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FULL PAPER

Synthesis, photophysical, photochemical and electrochemical properties of rhenium(I) diimine complexes with photoisomerizable pyridyl-azo, -ethenyl or -ethyl ligands

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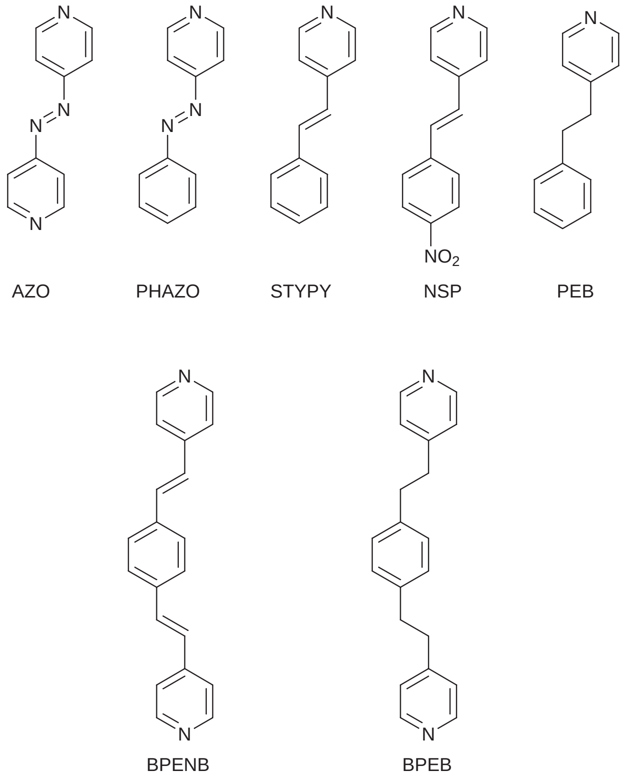
A series of rhenium(I) diimine complexes with pyridyl-azo, -ethenyl or -ethyl type ligands, $[Re(CO)_3(N-N)L]ClO_4$ and $[\{Re(CO)_3(N-N)\}_2L'][ClO_4]_2$ {N–N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen); L = 4-phenylazopyridine (PHAZO), 4-styrylpyridine (STYPY), [2-(4-pyridyl)ethyl]benzene (PEB), 4-(4-nitrostyryl)pyridine (NSP); L′ = 4,4′-azopyridine (AZO), 1,4-bis[2-(4-pyridyl)ethenyl]benzene (BPENB), 1,4-bis[2-(4-pyridyl)ethyl]benzene (BPEB)} have been synthesized and their photophysical properties studied. The quantum yields for the photoinduced isomerization of the complexes $[Re(CO)_3(bpy)(NSP)]^+$ and $[Re(CO)_3(phen)(NSP)]^+$ have been determined.

Photochromic molecules and their photoisomerization reactions have been the subject of extensive investigation in the field of molecular photochemistry.[1,2] Incorporation of a photoresponsive component into a supramolecular structure can lead to artificial photoresponsive species that may be quite valuable as model systems for theoretical studies and as photochemical molecular devices.[1,2] The basic requirements for the design of artificial photoresponsive supramolecular systems are as follows: (a) a component of the supramolecular system must be able to absorb light; (b) as a consequence of light excitation, the chromophoric component (or another component) must undergo a structural change; (c) such a molecular structural change must cause a 'functional' change (that is a change in some properties relevant to a function) in another component or in the whole supramolecular structure.[1,2] With the photoisomerizable properties of pyridyl-azo or -ethenyl type ligands and our recent interests in the design of luminescent metal complexes,[3] it would be extremely interesting to extend our studies to inorganic systems and supramolecular systems of photoswitchable materials. In this paper, the synthesis, photophysics, photochemistry and electrochemistry of $[Re(CO)_3(N-N)L]ClO_4$ and $[\{Re(CO)_3(N-N)\}_2L'][ClO_4]_2$ {N–N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen); L = 4-phenylazopyridine (PHAZO), 4-styrylpyridine (STYPY), [2-(4-pyridyl)ethyl]benzene (PEB), 4-(4-nitrostyryl)pyridine (NSP); L′ = 4,4′-azopyridine (AZO), 1,4-bis[2-(4-pyridyl)ethenyl]benzene (BPENB), 1,4-bis[2-(4-pyridyl)ethyl]benzene (BPEB)} are described; some of which have been previously communicated.[3a,b] The structures of these ligands are shown in Scheme 1. The quantum yields for the photoinduced isomerization of the complexes $[Re(CO)_3(bpy)(NSP)]^+$ and $[Re(CO)_3(phen)(NSP)]^+$ have been determined.

Experimental

Materials

The compound $[Re(CO)_5Cl]$ was purchased from Strem Chemicals Inc. and used as received. 2,2′-Bipyridine, 1,10-phenanthroline, silver trifluoromethanesulfonate Ag(OTf) and substituted pyridines which were used for subsequent ligand synthesis were obtained from Aldrich Chemical Co. Ltd. All solvents for synthesis were of analytical grade and were used without further purification.



Scheme 1 The schematic drawings of the pyridyl-azo, -ethenyl and -ethyl ligands

Physical measurements

The UV/VIS absorption 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. A narrow slit width was selected for all emission measurements, in particular those of complexes **1**–**9** which contain a photoisomerizable moiety. The complexes were found to be relatively stable and showed no significant UV/VIS spectral change before and after the measurements were taken. Proton NMR spectra were recorded either on a JEOL JNM-GSX270 (270 MHz) or a Bruker DPX300 (300 MHz) Fourier-transform NMR spectrometer. Electron-impact (EI) and positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the newly synthesized complexes were performed either by Butterworth Laboratories Ltd. or 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 Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals were recorded on a Tektronix model TDS-620A (500 MHz) digital oscilloscope, and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a round-bottomed flask (10 ml) equipped with a side-arm fluorescence cuvette (1 cm) and sealed from the atmosphere by a Kontes quick-release 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 an IBM-compatible personal computer. The ferrocenium–ferrocene couple was used as the internal reference in the electrochemical measurements in acetonitrile (0.1 M $Bu^n_4NPF_6$). The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode, with a Ag–$AgNO_3$ (0.1 M in MeCN) electrode as the reference electrode and a platinum foil acting as the counter electrode.

Chemical actinometry was employed for the photochemical quantum yield determination.[4] Incident light intensities were taken from the average values measured just before and after each photolysis experiment using ferrioxalate actinometry.[4] The time of irradiation was chosen to monitor 10% or less of the photolysis reaction in order to minimize any effects arising from secondary photolysis.

Synthesis of pyridyl-azo, -ethenyl or -ethyl type ligands

The ligands AZO,[5] PHAZO,[5] STYPY[6] and BPENB[6] were synthesized according to literature procedures.

