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Synthesis, Photophysical Properties, and Photoinduced Luminescence Switching of Trinuclear Diimine Rhenium(I) Tricarbonyl Complexes Linked by an Isomerizable Stilbene-like Ligand

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Two series of trinuclear diimine rhenium(I) tricarbonyl complexes bridged by 1,3,5-tris(4-ethenylpyridyl)benzene (L1) or 1,3,5-tris(4-ethynylpyridyl)benzene (L2) have been synthesized and characterized. The L2-bridged complexes (group B) exhibit strong luminescence and long emission lifetimes in room-temperature solution which are typical of decay from ^{3}MLCT excited states, while the L1-bridged complexes (group A) show only very weak luminescence and short lifetimes under the same experimental conditions, although the emission positions and profiles do not vary that much. The low emission quantum yields and short lifetimes in group A complexes are attributed to intramolecular sensitization of the $^3\pi\pi^*$ excited state localized on the olefin link of the bridging ligand accompanied by a subsequent trans−cis isomerization process. The effects of different diimine ligand substitutents on the triplet−triplet energy transfer mechanisms are explored. The excited-state decay of group B complexes follows the energy gap law on the basis of an observed linear relationship between ln k_{nr} and emission energy.

Introduction

There has been considerable interest in polynuclear transition-metal complexes containing multi-chromophoric units capable of performing light-induced processes. In particular, metal complexes exhibiting long-lived metal-to-ligand charge-transfer (MLCT) excited states have received much attention.[1] Although Ru(bpy)$_3^{2+}$ and its derivatives have been extensively studied,[2] the relatively straightforward synthesis, tunable excited state and redox properties, and photochemical stability of organometallic (α-diimine)Re^I(CO)$_3$L complexes result in them also occupying an important position in the field of transition-metal photophysics and photochemistry.[3] In this regard, polypyridyl Re(I) tricarbonyl complexes have been widely used in a variety of studies, including fundamental excited-state properties such as photoinduced electron and energy transfer[4] and potential applications such as catalysts,[5] sensors,[6] probes for photopolymerization,[3a,7] photocleavage of DNA,[8] nonlinear optical materials,[9] and optical switches.[10] Recently, we have synthesized a series of trinuclear diimine rhenium(I) tricarbonyl complexes linked by a stilbene-like bridging ligand.[10a] We have found that the energy transfer quenching process is switchable by photomodulation of the relative excited-

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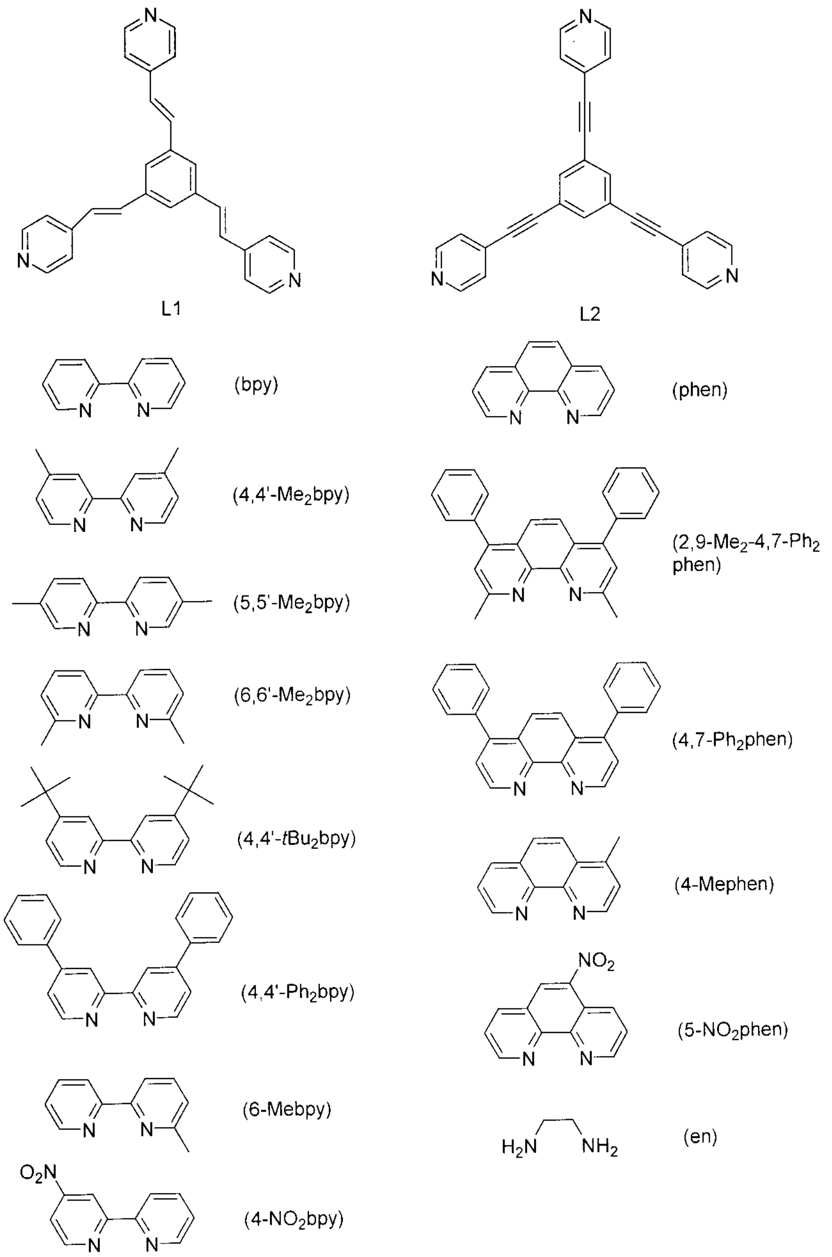
Chart 1



state positions between the emitting chromophore and quencher and, therefore, these complexes have the potential to be developed as molecular switches. By definition, a molecular switch is a system that possesses at least two interconvertible states and the output properties from these two states can be switched on/off through external stimuli.[11] The photoinduced trans–cis isomerization of stilbene and its derivatives have been intensely investigated from the viewpoint of both fundamental mechanistic interests and practical applications.[12] Consequently, the incorporation of stilbene units into molecular systems which are designed for the development of photochromic materials has been shown to be a very promising research area.[4c,10a,b,d] Previously, several papers have reported that the ^{3}MLCT excited state of a transition-metal chromophore can very efficiently sensitize the $^3\pi-\pi^*$ excited-state localized on stilbene-like ligands; this is significant, as the $^3\pi-\pi^*$ levels are sometimes not accessible by direct irradiation. However, subsequent isomerization of the olefin double bonds from a trans to cis configuration shifts the $^3\pi-\pi^*$ excited state to higher energy, with the result that strong ^{3}MLCT luminescence is again observed from the metal chromophore.[4c,e,10] In this paper, we wish to report detailed studies of the photoswitching properties of an extensive series of polynuclear *fac*-(diimine)Re(CO)$_3$ complexes linked by an isomerizable stilbene-like bridging ligand. The structures and abbreviations of all the ligands and complexes studied are illustrated in Charts 1 and 2, respectively.

Experimental Section

Materials and Synthesis. All chemicals are commercially available unless stated otherwise. All reactions and manipulations were carried out under N$_2$ or argon with the use of

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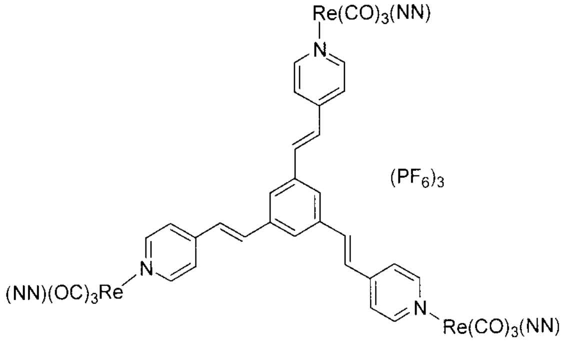
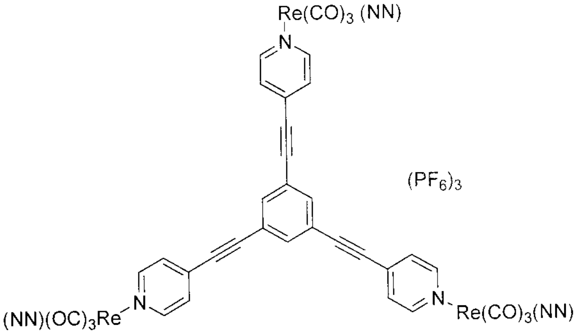
Chart 2



