, Adv. Organomet. Chem. 48 (2001) 71;
(d) M.I. Bruce, J.L. Paul, K. Costuas, J.F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949.

[7] (a) S. Mihan, T. Wedimann, V. Weinrich, D. Fenske, W. Beck, J. Organomet. Chem. 541 (1997) 423;
(b) S. Mihan, K. Sunkel, W. Beck, Chem. Eur. J. 5 (1999) 745.

[8] (a) R.D. Adams, U.H.F. Bunz, W. Fu, L. Nguyen, J. Organomet. Chem. 578 (1999) 91;
(b) R.D. Adams, U.H.F. Bunz, W. Fu, G. Roidl, J. Organomet. Chem. 578 (1999) 55.

[9] (a) T.C. Stoner, R.F. Dallinger, M.D. Hopkins, J. Am. Chem. Soc. 112 (1990) 5651;
(b) T.C. Stoner, S.J. Geib, M.D. Hopkins, J. Am. Chem. Soc. 114 (1992) 4201;
(c) T.C. Stoner, S.J. Geib, M.D. Hopkins, Angew Chem. Int. Ed. Engl. 32 (1993) 409;
(d) K.D. John, T.C. Stoner, M.D. Hopkins, Organometallics 15 (1997) 44948.

[10] M.S. Khan, A.K. Kakkar, N.J. Long, J. Lewis, P. Raithby, P. Nguyen, T.B. Marder, F. Wittmann, R.H. Friend, J. Mater. Chem. 4 (1994) 1227.

[11] (a) V.W.W. Yam, K.M.C. Wong, N. Zhu, J. Am. Chem. Soc. 124 (2002) 6506;
(b) V.W.W. Yam, R.P.L. Tang, K.M.C. Wong, K.K. Cheung, Organometallics 20 (2001) 4476;
(c) V.W.W. Yam, K.M.C. Wong, N. Zhu, Angew. Chem. Int. Ed. Engl., 42 (2003) in press.

[12] (a) V.W.W. Yam, Acc. Chem. Res. 35 (2002) 555;
(b) K.M.C. Wong, C.K. Hui, K.L. Yu, V.W.W. Yam, Coord. Chem. Rev. 229 (2002) 123;
(c) V.W.W. Yam, P.K.Y. Yeung, L.P. Chan, W.M. Kwok, D.L. Phillips, K.L. Yu, R.W.K. Wong, H. Yan, Q.J. Meng, Organometallics 17 (1998) 2590;
(d) V.W.W. Yam, C.K. Hui, K.M.C. Wong, N. Zhu, K.K. Cheung, Organometallics 21 (2002) 4326;
(e) C.K. Hui, B.W.K. Chu, N. Zhu, V.W.W. Yam, Inorg. Chem. 41 (2002) 6178.

[13] (a) V.W.W. Yam, C.H. Tao, L. Zhang, K.M.C. Wong, K.K. Cheung, Organometallics 20 (2001) 453;
(b) V.W.W. Yam, L. Zhang, C.H. Tao, K.M.C. Wong, K.K. Cheung, J. Chem. Soc. Dalton Trans. (2001) 1111.

[14] (a) V.W.W. Yam, K.K.W. Lo, K.M.C. Wong, J. Organomet. Chem. 578 (1999) 3;
(b) V.W.W. Yam, K.K.W. Lo, Chem. Soc. Rev. 28 (1999) 323;
(c) V.W.W. Yam, W.K.M. Fung, K.K. Cheung, Angew. Chem. Int. Ed. Engl. 35 (1996) 1100;
(d) V.W.W. Yam, W.K.M. Fung, K.K. Cheung, Chem. Commun. (1997) 963.;
(e) V.W.W. Yam, W.K.M. Fung, K.K. Cheung, Organometallics 16 (1997) 2032;
(f) V.W.W. Yam, W.K.M. Fung, K.K. Cheung, Organometallics 17 (1998) 3293.

[15] (a) V.W.W. Yam, W.K. Lee, K.K. Cheung, J. Chem. Soc. Dalton Trans. (1996) 2335.;
(b) V.W.W. Yam, S.W.K. Choi, C.L. Chan, K.K. Cheung, J. Chem. Soc. Chem. Commun. (1996) 2067.;
(c) V.W.W. Yam, W.K.M. Fung, K.K. Cheung, J. Cluster Sci. 10 (1999) 37;
(d) V.W.W. Yam, A.C.H. Lam, N. Zhu, Inorg. Chim. Acta 331 (2002) 239.