4-(4-Nitrostyryl)pyridine NSP. This was prepared by modification of a procedure reported by McCleverty and co-workers.[7] A mixture of 4-ethenylpyridine (1.97 g, 18.8 mmol), 4-bromonitrobenzene (3.03 g, 15 mmol), palladium(II) acetate (34 mg, 0.15 mmol), triethylamine (1.90 g, 18.8 mmol) and PPh_3 (79 mg, 0.3 mmol) was sealed in a Schlenk tube under N_2, and heated to 100 °C for 3 d. The resulting solid was partitioned between dichloromethane and water. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and evaporated to dryness, and the crude product was recrystallized from acetone. Yield 2.37 g, 70%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to $SiMe_4$): δ 7.08–7.10, 7.20–7.26 (2 H, d, vinyl H, $J_{HH(trans)}$ = 16 Hz), 7.40–7.41 (2 H, d, pyridyl H *meta* to the N), 7.70–7.77, 8.23–8.35 (4 H, dd, phenyl H), 8.64–8.66 (2 H, dd, pyridyl H *ortho* to N). Positive-ion EI-MS: ion clusters at *m*/*z* 226 $\{M\}^+$ (Found: C, 68.73; H, 4.16; N, 12.31. Calc. for $C_{13}H_{10}N_2O_2$: C, 69.03; H, 4.42; N, 12.39%).

1,4-Bis[2-(4-pyridyl)ethyl]benzene BPEB. The ligand was synthesized by modification of a literature method reported by Osuch and Levine.[8] 4-Methylpyridine (0.93 g, 1 ml, 11.8 mmol) was dissolved in degassed tetrahydrofuran, and methyllithium (7.3 ml of 1.4 M solution in hexane) was added to the solution mixture at 0 °C under an inert atmosphere of nitrogen, during which the colorless solution turned orange-red. The solution was then allowed to reflux for 2 h. The reaction mixture was allowed to cool down, and a solution of 1,4-bis(bromomethyl)benzene in degassed tetrahydrofuran was added at 0 °C under nitrogen, and allowed to reflux overnight. Any unreacted 4-methylpyridine was distilled off. The reaction mixture was then poured into an ice–water mixture, and extracted with diethyl ether (3 × 10 ml). The ethereal layer was dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum. The solid residue was then purified by column chromatography on silica gel with diethyl ether as eluent. The first band was the unreacted 1,4-bis(bromomethyl)benzene, while the second band was the desired product. Yield 1.53 g, 45%. ^{1}H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 2.91 (8 H, s, CH_2CH_2 of BPEB), 7.05–7.27 (8 H, br, phenyl H and pyridyl H *meta* to N), 8.44–8.49 (4 H, d, pyridyl H *ortho* to N). Positive-ion EI-MS: ion clusters at *m*/*z* 287 $\{M\}^+$ (Found: C, 83.05; H, 7.01; N, 9.39. Calc. for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72%).

[2-(4-Pyridyl)ethyl]benzene PEB. The procedure was similar to that of BPEB except 1 equivalent of benzyl bromide was used instead of 1,4-bis(bromomethyl)benzene. Yield 1.51 g, 70%. ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, relative to $SiMe_4$): δ 2.92 (4 H, s, CH_2CH_2 of PEB), 7.04–7.10 (2 H, dd, pyridyl H *meta* to N), 7.13–7.27 (5 H, m, phenyl H), 8.44–8.51 (2 H, dd, pyridyl H *ortho* to N). Positive-ion EI-MS: ion clusters at *m*/*z* 183 $\{M\}^+$ (Found: C, 85.23; H, 7.23; N, 7.45. Calc. for $C_{13}H_{13}N$: C, 85.25; H, 7.10; N, 7.65%).

Synthesis of rhenium complexes

The rhenium complexes $[Re(CO)_3(N{-}N)Cl]$ and $[Re(CO)_3(N{-}N)(MeCN)]OTf$ (N–N = bpy, phen) were prepared by literature methods.[9,10]

General synthesis of $[Re(CO)_3(N{-}N)L]ClO_4$. This was synthesized by modification of a reported procedure.[9m,10j–l] A mixture of $[Re(CO)_3(N{-}N)(MeCN)]OTf$ (1 equivalent) and ligand L (1.5 equivalents) in tetrahydrofuran was heated to reflux under an inert atmosphere of nitrogen for 12 h. The resulting solution was allowed to cool, and evaporated to dryness under vacuum to give a bright yellow-orange residue, which was then dissolved in methanol and metathesized to its ClO_4^- salt upon addition of a saturated methanolic solution of $LiClO_4$. The yellow-orange solid obtained was recrystallized by vapor diffusion of diethyl ether into an acetonitrile solution of the product. Yields of the product ranged from 75 to 95%.

General synthesis of $[\{Re(CO)_3(N{-}N)\}_2L'][ClO_4]_2$. This was similar to the procedure for the synthesis of $[Re(CO)_3(N{-}N)L]ClO_4$ except 0.5 equivalent of L′ was used in place of 1.5 equivalents of L.[9m,10j–l]

$[\{Re(CO)_3(bpy)\}_2(AZO)][ClO_4]_2$ **1**. Orange solid, yield 80%. ^{1}H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 7.80–7.83 (2 H, dd, pyridyl H *meta* to N), 7.95–8.00 (2 H, td, 5,5′-H of bpy), 8.05–8.10 (2 H, td, 4,4′-H of bpy), 8.50–8.53 (2 H, d, 3,3′-H of bpy), 8.84–8.87 (2 H, d, pyridyl H *ortho* to N), 9.21–9.25 (2 H, td, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1922, 1938, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 1138 $\{M{\cdot}ClO_4\}^+$, 1038 $\{M\}^+$, 611 $\{M - Re(CO)_3(bpy)\}^+$, 427 $\{Re(CO)_3(bpy)\}^+$ (Found: C, 33.01; H, 2.01; N, 8.18. Calc. for $C_{36}H_{24}Cl_2N_8O_{14}Re_2{\cdot}1.5CH_2Cl_2$: C, 33.02; H, 1.98; N, 8.22%).

$[Re(CO)_3(bpy)(PHAZO)]ClO_4$ **2**. Orange crystalline solid, yield 82%. ^{1}H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 7.60–7.70 (5 H, m, 2,4,6-H of phenyl ring and pyridyl H *meta* to N), 7.78–7.80 (2 H, dd, pyridyl H *ortho* to N), 7.90–8.00 (2 H, dd, 3,5-H of phenyl ring), 8.05–8.10 (2 H, td, 5,5′-H of bpy), 8.45–8.55 (2 H, 4,4′-H of bpy), 8.78–8.84 (4 H, td, 3,3′-H of bpy), 9.50–9.55 (2 H, dd, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1911, 1941, 2031. Positive-ion FAB-MS: ion clusters at *m*/*z* 610 $\{M\}^+$, 427 $\{M - PHAZO\}^+$ (Found: C, 39.58; H, 2.49; N, 9.44. Calc. for $C_{24}H_{17}ClN_5O_7Re{\cdot}H_2O$: C, 39.63; H, 2.61; N, 9.63%).