NN = bpy (**1**)
NN = 4,4'-Me$_2$bpy (**3**)
NN = 4-NO$_2$bpy (**5**)
NN = 4,4'-Ph$_2$bpy (**6**)
NN = 4,4'-*t*Bu$_2$bpy (**8**)
NN = 5,5'-Me$_2$bpy (**10**)
NN = 6,6'-Me$_2$bpy (**12**)
NN = 6-Mebpy (**14**)
NN = phen (**16**)
NN = 4-Mephen (**18**)
NN = 4,7-Ph$_2$phen (**20**)
NN = 2,9-Me$_2$-4,7-Ph$_2$phen (**22**)
NN = 5-NO$_2$phen (**24**)
NN = en (**26**)



NN = bpy (**2**)
NN = 4,4'-Me$_2$bpy (**4**)
NN = 4,4'-Ph$_2$bpy (**7**)
NN = 4,4'-*t*Bu$_2$bpy (**9**)
NN = 5,5'-Me$_2$bpy (**11**)
NN = 6,6'-Me$_2$bpy (**13**)
NN = 6-Mebpy (**15**)
NN = phen (**17**)
NN = 4-Mephen (**19**)
NN = 4,7-Ph$_2$phen (**21**)
NN = 2,9-Me$_2$-4,7-Ph$_2$phen (**23**)
NN = 5-NO$_2$phen (**25**)
NN = en (**27**)

standard inert-atmosphere and Schlenk techniques. Solvents used for synthesis were dried by standard procedures and stored under N_2.[13] Solvents used in luminescent and electrochemical studies were of spectroscopic and anhydrous grades, respectively. The compounds 1,3,5-tris(4-ethenylpyridyl)benzene(L1),[14] 1,3,5-tris(4-ethynylpyridyl)benzene(L2),[15] (en)Re(CO)$_3$Br (en = 1,2-ethylenediamine),[16] and (NN)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (NN = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives)[17] were prepared according to published procedures. Tetrabutylammonium hexafluorophosphate (TBAH) used as supporting electrolyte was rigorously dried (in vacuo at 100 °C for 18 h) prior to use. Nitrogen used for the synthesis and purging experiments was dried and deoxygenated according to a previously reported method.[18]

General Procedure for Preparation of the Ligand-Bridged Trinuclear Complexes [(NN)Re(CO)$_3$]$_3$(μ-L)(PF$_6$)$_3$. Method A. A 100 mL flask was charged with (NN)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (0.52 mmol) and bridging ligand (0.17 mmol). To this mixture was added 30 mL of THF, and the resulting suspension was refluxed for 5 h before it was cooled to 5 °C in an ice bath. The precipitate was collected by suction filtration, washed with cold THF (5 mL × 2), and dried under vacuum to afford a pure product.

Method B. A 100 mL flask was charged with (NN)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (0.52 mmol) and bridging ligand (0.17 mmol). To this mixture was added 30 mL of THF, and the resulting suspension was refluxed for 5 h. The solvent was removed under reduced pressure. Subsequently, 20 mL of CH$_3$CN was added to redissolve the solid, and the solution was filtered to remove any undissolved solid. Slow diffusion of diethyl ether into a CH$_3$CN solution afforded the analytically pure product.

Method C. A 100 mL flask was charged with (NN)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (0.52 mmol) and bridging ligand (0.17 mmol). To this mixture was added 30 mL of THF, and the resulting suspension was refluxed for 5 h. The solution was cooled to room temperature and filtered to remove the brown precipitate. The deep yellow filtrate was added to cold pentane to precipitate the pale yellow solid. The pale yellow solid was collected on a frit. Recrystallization from CH$_3$CN and ether afforded a microcrystalline solid.

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Method D. A 100 mL flask was charged with (NN)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (0.52 mmol) and bridging ligand (0.17 mmol). To this mixture was added 30 mL of THF, and the resulting suspension was refluxed for 5 h. The solvent was removed under reduced pressure. The residue was subjected to column chromatography (neutral alumina), with a CH$_3$CN/toluene mixture as eluant.

[(bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (1). Method A. Yield: 73%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2035, 1931. ^{1}H NMR (DMSO-d_6; δ): 9.34 (d, 6 H, J = 4.9 Hz, H$_{6,6'}$ bpy), 8.70 (d, 6 H, J = 8.2 Hz, H$_{3,3'}$ bpy), 8.40 (t, 6 H, J = 7.1 Hz, H$_{4,4'}$ bpy), 8.32 (d, 6 H, J = 6.3 Hz, H$_\alpha$ py), 7.91 (t, 6 H, J = 6.3 Hz, H$_{5,5'}$ bpy), 7.79 (s, 3 H, ph), 7.55 (d, 3 H, J = 16.3 Hz, py−C*H*═CH−ph), 7.51 (d, 6 H, J = 6.5 Hz, H$_\beta$ py), 7.23 (d, 3 H, J = 16.4 Hz, py−CH═C*H*−ph). ^{13}C NMR (DMSO-d_6; δ): 195.5, 192.1, 155.1, 154.1, 151.9, 147.5, 141.4, 136.7, 135.9, 129.1, 127.1, 125.4, 124.8, 123.4. ESI-MS (*m/z*): 1958.9 ([M − PF$_6$]$^+$, calcd *m/z* 1958.1). Anal. Calcd for C$_{66}$H$_{45}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 37.72; H, 2.16; N, 6.00. Found: C, 37.58; H, 2.28; N, 5.58.

[(bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (2). Method A. Yield: 60%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2036, 1933. ^{1}H NMR (DMSO-d_6; δ): 9.31 (d, 6 H, J = 4.8 Hz, H$_{6,6'}$ bpy), 8.70 (d, 6 H, J = 8.1 Hz, H$_{3,3'}$ bpy), 8.44−8.38 (m, 12 H, H$_{4,4'}$ bpy; H$_\alpha$ py), 7.95−7.88 (m, 9 H, H$_{5,5'}$ bpy), 7.87 (s, ph), 7.48 (d, 6 H, J = 6.6 Hz, H$_\beta$ py). ^{13}C NMR (DMSO-d_6; δ): 195.3, 192.0, 155.1, 154.0, 153.5, 152.2, 141.4, 132.9, 129.1, 128.3, 124.9, 122.2, 94.9, 87.1. ESI-MS (*m/z*): 1953.0 ([M − PF$_6$]$^+$, calcd *m/z* 1952.1). Anal. Calcd for C$_{66}$H$_{39}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 37.77; H, 1.87; N, 6.01. Found: C, 38.01; H, 1.99; N, 5.82.

[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (3). Method A. Yield: 69%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2032, 1928. ^{1}H NMR (DMSO-d_6; δ): 9.15 (d, 6 H, J = 5.6 Hz, H$_{6,6'}$ bpy), 8.58 (s, 6 H, H$_{3,3'}$ bpy), 8.32 (d, 6 H, J = 6.1 Hz, H$_\alpha$ py), 7.80 (s, 3 H, ph), 7.74 (d, 6 H, J = 5.3 Hz, H$_{5,5'}$ bpy), 7.57 (d, 3 H, J = 16.6 Hz, py−C*H*═CH−ph), 7.53 (d, 6 H, J = 6.4 Hz, H$_\beta$ py), 7.23 (d, 3 H, J = 16.3 Hz, py−CH═C*H*−ph), 2.54 (s, 18 H, C*H*$_3$). ^{13}C NMR (DMSO-d_6; δ): 195.6, 192.5, 154.7, 153.7, 153.3, 151.9, 147.4, 136.7, 135.9, 129.5, 128.3, 127.1, 125.3, 123.4, 21.0. ESI-MS (*m/z*): 949.1 ([M − 2PF$_6$]$^{2+}$, calcd *m/z* 948.6). Anal. Calcd for C$_{72}$H$_{57}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 39.56; H, 2.63; N, 5.77. Found: C, 39.18; H, 3.09; N, 5.87.