[16] (a) V.W.W. Yam, S.W.K. Choi, K.K. Cheung, Organometallics 15 (1996) 1734;
(b) V.W.W. Yam, S.W.K. Choi, J. Chem. Soc. Dalton Trans. (1996) 4227.;
(c) V.W.W. Yam, K.L. Cheung, L.H. Yuan, K.M.C. Wong, K.K. Cheung, Chem. Commun. (2000) 1513.

[17] (a) V.W.W. Yam, Chem. Commun. (2001) 789.;
(b) V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, Organometallics 14 (1995) 2749;
(c) V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, Organometallics 15 (1996) 1740;
(d) V.W.W. Yam, S.H.F. Chong, K.K. Cheung, Chem. Commun. (1998) 2121.;
(e) V.W.W. Yam, S.H.F. Chong, K.M.C. Wong, K.K. Cheung, Chem. Commun. (1999) 1013.;
(f) V.W.W. Yam, S.H.F. Chong, C.C. Ko, K.K. Cheung, Organometallics 19 (2000) 5092.

[18] (a) F. Garnier, G. Horowitz, X.Z. Peng, D. Dichou, Adv. Mater. 2 (1990) 592;
(b) H.E. Katz, J. Mater. Chem. 7 (1997) 369;
(c) J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539;
(d) K. Uchiyama, H. Akimichi, S. Hotta, H. Noga, H. Sakaki, Synth. Met. 63 (1994) 57;
(e) N. Chawdhury, A. Köhler, E.H. Friend, J. Chem. Phys. 110 (1999) 4963;

(f) A. Buttinelli, E. Viola, E. Antonelli, C.L. Sterzo, Organometallics 17 (1998) 2574.

[19] T.B. Hadd, H.L. Bozec, Polyhedron 7 (1988) 75.

[20] M. Furue, K. Maruyama, T. Oguni, M. Naiki, M. Kamachi, Inorg. Chem. 31 (1992) 3792.

[21] T.B. Patrick, J.M. Disher, W.J. Probst, J. Org. Chem. 37 (1972) 4467.

[22] R. Rossi, A. Carpita, A. Lezzi, Tetrahedron 40 (1984) 2773.

[23] L.D. Ciana, A. Haim, J. Heterocyclic Chem. 21 (1984) 607.

[24] M.S. Wrighton, D.L. Morse, J. Am. Chem. Soc. 96 (1974) 998.

[25] (a) J.V. Caspar, T.J. Meyer, J. Phys. Chem. 23 (1983) 952;
(b) J.K. Hino, L.D. Ciana, W.J. Dressich, B.P. Sullivan, Inorg. Chem. 31 (1992) 1072;
(c) F. Paolucci, M. Marcaccio, C. Paradisi, S. Roffia, C.A. Bignozzi, C. Amatore, J. Phys. Chem. B 102 (1998) 4759.

[26] P. Zanello, F. Laschi, M. Fontani, L.C. Song, Y.H. Zhu, J. Organomet. Chem. 593 (1988) 7.

[27] (a) C.M. Che, K.Y. Wong, F.C. Anson, J. Electroanal. Chem. Interf. Electrochem. 226 (1987) 211;

(b) R.R. Gagne, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854.

[28] (a) J. Lewis, N.J. Long, P.R. Raithby, G.P. Shields, W.Y. Wong, M. Younus, J. Chem. Soc. Dalton Trans. (1997) 4283.;
(b) Y. Zhu, D.B. Millet, M.O. Wolf, S.J. Rettig, Organometallics 18 (1999) 1930.

[29] (a) M.K. De Armond, K.W. Hanck, D.W. Wertz, Coord. Chem. Rev. 64 (1985) 65;
(b) K. Kalyanasundaram, J. Chem. Soc. Faraday Trans. 2 (1986) 82;
(c) R. Lin, Y. Fu, C.P. Brock, T.F. Guarr, Inorg. Chem. 31 (1992) 4336.

[30] (a) S. Duclos, F. Conan, S. Triki, Y.L. Mest, M.L. Gonzalez, J.S. Pala, Polyhedron 18 (1999) 1935;
(b) P. Zanello, F. Laschi, M. Fontani, L.C. Song, Y.H. Zhu, J. Organomet. Chem. 7 (2000) 593.

[31] V.W.W. Yam, V.C.Y. Lau, unpublished results.