$[Re(CO)_3(phen)(PHAZO)]ClO_4$ **3**. Orange crystalline solid, yield 88%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 7.81–7.85 (2 H, d, pyridyl H *meta* to N), 7.40–7.50 (5 H, m, phenyl H of PHAZO), 8.35–8.40 (4 H, dd + s, dd 3,8-H of phen, s 5,6-H of phen), 8.55–8.60 (2 H, dd, 4,7-H of phen), 9.08–9.11 (2 H, dd, 2,9-H of phen), 9.12–9.15 (2 H, dd, pyridyl H *ortho* to N). IR (Nujol mull, cm^{-1}): ν(CO) 1907, 1945, 2030. Positive-ion FAB-MS: ion clusters at *m*/*z* 634 $\{M\}^+$, 451 $\{M - PHAZO\}^+$ (Found: C, 40.76; H, 2.19; N, 9.25. Calc. for $C_{26}H_{17}ClN_5O_7Re{\cdot}0.5CH_2Cl_2$: C, 40.98; H, 2.19; N, 9.02%).

$[Re(CO)_3(bpy)(STYPY)]ClO_4$ **4**. Yellow crystalline solid, yield 88%. ^1H NMR (270 MHz, CD_3CN, 298 K, relative to $SiMe_4$): δ 7.03–7.04 (1 H, d, vinyl H), 7.40–7.44 (3 H, m, aryl H and pyridyl H *meta* to N), 7.49–7.56 (1 H, d, vinyl H), 7.58–7.60 (2 H, m, aryl H), 7.75–7.82 (2 H, td, 5,5′-H of bpy), 8.12–8.15 (2 H, d, pyridyl H *ortho* to N), 8.27–8.30 (2 H, td, 4,4′-H of bpy), 8.41–8.44 (2 H, d, 3,3′-H of bpy), 9.22–9.24 (2 H, d, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1920, 1943, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 608 $\{M\}^+$, 427 $\{M - STYPY\}^+$ (Found: C, 43.29; H, 2.56; N, 5.89. Calc. for $C_{26}H_{19}ClN_3O_7Re{\cdot}0.5H_2O$: C, 43.57; H, 2.79; N, 5.86%).

$[Re(CO)_3(phen)(STYPY)]ClO_4$ **5**. Yellow crystalline solid, yield 90%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 6.94–6.97 (1 H, d, vinyl-H of STYPY), 7.25–7.27 (2 H, dd, pyridyl H *meta* to N), 7.33–7.58 (5 H, m, phenyl H of STYPY), 8.01–8.04 (2 H, dd, pyridyl H *ortho* to N), 8.10–8.24 (4 H, m, 3,8- and 5,6-H of phen), 8.83–8.86 (2 H, dd, 4,7-H of phen), 9.61–9.63 (2 H, dd, 2,9-H of phen). IR (Nujol mull, cm^{-1}): ν(CO) 1900, 1939, 2030. Positive-ion FAB-MS: ion clusters at *m*/*z* 632 $\{M\}^+$, 451 $\{M - STYPY\}^+$ (Found: C, 45.52; H, 2.54; N, 5.51. Calc. for $C_{28}H_{19}ClN_3O_7Re{\cdot}0.5H_2O$: C, 45.40; H, 2.70; N, 5.68%).

$[Re(CO)_3(bpy)(NSP)]ClO_4$ **6**. Yellow solid, yield 88%. ^1H NMR (300 MHz, CD_3CN, 298 K, relative to $SiMe_4$): δ 7.21–7.26 (1 H, d, vinyl H of NSP), 7.40–7.42 (2 H, d, pyridyl H *meta* to N), 7.49–7.55 (1 H, d, vinyl H *ortho* to N), 7.74–7.79 (4 H, d + t, d phenyl H of NSP and t 5,5′-H of bpy), 8.18–8.29 (6 H, 2d + t, one d phenyl H of NSP, one d pyridyl H *ortho* to N and t 4,4′-H of bpy), 8.36–8.39 (2 H, d, 3,3′-H of bpy), 9.22–9.24 (2 H, d, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1907, 1922, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 659 $\{M\}^+$, 427 $\{M - NSP\}^+$ (Found: C, 40.48; H, 2.23; N, 7.38. Calc. for $C_{26}H_{18}ClN_4O_9Re{\cdot}0.5H_2O$: C, 40.98; H, 2.49; N, 7.36%).

$[Re(CO)_3(phen)(NSP)]ClO_4$ **7**. Yellow crystalline solid, yield 90%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 7.30–7.40, 7.60–7.70 (2 H, d, vinyl H of NSP), 7.51–7.55 (2 H, d, pyridyl H *meta* to N), 7.80–7.88, 8.20–8.26 (4 H, d, phenyl H of NSP), 8.35–8.40 (4 H, dd + s, dd 3,8-H of phen, s 5,6-H of phen), 8.55–8.60 (2 H, dd, pyridyl H *ortho* to N), 9.08–9.11 (2 H, dd, 4,7-H of phen), 9.92–9.95 (2 H, dd, 2,9-H of phen). IR (Nujol mull, cm^{-1}): ν(CO) 1902, 1934, 2026. Positive-ion FAB-MS: ion clusters at *m*/*z* 677 $\{M\}^+$, 451 $\{M - NSP\}^+$ (Found: C, 38.92; H, 2.11; N, 6.62. Calc. for $C_{28}H_{18}ClN_4O_9Re{\cdot}1.5CH_2Cl_2$: C, 39.16; H, 2.32; N, 6.20%).

$[\{Re(CO)_3(bpy)\}_2(BPENB)][ClO_4]_2$ **8**. Yellow crystalline solid, yield 77%. ^1H NMR (270 MHz, CD_3CN, 298 K, relative to $SiMe_4$): δ 7.09–7.15 (2 H, d, vinyl-H of BPENB), 7.43–7.48 (6 H, 2d, d vinyl-H of BPENB and d pyridyl-H *meta* to N), 7.55 (4 H, s, phenyl H of BPENB), 8.05–8.10 (2 H, td, 5,5′-H of bpy), 8.45–8.55 (2 H, 4,4′-H of bpy), 8.78–8.84 (4 H, td, 3,3′-H of bpy), 9.50–9.55 (2 H, dd, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1922, 1950, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 1237 $\{M{\cdot}ClO_4\}^+$, 711 $\{M - Re(CO)_3(bpy)\}^+$, 427 $\{M - Re(CO)_3(bpy) - BPENB\}^+$ (Found: C, 40.65; H, 2.38; N, 6.16. Calc. for $C_{46}H_{32}Cl_2N_6O_{14}Re_2{\cdot}H_2O$: C, 40.76; H, 2.51; N, 6.20%).