[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (4). Method D. Yield: 56%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2034, 1929. ^{1}H NMR (DMSO-d_6; δ): 9.13 (d, 6 H, J = 5.7 Hz, H$_{6,6'}$ bpy), 8.58 (s, 6 H, H$_{3,3'}$ bpy), 8.43 (d, 6 H, J = 6.6 Hz, H$_\alpha$ py), 7.87 (s, 3 H, Ph), 7.73 (d, 6 H, J = 5.0 Hz, H$_{5,5'}$ bpy), 7.50 (d, 6 H, J = 6.7 Hz, H$_\beta$ py), 2.54 (s, 18 H, C*H*$_3$). ^{13}C NMR (DMSO-d_6; δ): 195.4, 192.3, 154.7, 153.7, 153.2, 152.2, 136.0, 132.9, 129.5, 128.3, 125.4, 122.2, 94.9, 87.1, 21.0. ESI-MS (*m/z*): 945.9 ([M − 2PF$_6$]$^{2+}$, calcd *m/z* 945.6). Anal. Calcd for C$_{72}$H$_{51}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 39.67; H, 2.36; N, 5.78. Found: C, 39.44; H, 2.56; N, 5.61.

[(4-NO$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (5). Method D. Yield: 32%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2035, 1939. ^{1}H NMR (DMSO-d_6; δ): 9.45 (d, 3 H, J = 2.0 Hz, H$_3$ NO$_2$bpy), 9.39 (d, 3 H, J = 6.1 Hz, H$_6$ NO$_2$bpy), 9.18 (d, 3 H, J = 8.3 Hz, H$_{6'}$ NO$_2$bpy), 9.12 (d, 3 H, J = 4.6 Hz, H$_{3'}$ NO$_2$bpy), 8.50−8.42 (m, 6 H, H$_{5,4'}$ NO$_2$bpy), 8.31 (d, 6 H, J = 6.3 Hz, H$_\alpha$ py), 7.92 (t, 3 H, J = 6.5 Hz, H$_5$ NO$_2$bpy), 7.77 (s, 3 H, Ph), 7.52 (d, 3 H, J = 16.1 Hz, py−C*H*═CH−ph), 7.50 (d, 6 H, J = 6.4 Hz, H$_\beta$ py), 7.22 (d, 3 H, J = 16.3 Hz, py−CH═C*H*−ph). ESI-MS (*m/z*): 973.3 ([M − 2PF$_6$]$^{2+}$, calcd *m/z* 974.1). Anal. Calcd for C$_{66}$H$_{42}$N$_{12}$O$_{15}$Re$_3$P$_3$F$_{18}$: C, 35.44; H, 1.89; N, 7.51. Found: C, 35.01; H, 1.97; N, 7.69.

[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(OTf)$_3$ (6). Method B. Yield: 53%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2033, 1929. ^{1}H NMR (DMSO-d_6; δ): 9.33 (d, 6 H, J = 5.9 Hz, H$_{6,6'}$ ph$_2$bpy), 9.17 (s, 6 H, H$_{3,3'}$ ph$_2$bpy), 8.40 (d, 6 H, J = 5.9 Hz, H$_\alpha$ py), 8.22 (d, 6 H, J = 5.9 Hz, H$_{5,5'}$ ph$_2$bpy), 8.11−8.08 (m, 12 H, H$_o$ ph), 7.74 (s, 3 H, ph), 7.64−7.62 (m, 18 H, H$_m$ ph, H$_\beta$ py), 7.58−7.50 (m, 9 H, H$_p$ ph, py−C*H*═CH−ph), 7.20 (d, 3 H, J = 16.3 Hz, py−CH═C*H*−ph). ^{13}C NMR (DMSO-d_6; δ): 195.7, 192.2, 155.8, 154.1, 152.0, 151.6, 150.1, 147.4, 136.7, 135.8, 134.7, 131.1, 129.4, 127.8, 125.8, 125.4, 123.5, 122.3. ESI-MS (*m/z*): 1137.7 ([M − 2OTf]$^{2+}$, calcd *m/z* 1136.7). Anal. Calcd for C$_{105}$H$_{69}$N$_9$Re$_3$O$_{18}$S$_3$F$_9$: C, 49.06; H, 2.71; N, 4.90. Found: C, 49.25; H, 2.99; N, 4.82.

[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(OTf)$_3$ (7). Method B. Yield: 66%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2034, 1931. ^{1}H NMR (DMSO-d_6; δ): 9.31 (d, 6 H, J = 5.8 Hz, H$_{6,6'}$ ph$_2$bpy), 9.19 (s, 6 H, H$_{3,3'}$ ph$_2$bpy), 8.52 (d, 6 H, J = 5.4 Hz, H$_\alpha$ py), 8.22 (d, 6 H, J = 5.8 Hz, H$_{5,5'}$ ph$_2$bpy), 8.12−8.09 (m, 12 H, H$_o$ ph), 7.82 (s, 3 H, ph), 7.64 (m, 18 H, H$_{m,p}$ ph), 7.50 (d, 6 H, J = 5.3 Hz, H$_\beta$ py). ^{13}C NMR (DMSO-d_6; δ): 195.1, 192.2, 156.8, 152.4, 150.1, 149.6, 137.9, 135.6, 129.6, 129.4, 129.3, 127.7, 126.6, 122.2, 121.5, 120.1, 88.3, 76.9. ESI-MS (*m/z*): 1134.8 ([M − 2OTf]$^{2+}$, calcd *m/z* 1133.6). Anal. Calcd for C$_{105}$H$_{63}$N$_9$Re$_3$O$_{18}$S$_3$F$_9$: C, 49.18; H, 2.48; N, 4.92. Found: C, 49.32; H, 2.86; N, 4.78.

[(4,4′-*t*-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (8). Method B. Yield: 58%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2032, 1928. ^{1}H NMR (DMSO-d_6; δ): 9.21 (d, 6 H, J = 5.7 Hz, H$_{6,6'}$ bpy), 8.71 (s, 6 H, H$_{3,3'}$ bpy), 8.33 (d, 6 H, J = 5.6 Hz, H$_\alpha$ py), 7.86 (d, 6 H, J = 5.8 Hz, H$_{5,5'}$ bpy), 7.81 (s, 3 H, ph), 7.59 (d, 3 H, J = 16.1 Hz, py-CH═CH-ph), 7.56 (d, 6 H, J = 5.2 Hz, H$_\beta$ py), 7.25 (d, 3 H, J = 16.1 Hz, py-CH═CH-ph), 1.40 (s, 54 H, CH$_3$). ^{13}C NMR (DMSO-d_6; δ): 195.7, 192.4, 165.7, 155.1, 153.7, 151.9, 147.5, 136.8, 135.9, 127.2, 125.6, 125.5, 123.5, 122.3, 36.0, 29.8. ESI-MS (*m/z*): 2292.3 ([M − PF$_6$]$^+$, calcd *m/z* 2292.5). Anal. Calcd for C$_{90}$H$_{93}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 44.33; H, 3.84; N, 5.17. Found: C, 43.99; H, 3.69; N, 5.39.

[(4,4′-*t*-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (9). Method C. Yield: 53%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2034, 1929. ^{1}H NMR (DMSO-d_6; δ): 9.18 (d, 6 H, J = 5.8 Hz, H$_{6,6'}$ bpy), 8.70 (s, 6 H, H$_{3,3'}$ bpy), 8.44 (d, 6 H, J = 5.9 Hz, H$_\alpha$ py), 7.87 (s, 3 H, ph), 7.85 (d, 6 H, J = 5.9 Hz, H$_{5,5'}$ bpy), 7.53 (d, 6 H, J = 5.7 Hz, H$_\beta$ py), 1.40 (s, 54 H, CH$_3$). ^{13}C NMR (DMSO-d_6; δ): 195.5, 192.3, 165.7, 155.2, 153.7, 153.2, 152.2, 136.1, 133.0, 128.4, 125.6, 122.3, 94.9, 87.2, 36.0, 29.8. ESI-MS (*m/z*): 2285.4 ([M − PF$_6$]$^+$, calcd *m/z* 2286.5). Anal. Calcd for C$_{90}$H$_{87}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 44.44; H, 3.61; N, 5.18. Found: C, 43.97; H, 3.38; N, 5.54.