$[\{Re(CO)_3(phen)\}_2(BPENB)][ClO_4]_2$ **9**. Yellow crystalline solid, yield 85%. ^1H NMR (270 MHz, CD_3CN, 298 K, relative to $SiMe_4$): δ 7.09–7.15 (2 H, d, vinyl-H of BPENB), 7.43–7.48 (6 H, 2d, d vinyl-H of BPENB and d pyridyl-H *meta* to N), 7.55 (4 H, s, phenyl H of BPENB), 7.97–8.37 (8 H, m, 3,8- and 5,6-H of phen), 8.45–8.48 (4 H, d, pyridyl H *ortho* to N), 9.06–9.10 (4 H, dd, 4,7-H of phen), 9.88–9.91 (4 H, dd, 2,9-H of phen). IR (Nujol mull, cm^{-1}): ν(CO) 1909, 1933, 2032. Positive-ion FAB-MS: ion clusters at *m*/*z* 1285 $\{M{\cdot}ClO_4\}^+$, 735 $\{M - Re(CO)_3(phen)\}^+$, 427 $\{M - Re(CO)_3(phen) - BPENB\}^+$ (Found: C, 42.20; H, 2.32; N, 5.79. Calc. for $C_{48}H_{32}Cl_2N_6O_{14}Re_2{\cdot}0.5CH_2Cl_2$: C, 42.44; H, 2.38; N, 5.88%).

$[Re(CO)_3(bpy)(PEB)]ClO_4$ **10**. Yellow crystalline solid, yield 90%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 2.66–2.81 (4 H, m, CH_2CH_2 of PEB), 6.93–7.00 (4 H, m, pyridyl H *meta* to N and 3-H of phenyl ring of PEB), 7.10–7.14 (3 H, m, 2,4-H of phenyl ring of PEB), 7.75–7.80 (2 H, td, 5,5′-H of bpy), 8.02–8.05 (2 H, dd, pyridyl H *ortho* to N), 8.23–8.29 (2 H, td, 4,4′-H of bpy), 8.30–8.40 (2 H, d, 3,3′-H of bpy), 9.18–9.21 (2 H, dd, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1923, 1940, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 610 $\{M\}^+$, 427 $\{M - PEB\}^+$ (Found: C, 43.42; H, 2.90; N, 5.83. Calc. for $C_{26}H_{21}ClN_3O_7Re{\cdot}0.5H_2O$: C, 43.45; H, 3.06; N, 5.85%).

$[Re(CO)_3(phen)(PEB)]ClO_4$ **11**. Yellow crystalline solid, yield 92%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 2.66–2.81 (4 H, m, CH_2CH_2 of PEB), 6.93–7.00 (4 H, m, pyridyl H *meta* to N and 3-H of phenyl ring of PEB), 7.10–7.14 (3 H, m, 2,4-H of phenyl ring of PEB), 8.07–8.10 (4 H, d + dd, d pyridyl H *ortho* to N, dd 3,8-H of phen), 8.18 (2 H, s, 5,6-H of phen), 8.82–8.86 (2 H, dd, 4,7-H of phen), 9.58–9.60 (2 H, dd, 2,9-H of phen). IR (Nujol mull, cm^{-1}): ν(CO) 1922, 1942, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 634 $\{M\}^+$, 451 $\{M - PEB\}^+$ (Found: C, 45.59; H, 2.76; N, 5.68. Calc. for $C_{28}H_{21}ClN_3O_7Re$: C, 45.86; H, 2.87; N, 5.73%).

$[\{Re(CO)_3(bpy)\}_2(BPEB)][ClO_4]_2$ **12**. Yellow crystalline solid, yield 95%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 2.50–2.82 (8 H, m, CH_2CH_2 of BPEB), 6.82 (4 H, s, phenyl H of BPEB), 6.96–6.99 (4 H, d, pyridyl H *meta* to N), 7.92–7.98 (8 H, td, 5,5′-H of bpy), 8.30–8.39 (4 H, d, pyridyl H *ortho* to N), 8.43–8.45 (4 H, td, 4,4′-H of bpy), 8.65–8.68 (4 H, d, 3,3′-H of bpy), 9.40–9.42 (4 H, dd, 6,6′-H of bpy). IR (Nujol mull, cm^{-1}): ν(CO) 1922, 1935, 2027. Positive-ion FAB-MS: ion clusters at *m*/*z* 1283 $\{M{\cdot}ClO_4{\cdot}CH_3CN\}^+$, 714 $\{M - Re(CO)_3(bpy)\}^+$, 427 $\{M - Re(CO)_3(bpy) - BPEB\}^+$ (Found: C, 41.00; H, 2.57; N, 6.23. Calc. for $C_{46}H_{34}Cl_2N_6O_{14}Re_2$: C, 41.27; H, 2.54; N, 6.28%).

$[\{Re(CO)_3(phen)\}_2(BPEB)][ClO_4]_2$ **13**. Yellow crystalline solid, yield 90%. ^1H NMR [270 MHz, $(CD_3)_2CO$, 298 K, relative to $SiMe_4$]: δ 2.50–2.82 (8 H, m, CH_2CH_2 of BPEB), 6.82 (4 H, s, phenyl H of BPEB), 6.96–6.99 (4 H, dd, pyridyl H *meta* to N), 8.02–8.14 (8 H, 2dd, dd pyridyl H *ortho* to N and dd 3,8-H of phen), 8.16 (4 H, s, 5,6-H of phen), 8.81–8.85 (4 H, dd, 4,7-H of phen), 9.58–9.60 (4 H, dd, 2,9-H of phen). IR (Nujol mull, cm^{-1}): ν(CO) 1916, 1945, 2030. Positive-ion FAB-MS: ion clusters at *m*/*z* 1287 $\{M{\cdot}ClO_4\}^+$, 738 $\{M - Re(CO)_3(phen)\}^+$, 451 $[M - Re(CO)_3(phen) - BPEB\}^+$ (Found: C, 42.43; H, 2.84; N, 5.72. Calc. for $C_{48}H_{34}Cl_2N_6O_{14}Re_2{\cdot}0.5CH_2Cl_2$: C, 42.38; H, 2.59; N, 5.87%).