[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (10). Method C. Yield: 73%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2033, 1929. ^{1}H NMR (DMSO-d_6; δ): 9.14 (s, 6 H, H$_{6,6'}$ bpy), 8.50 (d, 6 H, J = 8.4 Hz, H$_{3,3'}$ bpy), 8.39 (d, 6 H, J = 6.0 Hz, H$_\alpha$ py), 8.18 (d, 6 H, J = 8.5 Hz, H$_{4,4'}$ bpy), 7.79 (s, 3 H, ph), 7.57 (d, 3 H, J = 16.5 Hz, py−C*H*═CH−ph), 7.51 (d, 6 H, J = 6.5 Hz, H$_\beta$ py), 7.22 (d, 3 H, J = 16.4 Hz, py−CH═C*H*−ph), 2.55 (s, 18 H, C*H*$_3$). ^{13}C NMR (DMSO-d_6; δ): 195.5, 192.5, 153.8, 152.6, 152.2, 147.5, 141.6, 139.4, 136.8, 135.9, 127.1, 125.5, 123.7, 123.4, 18.0. ESI-MS (*m/z*): 2039.8 ([M − PF$_6$]$^+$, calcd *m/z* 2040.2). Anal. Calcd for C$_{72}$H$_{57}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 39.56; H, 2.63; N, 5.77. Found: C, 39.12; H, 2.41; N, 6.15.

[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (11). Method B. Yield: 73%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2034, 1931. ^{1}H NMR (DMSO-d_6; δ): 9.09 (s, 6 H, H$_{6,6'}$ bpy), 8.48 (m, 12 H, H$_{3,3'}$ bpy, H$_\alpha$ py), 8.16 (d, 6 H, J = 8.6 Hz, H$_{4,4'}$ bpy), 7.85 (s, 3 H, ph), 7.47 (d, 6 H, J = 5.0 Hz, H$_\beta$ py), 2.52 (s, 18 H, C*H*$_3$). ^{13}C NMR (DMSO-d_6; δ): 195.4, 192.5, 153.8, 152.7, 152.4, 142.0, 139.6, 136.2, 133.1, 128.4, 123.8, 122.4, 95.0, 87.2, 18.1. ESI-MS (*m/z*): 944.5 ([M − 2PF$_6$]$^{2+}$, calcd *m/z* 944.5). Anal. Calcd for C$_{72}$H$_{51}$N$_9$O$_9$Re$_3$P$_3$F$_{18}$: C, 39.67; H, 2.36; N, 5.78. Found: C, 39.39; H, 2.19; N, 6.05.

[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (12). Method B. Yield: 62%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2033, 1929. ^{1}H NMR (DMSO-d_6; δ): 8.34 (d, 6 H, J = 8.3 Hz, H$_{3,3'}$ bpy), 8.20 (t, 6 H, J = 7.9 Hz, H$_{4,4'}$ bpy), 7.91 (d, 6 H, J = 7.8 Hz, H$_{5,5'}$ bpy), 7.85 (d, 6 H, J = 6.8 Hz, H$_\alpha$ py), 7.84 (s, 3 H, ph), 7.60 (d, 3 H, J = 16.4 Hz, py−C*H*═CH−ph), 7.42 (d, 6 H, J = 5.6 Hz, H$_\beta$ py), 7.25 (d, 3 H, J = 16.5 Hz, py−CH═C*H*−ph), 3.17 (s, 18 H, C*H*$_3$).^{13}C NMR (DMSO-d_6; δ): 195.4, 192.3, 162.9, 156.4, 152.7, 147.4, 141.0, 136.7, 136.1, 128.4, 127.2, 125.5, 123.3, 122.3, 29.7. ESI-MS (*m/z*): 2039.3 ([M − PF$_6$]$^+$, calcd *m/z* 2040.2).

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Anal. Calcd for $C_{72}H_{57}N_9O_9Re_3P_3F_{18}$: C, 39.56; H, 2.63; N, 5.77. Found: C, 39.15; H, 2.46; N, 5.30.

[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(*μ*-L2)(PF$_6$)$_3$ (13). Method B. Yield: 59%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2034, 1931. ^1H NMR (DMSO-d_6; δ): 8.34 (d, 6 H, J = 8.2 Hz, $H_{3,3'}$ bpy), 8.20 (t, 6 H, J = 7.9 Hz, $H_{4,4'}$ bpy), 7.98 (d, 6 H, J = 6.8 Hz, H_α py), 7.92 (s, 3 H, ph), 7.91 (d, 6 H, J = 7.8 Hz, $H_{5,5'}$ bpy), 7.39 (d, 6 H, J = 6.6 Hz, H_β py), 3.14 (s, 18 H, CH_3).^{13}C NMR (DMSO-d_6; δ): 195.2, 192.2, 162.9, 156.3, 152.9, 150.0, 141.1, 136.2, 132.9, 128.5, 128.1, 122.4, 95.2, 87.0, 29.7. ESI-MS (m/z): 949.5 ([M − 2PF$_6$]$^{2+}$, calcd m/z 948.6). Anal. Calcd for $C_{72}H_{51}N_9O_9Re_3P_3F_{18}$: C, 39.67; H, 2.36; N, 5.78. Found: C, 39.91; H, 2.06; N, 5.66.

[(6-Mebpy)Re(CO)$_3$]$_3$(*μ*-*t*-L1)(PF$_6$)$_3$ (14). Method B. Yield: 79%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2034, 1932. ^1H NMR (DMSO-d_6; δ): 9.33 (d, 3 H, J = 5.3 Hz, H_6 bpy), 8.60 (d, 3 H, J = 8.3 Hz, $H_{3'}$ bpy), 8.48 (d, 3 H, J = 8.1 Hz, H_3 bpy), 8.36 (t, 3 H, J = 7.8 Hz, $H_{4'}$ bpy), 8.25 (t, 3 H, J = 7.7 Hz, H_4 bpy), 8.04 (d, 6 H, J = 5.0 Hz, H_α py), 7.97 (d, 3 H, J = 7.9 Hz, $H_{5'}$ bpy), 7.88 (t, 3 H, J = 6.1 Hz, H_5 bpy), 7.81 (s, 3 H, ph), 7.56 (d, 3 H, J = 16.1 Hz, py−C*H*═CH−ph), 7.47 (d, 6 H, J = 5.7 Hz, H_β py), 7.24 (d, 3 H, J = 15.9 Hz, py−CH═C*H*−ph), 3.16 (s, 9 H, CH_3). ^{13}C NMR (DMSO-d_6; δ): 196.3, 194.9, 192.0, 162.7, 155.8, 155.7, 153.7, 152.2, 147.4, 141.4, 141.2, 136.7, 136.0, 129.1, 128.8, 127.2, 125.4, 125.0, 123.5, 122.4, 30.4. ESI-MS (m/z): 1997.5 ([M − PF$_6$]$^+$, calcd m/z 1998.2). Anal. Calcd for $C_{69}H_{51}N_9O_9Re_3P_3F_{18}$: C, 38.66; H, 2.40; N, 5.88. Found: C, 38.27; H, 2.22; N, 6.02.

[(6-Mebpy)Re(CO)$_3$]$_3$(*μ*-L2)(PF$_6$)$_3$ (15). Method A. Yield: 72%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2035, 1933. ^1H NMR (DMSO-d_6; δ): 9.30 (d, 3 H, J = 5.4 Hz, H_6 bpy), 8.61 (d, 3 H, J = 8.3 Hz, $H_{3'}$ bpy), 8.48 (d, 3 H, J = 7.9 Hz, H_3 bpy), 8.36 (t, 3 H, J = 7.7 Hz, $H_{4'}$ bpy), 8.25 (t, 3 H, J = 7.2 Hz, H_4 bpy), 8.16 (d, 6 H, J = 5.2 Hz, H_α py), 7.97 (d, 3 H, J = 7.3 Hz, $H_{5'}$ bpy), 7.89 (s, 3 H, ph), 7.87 (t, 3 H, J = 5.3 Hz, H_5 bpy), 7.44 (d, 6 H, J = 5.2 Hz, H_β py), 3.14 (s, 9 H, CH_3). ^{13}C NMR (DMSO-d_6; δ): 196.1, 194.6, 191.8, 162.7, 155.8, 155.7, 153.7, 152.5, 141.5, 141.3, 136.1, 132.9, 129.1, 128.8, 128.3, 125.1, 122.5, 122.2, 95.0, 87.0, 30.4. ESI-MS (m/z): 1991.5 ([M − PF$_6$]$^+$, calcd m/z 1991.1). Anal. Calcd for $C_{69}H_{45}N_9O_9Re_3P_3F_{18}$: C, 38.77; H, 2.12; N, 5.90. Found: C, 38.72; H, 2.32; N, 5.68.