Results and Discussion

The complexes $[Re(CO)_3(N\text{–}N)L]ClO_4$ and $[\{Re(CO)_3(N\text{–}N)\}_2L'][ClO_4]_2$ were prepared by refluxing $[Re(CO)_3(N\text{–}N)(MeCN)]OTf$ (1 equivalent) and the corresponding ligand L (1.5 equivalents) or L′ (0.5 equivalent) in dry THF under an inert atmosphere of nitrogen, respectively. After allowing the reaction mixture to heat to reflux overnight, the solvent was removed under vacuum, and the solid residue was dissolved in methanol, filtered and the filtrate was reduced in volume, and metathesized to the perchlorate salt. Subsequent recrystalliz-

Table 1 Photophysical data of rhenium(I) diimine complexes

	Complex	Solvent (*T*/K)	Absorption λ_{max}/nm (ε/M^{-1} cm^{-1})	Emission λ_{em}/nm(τ_0/μs)
1	$[\{Re(CO)_3(bpy)\}_2(AZO)][ClO_4]_2$	CH_2Cl_2 (298)	250 (10 100), 272 (9970), 321 (6540), 366 (4090)	535 (1.04)
2	$[Re(CO)_3(bpy)(PHAZO)]ClO_4$	CH_2Cl_2 (298)	300 (sh) (25 400), 315 (40 000), 321 (sh) (9400), 344 (3350)	550 (0.50)
3	$[Re(CO)_3(phen)(PHAZO)]ClO_4$	CH_2Cl_2 (298)	232 (16 100), 260 (11 000), 279 (13 000), 300 (9400), 343 (11 800), 450 (sh) (5000)	563 (0.2, 1.5)[a]
4	$[Re(CO)_3(bpy)(STYPY)]ClO_4$	CH_2Cl_2 (298)	288 (sh) (6000), 324 (9550), 340 (9330)	530 (0.63)
		CH_3CN (298)	240 (20 200), 266 (sh) (17 100), 312 (28 400), 320 (sh) (33 700), 334 (29 100)	540 (0.46)
5	$[Re(CO)_3(phen)(STYPY)]ClO_4$	CH_2Cl_2 (298)	276 (24 200), 338 (24 500), 400 (sh) (2910)	548 (2.3)
6	$[Re(CO)_3(bpy)(NSP)]ClO_4$	CH_3CN (298)	242 (25 700), 282 (sh) (26 700), 312 (sh) (32 400), 320 (38 200), 346 (36 800)	540[b]
7	$[Re(CO)_3(phen)(NSP)]ClO_4$	CH_2Cl_2 (298)	258 (sh) (21 500), 278 (26 100), 294 (sh) (20 500), 348 (34 000)	550[b]
		CH_3CN (298)	230 (sh) (32 000), 254 (sh) (19 000), 278 (26 100), 346 (33 000)	550[b]
8	$[\{Re(CO)_3(bpy)\}_2(BPENB)][ClO_4]_2$	CH_3CN (298)	244 (54 200), 276 (41 700), 310 (43 300), 320 (49 300), 360 (43 300)	415 (<0.1), 556 (0.24)
9	$[\{Re(CO)_3(phen)\}_2(BPENB)][ClO_4]_2$	CH_3CN (298)	224 (96 200), 252 (64 200), 276 (67 100), 300 (sh) (35 900), 350 (sh) (59 800), 384 (94 300), 406 (sh) (66 000)	423 (<0.1), 540 (2.0)
10	$[Re(CO)_3(bpy)(PEB)]ClO_4$	CH_3CN (298)	249 (19 200), 263 (18 900), 305 (11 200), 319 (12 000), 348 (3530)	540 (0.23)
		Solid (298)		510 (1.5)
		Solid (77)		500
11	$[Re(CO)_3(phen)(PEB)]ClO_4$	CH_2Cl_2 (298)	259 (27 500), 276 (30 000), 294 (sh) (16 300), 334 (sh) (5340), 368 (sh) (4310)	550 (2.0)
		CH_3CN (298)	230 (sh) (11 800), 276 (9600), 308 (sh) (7400), 322 (8290), 363 (sh) (3550)	571 (1.4)
		Solid (298)		515 (1.9)
		Solid (77)		500
12	$[\{Re(CO)_3(bpy)\}_2(BPEB)][ClO_4]_2$	CH_3CN (298)	249 (38 300), 263 (37 400), 305 (21 700), 319 (22 900), 347 (6710)	586 (0.2)
		Solid (298)		508 (1.2)
		Solid (77)		508
13	$[\{Re(CO)_3(phen)\}_2(BPEB)][ClO_4]_2$	CH_2Cl_2 (298)	259 (43 200), 275 (47 700), 295 (sh) (24 600), 329 (sh) (8490), 383 (sh) (5830)	550 (2.5)
		CH_3CN (298)	258 (sh) (38 100), 276 (45 000), 327 (sh) (9350), 368 (sh) (6130)	570 (1.5)
		Solid (298)		557 (1.1)
		Solid (77)		540

[a] It is a biexponential decay. [b] As the complexes were rather light-sensitive as reflected by a change in the UV/VIS absorption spectra after laser-flash excitation, no lifetime measurements were made.

ation from acetonitrile–diethyl ether or dichloromethane–diethyl ether gave the analytically pure complexes. All the newly synthesized complexes were characterized by ^{1}H NMR and IR spectroscopy, FAB-MS and gave satisfactory elemental analyses. All complexes showed three ν(CO) stretches in the IR spectra, typical of Re(I) diimine tricarbonyl complexes with the carbonyls arranged in a facial configuration.[9a–j]

Electronic absorption spectroscopy

The electronic absorption spectral data of the rhenium(I) complexes are shown in Table 1 and those of the ligands are summarized in Table 2. The electronic absorption spectra of complexes **1**–**5** and **13** in dichloromethane and complexes **6**–**12** in acetonitrile all show an absorption band/shoulder at *ca.* 320–400 nm at 298 K. With reference to previous spectroscopic work on related rhenium(I) diimine systems,[9,10] this absorption band is most likely assigned as the $d\pi(Re) \longrightarrow \pi^*$(bpy/phen) metal-to-ligand charge-transfer (MLCT) transition. However, with complexes **1**–**9**, closer scrutiny on their absorption spectra showed that the band in this region has an absorption coefficient of the order of 10^4, which is much larger than an order of 10^3 M^{-1} cm^{-1} commonly observed for rhenium(I) diimine MLCT transitions. Further examination of the free ligands associated with complexes **1**–**9**, that is the AZO, PHAZO, NSP, STYPY and BPENB ligands, showed that they absorbed strongly in the same region with absorption coefficients of the order of 10^4 M^{-1} cm^{-1}. Therefore it is likely that the lowest energy absorption band in complexes **1**–**9** may consist of an admixture of intraligand (IL) $\pi \longrightarrow \pi^*$ (L or L′) and MLCT character. On the other hand, the electronic absorption spectra of complexes **10**–**13** which do not contain the conjugated pyridyl ligands showed low energy absorption bands with absorption coefficients of 10^3 M^{-1} cm^{-1}, typical of MLCT transitions of rhenium(I) diimine systems. Moreover, for complexes **12** and **13**, where the two rhenium(I) centers were bridged by a non-conjugated BPEB ligand which does not show any appreciable absorption beyond 300 nm, the absorption coefficients for the lowest energy absorption band/shoulder are about twice that observed for the respective mononuclear complexes **10** and **11**. These findings suggest that the lowest energy absorption band/shoulders in

Table 2 Electronic absorption spectral data of the pyridyl ligands in MeCN at 298 K

Compound	Absorption λ_{max}/nm (ε/M^{-1} cm^{-1})
AZO	252 (3830), 312 (7160), 460 (295)
PHAZO	228 (9470), 310 (23 360), 450 (265)
STYPY	228 (21 160), 236 (sh) (16 340), 292 (31 300), 320 (sh) (15 435)
NSP	218 (sh) (14 345), 234 (10 865), 276 (17 755), 332 (30 875)
BPENB	238 (15 655), 246 (12 925), 334 (47 070), 350 (57 120), 370 (sh) (38 000)
PEB	258 (2145), 288 (sh) (230)
BPEB	222 (14 920), 266 (14 270), 280 (13 050)

complexes **10**–**13** are pure MLCT transitions. Similar observations have been reported in other related binuclear and supramolecular Re(I) and Ru(II) polypyridine systems.[9,10,11a,b]

Emission spectroscopy

Excitation of the complexes at $\lambda \geqslant 350$ nm in fluid solution at room temperature results in a yellowish-green luminescence centered at *ca.* 510–580 nm. The detailed photophysical data are summarized in Table 1. The large Stokes shift together with the relatively long radiative lifetime observed are suggestive of an emissive origin of triplet parentage, possibly derived from the ^{3}MLCT [dπ(Re) $\longrightarrow$ π^*(bpy/phen)] state. The emission energies of the complexes are comparable to those of other rhenium(I) tricarbonyl diimine systems, such as [Re(CO)$_3$(bpy)(4-Etpy)]ClO$_4$[10j] and [Re(CO)$_3$(phen)(py)]ClO$_4$,[9n,o] suggesting the relative insensitivity of the emission energy to the nature of the pyridyl ligand.[11]

The almost identical excited-state lifetimes and emission maxima of the binuclear complexes **8**, **9**, **12** and **13** with their respective mononuclear complexes **4**, **5**, **10** and **11** are suggestive of weak to no interaction between the two rhenium centers, typical of complexes containing weakly conjugated/non-conjugated bridging ligands. It is interesting to note that for the complexes which contain photoisomerizable bridging C=C or N=N units, in particular, complexes **1**–**3**, **6** and **7**, their radiative lifetimes are found to be shorter than those of complexes **10**–**13**. This may be rationalized by the presence of an intramolecular excited-state energy transfer to the photoisomerizable unit to effect a *trans–cis* isomerization process, *i.e.* the presence of an additional non-radiative decay pathway in **1**–**3**, **6** and **7** as compared to complexes **10**–**13**.

Photoisomerization studies

Spectroscopic measurements. With complexes **1**–**9** which contained a photoisomerizable C=C or N=N unit, a photoinduced *trans–cis* isomerization was observed upon visible light excitation. Upon irradiation of a degassed dichloromethane solution of [Re(N–N)(CO)$_3$L]$^+$ or [{Re(N–N)(CO)$_3$}$_2$L′]$^{2+}$, where L and L′ contain an isomerizable pyridyl ligand, at $\lambda > 350$ nm, UV/VIS spectral changes with a clean and well defined isosbestic point were observed. For example, a solution of complex **2** gives a clean UV/VIS spectral trace with an isosbestic point at *ca.* 310 nm (Fig. 1). The spectral changes were suggested to result from the *trans–cis* isomerization of the azo unit of the PHAZO ligand. To our surprise, the emission intensity was shown to be greatly enhanced after steady-state photolysis for 12 h, using a conventional 200 W xenon lamp as the light source. The luminescence quantum yield (φ_{lum}) measured after photolysis was *ca.* 40 times greater than that before photolysis, and its emission maximum is red-shifted by *ca.* 20 nm from 550 nm to 570 nm [$\approx$0.08 eV, eV $\approx 1.602 \times 10^{-19}$ J] (Fig. 2). It is well known that for the free azo chromophore the triplet-state energy for the *trans* isomer is generally lower than that of the *cis* counterpart as a result of the steric constraints in the *cis* isomer which reduces the π electron delocalization.[4b] Thus it is likely that in the ^{3}MLCT excited state some of its excited-state energy is intramolecularly transferred to the *trans*-azo moiety, providing an additional non-radiative deactivation pathway. On the contrary, with the *cis*-azo ligand formed upon photolysis, such intramolecular energy-transfer processes are highly disfavored or blocked owing to the higher triplet-state energy of the *cis* isomer, and hence resulting in a higher luminescence quantum yield [for complex **2**, $\varphi_{\text{lum}}(trans) = 7.2 \times 10^{-4}$; $\varphi_{\text{lum}}(cis) = 0.027$].[3a,b]

In order to further our understanding on the photoinduced *trans–cis* isomerization processes in these complexes, a comparison of their photoreactivities with the bridging C=C analog, *i.e.* the styrylpyridine ligand was made. As expected, due to the relatively higher triplet-state energy of the ethylene moiety compared to the azo analog,[4b] the steady-state photolysis reaction of complex **4** was found to be extremely slow under similar experimental conditions. However, upon replacement of styrylpyridine with NSP, an enhancement in the efficiency of the isomerization process was obtained.

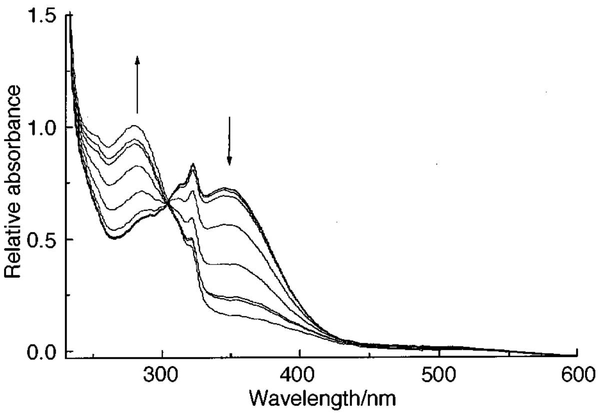


Fig. 1 The UV/VIS spectral trace of complex **2** upon steady-state photolysis at $\lambda > 350$ nm at 0, 125, 190, 250, 370, 490 and 790 min in degassed CH$_2$Cl$_2$

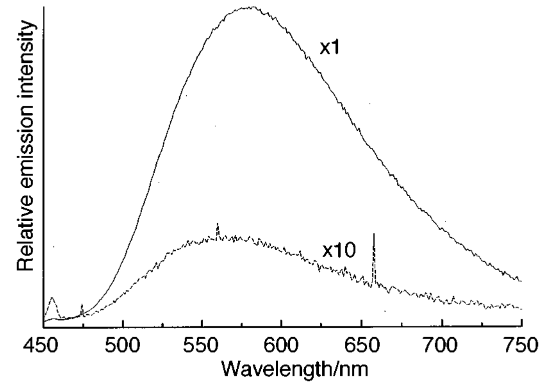


Fig. 2 The emission spectra of complex **2** before (– – – – – –) and after (———) photolysis