[(phen)Re(CO)$_3$]$_3$(*μ*-*t*-L1)(PF$_6$)$_3$ (16). Method A. Yield: 66%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2035, 1931. ^1H NMR (DMSO-d_6; δ): 9.76 (d, 6 H, J = 5.0 Hz, $H_{2,9}$ phen), 9.02 (d, 6 H, J = 8.2 Hz, $H_{4,7}$ phen), 8.35 (d, 6 H, J = 6.1 Hz, H_α py), 8.29 (s, 6 H, $H_{5,6}$ phen), 8.24 (dd, 6 H, J = 5.2 Hz, $H_{3,8}$ phen), 7.66 (s, 3 H, ph), 7.43 (d, 3 H, J = 16.2 Hz, py−C*H*═CH−ph), 7.37 (d, 6 H, J = 6.3 Hz, H_β py), 7.09 (d, 3 H, J = 16.1 Hz, py−CH═C*H*−ph). ^{13}C NMR (DMSO-d_6; δ): 195.4, 192.0, 155.0, 151.9, 150.2, 147.4, 145.5, 140.5, 136.6, 135.7, 130.6, 128.1, 127.4, 125.3, 123.3. ESI-MS (m/z): 943.3 ([M − 2PF$_6$]$^{2+}$, calcd m/z 942.6). Anal. Calcd for $C_{72}H_{45}N_9Re_3O_9P_3F_{18}$: C, 39.72; H, 2.09; N, 5.79. Found: C, 39.89; H, 2.11; N, 5.46.

[(phen)Re(CO)$_3$]$_3$(*μ*-L2)(PF$_6$)$_3$ (17). Method A. Yield: 60%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2036, 1933. ^1H NMR (DMSO-d_6; δ): 9.74 (d, 6 H, J = 5.0 Hz, $H_{2,9}$ phen), 9.02 (d, 6 H, J = 8.3 Hz, $H_{4,7}$ phen), 8.47 (d, 6 H, J = 6.2 Hz, H_α py), 8.30 (s, 6 H, $H_{5,6}$ phen), 8.23 (dd, 6 H, J = 4.8 Hz, $H_{3,8}$ phen), 7.74 (s, 3 H, ph), 7.34 (d, 6 H, J = 5.9 Hz, H_β py). ^{13}C NMR (DMSO-d_6; δ): 195.2, 191.9, 155.0, 152.1, 145.6, 140.5, 135.9, 132.8, 130.6, 128.11, 128.07, 127.4, 122.1, 94.7, 87.0. ESI-MS (m/z): 939.0 ([M − 2PF$_6$]$^{2+}$, calcd m/z 939.6). Anal. Calcd for $C_{72}H_{39}N_9Re_3O_9P_3F_{18}$: C, 39.83; H, 1.81; N, 5.81. Found: C, 39.99; H, 2.03; N, 5.49.

[(4-Mephen)Re(CO)$_3$]$_3$(*μ*-*t*-L1)(PF$_6$)$_3$ (18). Method B. Yield: 73%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2034, 1930. ^1H NMR (DMSO-d_6; δ): 9.76 (d, 3 H, J = 4.9 Hz, H_9 phen), 9.61 (d, 3 H, J = 5.3 Hz, H_2 phen), 9.03 (d, 3 H, J = 8.6 Hz, H_7 phen), 8.40−8.35 (m, 9 H, H_5 phen, H_α), 8.31 (d, 3 H, J = 9.1 Hz, H_6 phen), 8.23 (dd, 3 H, J = 5.1 Hz, H_8 phen), 8.09 (d, 3 H, J = 5.2 Hz, H_3 phen), 7.67 (s, 3 H, ph), 7.43 (d, 3 H, J = 16.5 Hz, py−C*H*═CH−ph), 7.38 (d, 6 H, J = 6.1 Hz, H_β), 7.09 (d, 3 H, J = 16.4 Hz, py−CH═C*H*−ph), 2.94 (s, 9 H, CH_3). ^{13}C NMR (DMSO-d_6; δ): 195.5, 192.2, 155.2, 154.3, 151.8, 151.1, 150.1, 147.3, 145.6, 145.1, 140.4, 136.6, 135.7, 130.3, 130.2, 127.8, 127.7, 127.3, 125.3, 124.9, 123.2, 18.7. ESI-MS (m/z): 964.5 ([M − 2PF$_6$]$^{2+}$, calcd m/z 963.6). Anal. Calcd for $C_{75}H_{51}N_9Re_3O_9P_3F_{18}$: C, 40.65; H, 2.32; N, 5.69. Found: C, 40.85; H, 2.39; N, 5.55.

[(4-Mephen)Re(CO)$_3$]$_3$(*μ*-L2)(PF$_6$)$_3$ (19). Method B. Yield: 67%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2035, 1932. ^1H NMR (DMSO-d_6; δ): 9.73 (d, 3 H, J = 4.9 Hz, H_9 phen), 9.58 (d, 3 H, J = 5.2 Hz, H_2 phen), 9.03 (d, 3 H, J = 8.1 Hz, H_7 phen), 8.47 (d, 6 H, J = 6.1 Hz, H_α), 8.39 (d, 3 H, J = 9.3 Hz, H_5 phen), 8.32 (d, 3 H, J = 9.1 Hz, H_6 phen), 8.23 (dd, 3 H, J = 5.2 Hz, H_8 phen), 8.09 (d, 3 H, J = 5.2 Hz, H_3 phen), 7.74 (s, 3 H, ph), 7.35 (d, 6 H, J = 6.5 Hz, H_β), 2.94 (s, 9 H, CH_3). ^{13}C NMR (DMSO-d_6; δ): 195.3, 192.0, 155.1, 154.2, 152.1, 151.1, 145.7, 145.2, 140.4, 135.9, 132.8, 130.3, 130.2, 128.1, 127.8, 127.7, 127.3, 124.9, 122.1, 94.7, 87.0, 18.7. ESI-MS (m/z): 960.1 ([M − 2PF$_6$]$^{2+}$, calcd m/z 960.6). Anal. Calcd for $C_{75}H_{45}N_9Re_3O_9P_3F_{18}$: C, 40.77; H, 2.05; N, 5.70. Found: C, 40.91; H, 2.11; N, 5.93.

[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(*μ*-*t*-L1)(PF$_6$)$_3$ (20). Method B. Yield: 58%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2034, 1930. ^1H NMR (DMSO-d_6; δ): 9.57 (d, 2 H, J = 5.3 Hz, $H_{2,9}$ phen), 8.52 (bs, 6 H, H_α py), 8.21 (s, 6 H, $H_{5,6}$ phen), 8.14 (bs, 6 H, $H_{3,8}$ phen), 7.67 (s, 3 H, ph L1), 7.72−7.62 (m, 13 H, ph, py−C*H*═CH−ph), 7.48 (bs, 6 H, H_β py), 7.19 (d, 3 H, J = 16.0 Hz, py−CH═C*H*−ph). ^{13}C NMR (DMSO-d_6; δ): 195.5, 192.0, 154.6, 154.0, 152.1, 151.5, 147.4, 146.5, 136.7, 135.0, 130.1, 129.8, 129.6, 129.2, 128.3, 127.3, 127.0, 126.0, 123.4. ESI-MS (m/z): 1170.1 ([M − 2PF$_6$]$^{2+}$, calcd m/z 1170.7). Anal. Calcd for $C_{108}H_{69}N_9Re_3O_9P_3F_{18}$: C, 49.32; H, 2.64; N, 4.79. Found: C, 49.25; H, 2.97; N, 5.01.

[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(*μ*-L2)(PF$_6$)$_3$ (21). Method B. Yield: 51%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2030, 1930. ^1H NMR (DMSO-d_6; δ): 9.80 (d, 6 H, J = 5.5 Hz, $H_{2,9}$ phen), 8.63 (d, 6 H, J = 5.7 Hz, H_α py), 8.20 (d, 6 H, J = 5.3 Hz, $H_{3,8}$ phen), 8.14 (s, 6 H, $H_{5,6}$ phen), 7.80 (s, 3 H, ph L2), 7.67 (m, 30 H, ph), 7.45 (d, 6 H, J = 5.2 Hz, H_β py). ^{13}C NMR (DMSO-d_6; δ): 195.3, 191.9, 154.6, 152.3, 151.5, 150.1, 146.6, 135.9, 135.0, 132.9, 130.1, 129.8, 129.2, 128.3, 127.3, 126.0, 122.2, 94.7, 87.1. ESI-MS (m/z): 1168.6 ([M − 2PF$_6$]$^{2+}$, calcd m/z 1167.6). Anal. Calcd for $C_{108}H_{63}N_9Re_3O_9P_3F_{18}$: C, 49.43; H, 2.42; N, 4.80. Found: C, 49.55; H, 2.46; N, 4.51.

[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(*μ*-*t*-L1)(PF$_6$)$_3$(22). Method B. Yield: 63%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2032, 1930. ^1H NMR (DMSO-d_6; δ): 8.25 (s, 6 H, $H_{5,6}$ phen), 8.02 (d, 6 H, J = 5.5 Hz, H_α py), 7.92 (s, 6 H, $H_{3,8}$ phen), 7.75 (s, 3 H, ph L1), 7.49 (d, 3 H, J = 16.5 Hz, py−C*H*═CH−ph), 7.35 (bs, 6 H, H_β py), 7.17 (d, 3 H, J = 15.8 Hz, py−CH═C*H*−ph), 3.39 (s, 18 H, CH_3). ^{13}C NMR (DMSO-d_6; δ): 195.5, 192.0, 164.2, 152.5, 150.9, 147.2, 136.6, 135.8, 135.0, 129.9, 129.6, 129.1, 127.8, 127.1, 126.6, 126.3, 125.5, 124.6, 123.2, 30.5. ESI-MS (m/z): 1213.6 ([M − 2PF$_6$]$^{2+}$, calcd m/z 1212.7). Anal. Calcd for $C_{114}H_{81}N_9Re_3O_9P_3F_{18}$: C, 50.44; H, 3.01; N, 4.64. Found: C, 50.85; H, 3.40; N, 4.52.

[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(*μ*-L2)(PF$_6$)$_3$ (23). Method B. Yield: 55%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2033, 1932. ^1H NMR (DMSO-d_6; δ): 8.25 (s, 6 H, $H_{5,6}$ phen), 8.15 (d, 6 H, J = 5.3 Hz, H_α py), 7.92 (s, 6 H, $H_{3,8}$ phen), 7.85 (s, 3 H, ph L2), 7.63 (bs, 30 H, ph), 7.31 (d, 6 H, J = 5.4 Hz, H_β py), 3.37 (s, 18 H, CH_3). ^{13}C NMR (DMSO-d_6; δ): 195.3, 191.9, 164.3, 152.8, 151.0, 147.1, 136.1, 135.0, 132.8, 129.9, 129.6, 129.1, 128.1, 127.8, 126.6, 124.7, 122.1, 95.0, 87.1, 30.5. ESI-MS (m/z): 1210.3 ([M − 2PF$_6$]$^{2+}$, calcd m/z 1209.7). Anal. Calcd for $C_{114}H_{75}N_9Re_3O_9P_3F_{18}$: C, 50.56; H, 2.79; N, 4.65. Found: C, 50.99; H, 2.36; N, 4.41.

[(5-NO$_2$phen)Re(CO)$_3$]$_3$(*μ*-*t*-L1)(PF$_6$)$_3$ (24). Method B. Yield: 22%. IR ($\nu_{C\equiv O}$, CH_3CN; cm^{-1}): 2037, 1935. ^1H NMR (DMSO-d_6; δ): 9.89 (bt, 6 H, $H_{2,9}$ phen), 9.35 (s, 3 H, H_6 phen),

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9.33 (d, 3 H, *J* = 9.2 Hz, H_4 phen), 9.23 (d, 3 H, *J* = 8.1 Hz, H_7 phen), 8.40−8.35 (m, 12 H, $H_{3,8}$ phen, H_α py), 7.68 (s, 3 H, ph), 7.45 (d, 3 H, *J* = 16.9 Hz, py−C*H*═CH−ph), 7.39 (d, 6 H, *J* = 4.2 Hz, H_β), 7.12 (d, 3 H, *J* = 16.5 Hz, py−CH═C*H*−ph). ^{13}C NMR (DMSO-d_6; δ): 195.2, 191.5, 157.8, 156.1, 152.1, 150.1, 147.5, 147.4, 146.3, 144.4, 142.4, 136.9, 136.6, 135.7, 128.4, 127.9, 127.2, 127.0, 125.3, 123.4, 123.3. ESI-MS (*m*/*z*): 1010.9 ([M − 2PF$_6$]$^{2+}$, calcd *m*/*z* 1010.6). Anal. Calcd for $C_{72}H_{43}N_{12}Re_3O_{15}P_3F_{18}$: C, 37.44; H, 1.88; N, 7.28. Found: C, 37.66; H, 2.13; N, 7.02.

[(5-NO$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (25). Method B. Yield: 27%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2038, 1936. ^{1}H NMR (DMSO-d_6; δ): 9.87 (t, 6 H, *J* = 5.2 Hz, $H_{2,9}$ phen), 9.36 (s, 3 H, H_6 phen), 9.33 (d, 3 H, *J* = 8.9 Hz, H_4 phen), 9.23 (d, 3 H, *J* = 8.4 Hz, H_7 phen), 8.52 (d, 6 H, *J* = 5.5 Hz, H_α py), 8.37−8.34 (m, 6 H, $H_{3,8}$ phen), 7.76 (s, 3 H, ph), 7.37 (d, 6 H, *J* = 5.3 Hz, H_β py). ^{13}C NMR (DMSO-d_6; δ): 194.9, 191.4, 157.7, 156.1, 152.3, 147.5, 146.4, 144.4, 142.4, 136.9, 135.9, 132.8, 128.4, 128.1, 128.0, 127.9, 127.1, 123.4, 122.1, 94.6, 87.0. ESI-MS (*m*/*z*): 1008.6 ([M − 2PF$_6$]$^{2+}$, calcd *m*/*z* 1007.5). Anal. Calcd for $C_{72}H_{37}N_{12}Re_3O_{15}P_3F_{18}$: C, 37.54; H, 1.62; N, 7.30. Found: C, 37.82; H, 1.99; N, 7.22.

[(en)Re(CO)$_3$]$_3$(μ-*t*-L1)(OTf)$_3$ (26). Method D. Yield: 68%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2036, 1928. ^{1}H NMR (DMSO-d_6; δ): 8.64 (d, 6 H, *J* = 5.1 Hz, H_α py), 7.97 (s, 3 H, ph), 7.69 (d, 6 H, *J* = 5.5 Hz, H_β py), 7.56 (d, 3 H, *J* = 16.1 Hz, py−C*H*═CH−ph), 7.20 (d, 3 H, *J* = 16.0 Hz, py−CH═C*H*−ph), 5.91 (s, 12 H, NH), 2.94 (s, 12 H, CH$_2$). ^{13}C NMR (DMSO-d_6; δ): 193.6, 190.5, 150.1, 144.6, 134.9, 131.5, 124.5, 123.1, 122.2, 120.7, 46.4. ESI-MS (*m*/*z*): 1643.0 ([M − OTf]$^+$, calcd *m*/*z* 1642.1). Anal. Calcd for $C_{42}H_{45}N_9Re_3O_{18}S_3F_9$: C, 28.19; H, 2.53; N, 7.04. Found: C, 28.55; H, 2.46; N, 7.51.

[(en)Re(CO)$_3$]$_3$(μ-L2)(OTf)$_3$ (27). Method D. Yield: 71%. IR ($\nu_{C\equiv O}$, CH$_3$CN; cm^{-1}): 2036, 1927. ^{1}H NMR (acetone-d$_6$): 8.66 (d, 6 H, *J* = 5.8 Hz, H_α py), 7.88 (s, 3 H, ph), 7.53 (d, 6 H, *J* = 5.9 Hz, H_β py), 5.92 (s, 12 H, NH), 2.94 (s, 12 H, CH$_2$). ^{13}C NMR (DMSO-d_6; δ): 193.5, 190.7, 149.3, 135.6, 130.1, 127.6, 122.3, 121.5, 85.2, 78.6, 46.1. ESI-MS (*m*/*z*): 1634.9 ([M − OTf]$^+$, calcd *m*/*z* 1636.1). Anal. Calcd for $C_{42}H_{39}N_9Re_3O_{18}S_3F_9$: C, 28.28; H, 2.20; N, 7.07. Found: C, 28.75; H, 2.77; N, 7.01.