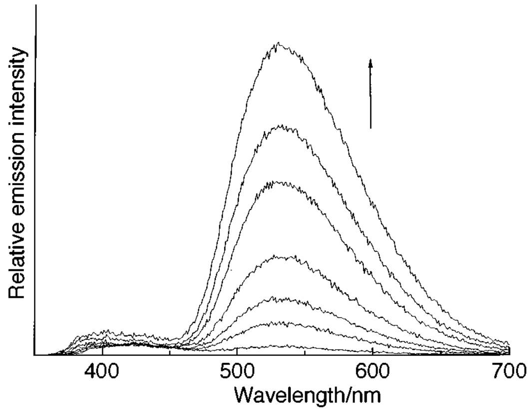


Fig. 3 The emission spectral traces of complex **7** upon irradiation at $\lambda = 330$ nm in degassed CH$_2$Cl$_2$

Steady-state photolysis of complex **7** under similar experimental conditions required *ca.* 4 h to give no further UV/VIS spectral changes with an isosbestic point at *ca.* 300 nm and a greater than 35 times increase in the luminescence quantum yield. The emission traces resulting from the photoisomerization of a degassed dichloromethane solution of complex **7** upon irradiation at $\lambda = 366$ nm are shown in Fig. 3. It is likely that irradiation of the lowest energy absorption band which

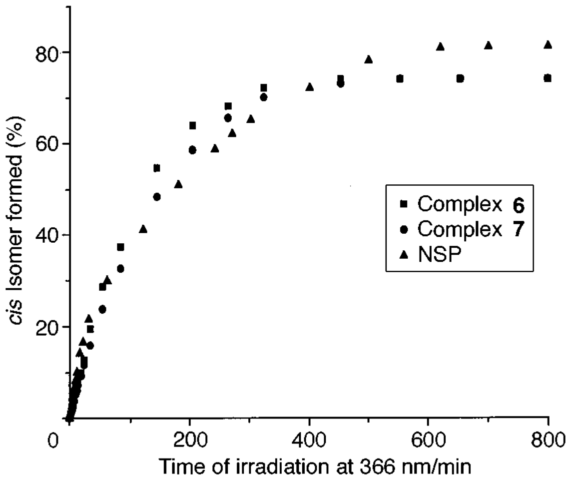


Fig. 4 Plots of the *cis* isomer of complexes **6**, **7** and the NSP ligand formed (%) against the time of irradiation at 366 nm

Table 3 Quantum yields for the photoisomerization processes of compounds **6**, **7** and NSP

Compound	Quantum yield, $\varphi_{trans\text{–}cis}$	*cis* Isomer formed (%)
6	0.66	74
7	0.47	74
NSP	0.81	80

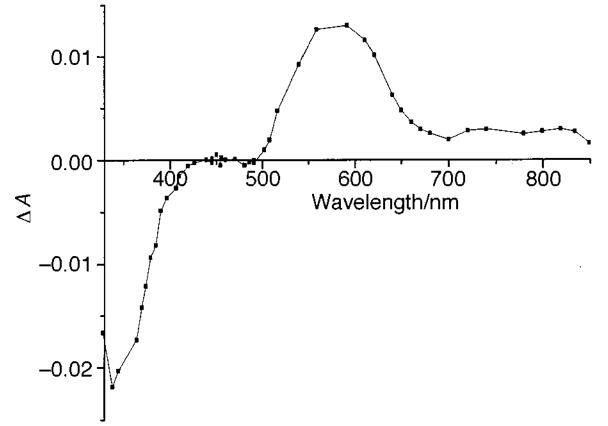


Fig. 5 Transient absorption difference spectrum for the intramolecular energy-transfer process of complex **3** (25 mM) recorded 10 µs after laser flash

was assigned as an admixture of MLCT–IL transitions resulted in an efficient *trans–cis* isomerization process.

Quantum yield measurements. In order to obtain a quantitative measure of the photoinduced isomerization processes of the rhenium(I) diimine complexes, the photochemical quantum yield for the *trans–cis* isomerization process of the complexes was determined using chemical actinometry. In the present study, complexes with the styrylpyridine moiety were chosen instead of those with 4-phenylazopyridine, as it contains a CH=CH group which shows a characteristic ^{1}H NMR coupling constant in the *trans* (16 Hz) and *cis* (12 Hz) forms, and could be conveniently used for monitoring the photoreaction. However, the photoreactions of the complexes with STYPY ligands were extremely slow. In this context, the complexes with the NSP ligand where an electron withdrawing NO_2 group was introduced to the 4-position of the phenyl ring, *i.e.* complexes **6** and **7**, were employed in the studies, which were extremely sensitive to light irradiation and showed effective photoisomerization. The photoreactions were monitored by ^{1}H NMR spectroscopy. Upon irradiation, the CH=CH signals for the *trans* isomers which occurred at δ 7.29–7.35 and 7.58–7.64 (2 H, J_{HH} 16 Hz) for **6** and **7** respectively in CD_3CN were found to decrease gradually while at the same time the signals due to the *cis* isomers which occurred at δ 6.47–6.51 and 6.80–6.90 (2 H, J_{HH} 12 Hz) (**6** and **7** respectively) gradually built up in intensity. From the ^{1}H NMR results, 74% of both $[Re(CO)_3(bpy)(\textit{cis}\text{-}NSP)]^+$ and $[Re(CO)_3(phen)(\textit{cis}\text{-}NSP)]^+$ were formed upon irradiation while in the case of the pure ligand, NSP, 80% of the *cis* isomer was formed. The plots of the percentage of *cis* isomer formed or the percentage of *trans* isomer disappeared against the time of irradiation for complexes **6**, **7** and the ligand NSP are depicted in Fig. 4. The quantum yields of the photochemical reactions are summarized in Table 3 where an order of NSP > **6** > **7** is observed. A control experiment to correct for the presence of any thermal *trans–cis* isomerization reaction was performed in each case, in which an equal amount of the complex/compound was dissolved in the same amount of degassed deuteriated acetonitrile and placed in the dark. A real-time monitoring of the thermal control by ^{1}H NMR spectroscopy was performed in each case, from which no observable *cis* isomer was formed in the absence of light.

Quenching studies

Excited-state absorption properties: transient absorption spectroscopic studies for intramolecular energy-transfer quenching. The transient absorption spectrum of complex **3** in CH_3CN at room temperature is shown in Fig. 5. The transient absorption difference spectrum of **3** showed a ground-state bleaching at *ca.* 350–425 nm, while for both complexes **2** and **3** a strong absorption at *ca.* 450–700 nm was observed. The broad, featureless transient absorption band of both complexes at *ca.* 600 nm was tentatively assigned as the triplet-state absorption of the *trans* PHAZO moiety. Similar assignments have been suggested by Shaw and co-workers.[11a,b] The triplet-state absorption of *trans*-4,4′-azopyridine has also been reported to occur at similar regions.[12] The observation of the triplet-state absorption of the PHAZO moiety is indicative of an intramolecular energy-transfer quenching mechanism.