Equipment and Procedures. ^{1}H NMR spectra were obtained using a Brüker AC 300 spectrometer, and ^{13}C and ^{31}P NMR spectra were obtained using a Brüker AM 360 spectrometer. Infrared spectra were measured on a Nicolet 20SXC Fourier transform infrared spectrophotometer. UV−vis spectra were obtained using an HP 8450A diode array spectrophotometer interfaced to an IBM computer. Emission spectra were recorded in deoxygenated solvent solution at 293 K with an SLM 48000S lifetime fluorescence spectrophotometer equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. Luminescence quantum yields were calculated relative to [Re(bpy)(CO)$_3$(4-Etpy)]PF$_6$ in acetonitrile (Φ = 0.027).[19] Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%. Luminescence lifetimes shorter than 30 ns were obtained using an SLM 48000S lifetime fluorescence spectrophotometer, and lifetimes longer than 30 ns were obtained using a Laser Photonics nitrogen laser as the excitation source (337 nm) and a Tektronix TDS 544A digitizer was used for decay data acquisition. Photolysis experiments were carried out with a 200 W medium-pressure Hg arc lamp with Ealing Corp. interference filters (10 nm band-pass) to isolate the excitation wavelength. The quantum efficiencies of photoisomerization (Φ_{iso}) in CH$_3$CN at 293 K were determined on the basis of the first 5% of the absorbance change, where the primary photoproducts were cis,trans,trans isomers which were confirmed by the controlled ^{1}H NMR experiments. The detailed procedures for the photophysical and photochemical measurements have been reported in a previous paper.[20]

Electrochemical measurements were recorded on an EG&G PAR Model 263A potentiostat/galvanostat. The electrochemical cell consisted of a platinum working electrode, a platinum-wire counter electrode, and a Ag/AgNO$_3$ (0.01 M in CH$_3$CN solution) reference electrode. Cyclic voltammograms were obtained in deoxygenated CH$_3$CN with the electroactive material (1.0 × 10^{-3} M) and 0.1 M TBAH as supporting electrolyte. Ferrocene (Fc) was used as an internal standard for both potential calibration and reversibility criteria. All potentials for the complexes in the study are reported relative to Fc/Fc$^+$. The scan rate was 200 mV/s. The measurements were uncorrected for liquid-junction potentials.

Results and Discussion

Synthesis, Characterization, and General Properties. The trinuclear Re(I) complexes were prepared by refluxing (NN)Re(CO)$_3$(CH$_3$CN)(PF$_6$) with the corresponding bridging ligand in THF solution.[19,21] In the case of NN = 4,4′-Ph$_2$bpy, the triflate salt (4,4′-Ph$_2$bpy)-Re(CO)$_3$(CH$_3$CN)(OTf) was used instead of the PF$_6^-$ salt due to the low solubility of the latter complex. The products were purified by standard workup procedures as described in the Experimental Section, and the resultant yields are typically 50−80%. However, the complexes containing the strongly electron withdrawing 4-NO$_2$bpy and 5-NO$_2$phen ligands exhibit particularly low yields (30% or less). Similarly, low yields have also been observed in the *fac*-(L)Re(CO)$_3$(Etpy) complexes, where L are bpy derivatives with electron-withdrawing groups in the 4,4′-positions and Etpy is 4-ethylpyridine.[22] The purity and composition of the complexes have been confirmed by NMR, elemental analysis, and electrospray mass spectrometry. These complexes do not decompose in the solid state under exposure to air over a 3 month period, although they do undergo decomposition in air-saturated CH$_3$CN solution in just a few days.

Infrared Spectra. The observation of two strong bands between 2040 and 1920 cm^{-1} in the infrared spectra recorded in CH$_3$CN solution in room temperature for all complexes confirms that the three carbonyl groups are in a facial arrangement with C_{3v} local symmetry.[23] The carbonyl stretching frequencies exhibit subtle differences between different complexes which roughly follow the order of the π-accepting ability of the coordinated diimine ligands.

Electrochemistry. Cyclic voltammograms were recorded in CH$_3$CN solution at ambient temperature, and the redox potentials are collected in Table 1. A single irreversible oxidation wave was observed for each of the complexes, which is assigned to the Re(I/II) oxidation process. The oxidation potentials vary over a small range (1.35−1.51 V), but they can be correlated to the electron donor/acceptor abilities of the diimine ligands; i.e., the strongest electron acceptors such as 5-NO$_2$phen and 4-NO$_2$bpy destabilize the Re(II) and result in the

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Table 1. Redox Potentials[a]

compd	E_{ox}	E_{red}
L1[b]		−2.24 (108)
L2[b]		−2.11 (136)
[(bpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**1**)	1.40 (i)	−1.56 (78), −1.76 (88)
[(bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**2**)	1.40 (i)	−1.64 (i)
[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**3**)	1.40 (i)	−1.63 (78)
[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**4**)	1.45 (i)	−1.72 (i)
[(4-NO$_2$bpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**5**)	1.49 (i)	−1.01 (i), −1.71 (i)
[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-t-L1)(OTf)$_3$ (**6**)	1.43 (i)	−1.46 (78), −1.66 (74)
[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(OTf)$_3$ (**7**)	1.45 (i)	−1.49 (i), −1.67 (i)
[(4,4′-t-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**8**)	1.39 (i)	−1.67 (117)
[(4,4′-t-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**9**)	1.38 (i)	−1.71 (i)
[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**10**)	1.42 (i)	−1.67 (i)
[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**11**)	1.42 (i)	−1.77 (i)
[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**12**)	1.37 (i)	−1.63 (97)
[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**13**)	1.36 (i)	−1.70 (i)
[(6-Mebpy)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**14**)	1.44 (i)	−1.57 (74), −1.74 (102)
[(6-Mebpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**15**)	1.46 (i)	−1.57 (76)
[(phen)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**16**)	1.40 (i)	−1.51 (i)
[(phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**17**)	1.42 (i)	−1.56 (i)
[(4-Mephen)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**18**)	1.38 (i)	−1.55 (i)
[(4-Mephen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**19**)	1.43 (i)	−1.55 (i)
[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**20**)	1.47 (i)	−1.55 (80), −1.83 (72)
[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**21**)	1.48 (i)	−1.57 (104), −1.82 (72)
[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**22**)	1.45 (i)	−1.56 (i), −1.85 (i)
[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**23**)	1.46 (i)	−1.65 (i), −1.78 (i)
[(5-NO$_2$phen)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**24**)	1.47 (i)	−0.91 (i), −1.46 (i), −1.77 (i)
[(5-NO$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**25**)	1.51 (i)	−0.90 (i), −1.51 (i), −1.72 (i)
[(en)Re(CO)$_3$]$_3$(μ-t-L1)(PF$_6$)$_3$ (**26**)	1.37 (i)	−1.86 (92)
[(en)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**27**)	1.37 (i)	−1.82 (106)

[a] Analyses were performed in 1 mM deoxygenated solutions containing 0.1 M TBAH; scan rates were 200 mV/s. All potentials are in volts vs [Fe(C$_5$H$_5$)$_2$]$^{0/+}$ (0.093 V with peak separation 82 mV in CH$_3$CN and 0.11 V with peak separation 86 mV in DMF); "i" denotes an irreversible process. Peak potentials are reported for irreversible processes. [b] In DMF solution.

highest oxidation potentials, while a good electron donor such as 6,6′-Me$_2$bpy exerts an opposite effect and gives rise to much lower oxidation potentials. The oxidation process occurs at the metal center to initially generate a 17-electron species, which subsequently undergoes a chemical reaction and, thus, an irreversible process is observed.[19,20,24] The observation of only one Re(I)-centered oxidation process suggests that there is negligible communication between the three individual chromophores. Similar noninteracting rhenium(I) diimine chromophores have also been reported in some self-assembly cyclic structures featuring tricarbonyl rhenium(I) moieties at the corners.[20,25]

The reduction processes are much more complicated for these complexes. In general, one or two reduction waves were observed. Apparently, the first reduction waves represent the process of adding electrons to the diimine ligands rather than the bridging ligands L1 or L2 because the reduction potentials correlate with the energy of the π^* acceptor level of the diimine ligands. Complexes with nitro-substituted diimine ligands exhibit the lowest first reduction potentials, while complexes with 6,6′-Me$_2$bpy display the highest reduction potentials. The second reduction potentials are more ambiguous to assign because the bridging ligand based reduction and metal-centered reduction are both likely to occur in that region.[10d,21a,26]