Intermolecular energy-transfer quenching. In order to provide further support on the intramolecular energy-transfer process occurring in the complexes such as complex **3**, an intermolecular energy-transfer quenching study of the related complex $[Re(CO)_3(phen)(py)]ClO_4$ by 4-phenylazopyridine and 4-(4-nitrostyryl)pyridine, respectively, in acetonitrile was performed. From the Stern–Volmer quenching plot, it was found that the excited-state luminescence properties of $[Re(CO)_3(phen)(py)]ClO_4$ were quenched effectively by both PHAZO and NSP. The diffusion-corrected quenching rate constants, k_q', were found to be in the order of 8.5×10^9 and 4.7×10^9 M^{-1} s^{-1}, respectively. Based on the intermolecular quenching data, it is envisaged that the corresponding intramolecular energy-transfer quenching in complex **3** would be very facile, with rate constants greater than that of 10^9 s^{-1}.

Electrochemical properties

Cyclic voltammetric data for the rhenium(I) complexes and their related compounds[9d,10c,h,j,n,o,13] are collected in Table 4. All the complexes showed a characteristic quasireversible to irreversible oxidation wave in the range of +1.72 to +1.78 V *vs.* SCE. This oxidation wave is assigned as the oxidation of the rhenium center, *i.e.* $Re^I \longrightarrow Re^{II}$, as similar findings have been reported in related systems.[13] The assignment of the oxidation as ligand-centered oxidation is unlikely since both the diimine ligand as well as the free pyridyl-azo, -ethenyl or -ethyl ligands do not show any oxidation wave in this region.

However, for the reductive scan, a more complicated picture is obtained. For the 2,2′-bipyridine systems, the cyclic voltam-

Table 4 Electrochemical data for rhenium(I) diimine complexes

Complex/ compound	Reduction $E_{\frac{1}{2}}$ or E_{pc}[a]/V *vs.* SCE (ΔE/mV)	Oxidation $E_{\frac{1}{2}}$[a,b]/V *vs.* SCE (ΔE/mV)
1	−1.27 (90), −1.52,[c] −1.63,[c] −1.73,[c] −2.14[c]	+1.77 (91)
2	−0.75 (79), −1.11 (57), −1.28 (67),[d] −1.83,[c] −2.05[d]	+1.78 (60)
3	−0.75 (70), −1.07 (60),[d] −1.27 (70),[d] −1.86,[c] −2.02[c]	+1.78 (60)
4	−1.18 (53), −1.39 (98),[d] −1.74,[c] −2.00,[c] −2.18[c]	+1.76 (113)
6	−0.98 (67), −1.14 (70), −1.29 (63),[d] −1.65,[c] −1.90,[c] −2.02,[c] −2.16,[c] −2.24[c]	+1.75 (96)
7	−0.96 (65), −1.13 (47),[d] −1.27 (87),[d] −1.82,[c] −2.12,[c] −2.20[c]	+1.72 (63)
8	−1.19 (30), −1.39 (94),[d] −1.81,[c] −2.11,[c] −2.31[c]	+1.77 (84)
9	−1.07 (197),[d] −1.44 (90),[d] −1.83,[c] −2.06,[c] −2.30[c]	+1.78 (54)
10	−1.18 (54), −1.40 (175)[d]	+1.74 (88)
12	−1.19 (90), −1.51 (37)[d]	+1.74 (62)
AZO[e]	−1.21 (70), −1.81 (110)	—
PHAZO[e]	−1.47 (90), −1.89 (180)	—
STYPY	−1.58 (73), −1.85,[c] −2.02 (107)[d]	—
NSP	−1.05 (104),[d] −1.70[c]	—
BPENB	−1.69 (120),[d] −1.94 (62),[d] −2.13 (85)[d]	—

[a] All the electrochemical measurements were done in MeCN (0.1 M $Bu^n{}_4NPF_6$); $E_{\frac{1}{2}} = (E_{pa} + E_{pc})/2$; E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential; working electrode, glassy carbon; scan rate, 100 mV s^{-1}; $\Delta E = |E_{pa} - E_{pc}|$ in mV. [b] All the oxidation waves are found to be dependent on the scan rate, and are quasireversible. [c] Irreversible reduction wave, the potential reported is E_{pc}. [d] The reductive wave is found to be dependent on the scan rate, and is quasireversible. [e] Taken from ref. 14.

mograms generally consist of a reversible–quasireversible reduction wave at *ca.* −1.15 V *vs.* SCE with $\Delta E \approx 60$ mV and a quasireversible to irreversible wave at *ca.* −1.35 V *vs.* SCE. Based on previous work on related systems,[9d,10c,h,j,n,o,13] the reduction couple at *ca.* −1.15 V is assigned as the reduction of the 2,2′-bipyridine ligand, bpy$^{0/-1}$. The reduction at *ca.* −1.35 V is assigned as the second reduction of the 2,2′-bipyridine, *i.e.* bpy$^{-1/-2}$, and this assignment has generally been supported by the findings of Demas and co-workers[9c] and Meyer and co-workers.[9h,j] However, according to the works by Moya and co-workers[13c,d] and Guarr and co-workers,[13e] the reduction wave at *ca.* −1.35 V is assigned as a metal-localized reduction, *i.e.* Re$^{I/0}$. Although we cannot completely exclude the possibility of this assignment, we favor its assignment as the bipyridine-centered reduction. For the 1,10-phenanthroline systems, the reversible–quasireversible wave at *ca.* −1.10 V *vs.* SCE is assigned as the reduction of the 1,10-phenanthroline ligand, *i.e.* phen$^{0/-1}$ as similar assignments have been reported in related rhenium(I)–phen systems.[9d,10c,h,j,n,o,13] Besides the above assigned diimine-based reduction waves, other reduction waves were probably due to the reduction of the pyridyl-azo, -ethenyl or -ethyl ligands. However, no attempts were made to unambiguously assign all the reduction waves, as the reduction of these Re diimine complexes is often complicated by coupled chemical processes. It is interesting to note that for complex **12** which contains the bridging ligand BPEB, only one metal-centered oxidation wave and two reduction waves for the bpy ligand are observed, which are suggestive of the non-interacting nature of the two rhenium diimine units, leading to the observation that the oxidation and reduction waves of the two units are indistinguishable.[15]

Acknowledgements

V. W.-W. Y. acknowledges financial support from the Research Grants Council and The University of Hong Kong. V. C.-Y. L. acknowledges the receipt of both the Croucher Foundation Studentship (1993–1995) and Scholarship (1995–1996), administered by the Croucher Foundation and a Sir Edward Youde Memorial Fund Fellowship, administered by the Sir Edward Youde Memorial Fund Council.

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Received 24*th February* 1998; *Paper* 8/01575I