Absorption Spectra. The absorption maxima and extinction coefficients of the metal complexes and free bridging ligands are summarized in Table 2. The free ligands L1 and L2 feature a very intense band in the 300 nm region which shows no obvious vibrational structure. The absorption spectra of all complexes feature a series of intense ligand localized $\pi \rightarrow \pi^*$ absorptions in the range of 220−320 nm. The lower energy bands which appear from ∼320 nm and extend past 400 nm are assigned to metal (dπ) to ligand (π^*) charge transfer (MLCT) bands by analogy with similar facial rhenium(I) tricarbonyl diimine complexes reported in the literature.[19,21] The two different MLCT bands associated with transitions to the diimine ligands and bridging ligand are substantially overlapping, and it is not possible to accurately assign their positions. However, complexes **26** and **27**, where the diimine ligands are replaced by ethylenediamine, exhibit only high-energy absorption bands, although a low-energy shoulder is also observed at 358 nm for complex **26**. The low extinction coefficient and solvent-independent nature of this latter band excludes the possibility of it being either a MLCT or $\pi\pi^*$ transition. A similar low-energy shoulder has been observed in the W(CO)$_4$(en) complex and has been attributed to a ^{3}LF transition;[27] hence, we tentatively assign this low-energy shoulder in complex **26** to a ^{3}LF band. It would appear, therefore, that the metal-to-diimine ligand charge-transfer bands are at a lower energy position than the corresponding metal-

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Table 2. Absorption Spectral Data of Bridging Ligands and Complexes in CH$_3$CN at 293 K

compd	$\lambda_{\max}$, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})
L1	325 (sh, 66), 309 (96), 223 (30)
L2	299 (66.7), 281 (73.8)
[(bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**1**)	341 (85.2), 320 (88.0), 280 (48.0), 239 (49.1)
[(bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**2**)	342 (sh, 47.4), 319 (87.7), 301 (93.8), 283 (83.8), 251 (66.5)
[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**3**)	354 (85.8), 318 (86.0), 280 (49.8), 240 (54.9)
[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**4**)	326 (sh, 75.0), 316 (94.6), 304 (93.8), 288 (78.8), 251 (70.7)
[(4-NO$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**5**)	402 (sh, 21.1), 336 (90.3), 285 (sh, 56.9), 238 (60.4)
[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(OTf)$_3$ (**6**)	350 (sh, 64.7), 331 (79.2), 290 (81.4), 260 (sh, 58.7)
[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(OTf)$_3$ (**7**)	331 (98.2), 297 (165), 283 (168)
[(4,4′-*t*-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**8**)	342 (125), 319 (116), 278 (70.8), 241 (79.5)
[(4,4′-*t*-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**9**)	341 (sh, 54.7), 317 (89.9), 305 (88.3), 282 (69.4), 249 (66.4)
[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**10**)	332 (163), 271 (67.3), 264 (66.9), 236 (66.2)
[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**11**)	322 (113), 282 (83.9), 260 (sh, 74.9)
[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**12**)	339 (150), 328 (179), 272 (94.8), 260 (94.8)
[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**13**)	326 (103), 317 (98.3), 279 (76.0), 260 (72.3)
[(6-Mebpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**14**)	340 (100), 327 (115), 278 (52.9), 230 (56.9)
[(6-Mebpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**15**)	324 (122), 315 (120), 283 (86.6), 253 (76.9)
[(phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**16**)	333 (81.9), 276 (73.9)
[(phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**17**)	322 (93.3), 299 (113), 276 (132), 257 (101), 220 (138)
[(4-Mephen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**18**)	345 (98.3), 331 (104), 276 (98.6), 223 (201)
[(4-Mephen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**19**)	321 (161), 299 (195), 276 (228), 258 (171), 218 (228)
[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**20**)	335 (105), 292 (127), 219 (125, sh)
[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**21**)	378 (19.6), 330 (45.8), 289 (120), 256 (68.4)
[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**22**)	335 (124), 299 (145), 260 (80.1), 226 (123)
[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**23**)	382 (sh, 31.8), 298 (269), 258 (154)
[(5-NO$_2$phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**24**)	339 (100), 271 (94.7)
[(5-NO$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**25**)	324 (139), 300 (153), 271 (189)
[(en)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**26**)	358 (sh, 9.6), 322 (42.0), 309 (53.4), 266 (39.3)
[(en)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**27**)	299 (39.6), 278 (51.9), 266 (54.5), 212 (263)

Table 3. Photophysical Data of Bridging Ligands and Complexes in CH$_3$CN at 293 K[a]

compd	λ_{em}, nm	$10^2\Phi_{\mathrm{em}}$[b]	τ, ns	k_{r}, s^{-1}	k_{nr}, s^{-1}
L1[c]	380	26	19.8	1.3×10^7	3.8×10^7
L2[c]	360	10.8	2.2	4.0×10^7	4.1×10^8
[(bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**1**)	574	0.14	15	9.3×10^4	4.0×10^6
[(bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**2**)	576	3.0	250	1.2×10^5	3.9×10^6
[(4,4′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**3**)	562	0.099	10	9.9×10^4	2.0×10^6
[(4,4′-Me$_2$-bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**4**)	566	6.1	510	1.2×10^5	1.9×10^6
[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(OTf)$_3$ (**6**)	582	0.43	15.5	2.8×10^5	5.0×10^6
[(4,4′-Ph$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(OTf)$_3$ (**7**)	582	4.0	220	1.8×10^5	4.4×10^6
[(4,4′-*t*-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**8**)	560	0.032	8.2	3.9×10^4	1.6×10^6
[(4,4′-*t*-Bu$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**9**)	562	2.6	610	4.3×10^4	1.6×10^6
[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**10**)	568	0.082	12.1	6.8×10^4	1.6×10^6
[(5,5′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**11**)	566	7.0	830	8.4×10^4	1.1×10^6
[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**12**)	556	0.076	9.9	7.7×10^4	1.8×10^6
[(6,6′-Me$_2$bpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**13**)	554	4.5	540	8.3×10^4	1.8×10^6
[(6-Mebpy)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**14**)	568	0.15	16.2	9.3×10^4	2.2×10^6
[(6-Mebpy)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**15**)	568	3.0	440	6.8×10^4	2.2×10^6
[(phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**16**)	560	0.15	17.6	8.5×10^4	1.0×10^6
[(phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**17**)	562	5.2	1850	2.8×10^4	5.1×10^5
[(4-Mephen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**18**)	554	0.037	5.4	6.9×10^4	1.0×10^7
[(4-Mephen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**19**)	552	3.5	2180	1.6×10^4	4.4×10^5
[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**20**)	578	0.17	20.5	1.3×10^5	2.6×10^7
[(4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**21**)	578	2.3	1070	2.1×10^4	9.1×10^5
[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**22**)	564	0.024	4.9	4.9×10^4	4.0×10^6
[(2,9-Me$_2$-4,7-Ph$_2$phen)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**23**)	562	2.7	1420	1.9×10^4	6.9×10^5
[(en)Re(CO)$_3$]$_3$(μ-*t*-L1)(PF$_6$)$_3$ (**26**)	538	~0.008	*d*		
[(en)Re(CO)$_3$]$_3$(μ-L2)(PF$_6$)$_3$ (**27**)	536	9.1	920	9.9×10^4	1.1×10^6

[a] The excitation wavelengths are 380 nm unless otherwise noted. [b] The emission quantum yields were determined using (bpy)Re(CO)$_3$(4-Etpy)(PF$_6$) ($\Phi_{\mathrm{em}}{}^{\mathrm{CH_3CN}} = 0.027$) and perylene ($\Phi_{\mathrm{em}}{}^{\mathrm{EtOH}} = 0.89$) as references. [c] The excitation wavelength is 330 nm. [d] The emission is too weak to obtain a reliable lifetime.

to-bridging ligand charge-transfer bands on the basis of the absorption results.

Photophysical Properties. The emission maxima, quantum yields, and lifetimes of complexes **1**−**27** as well as bridging ligands in CH$_3$CN are collected in Table 3. Both ligands L1 and L2 exhibit strong fluorescence in solution. Although two possible low-energy rotamers exist for L1,[28] only monoexponential decay was observed from the π−π^* excited state. This implies that one of the two rotamers is much favorable than the other in polar CH$_3$CN solution or both rotamers exhibit a very similar fluorescence lifetime.[29]

Our results illustrate that the series of complexes can be separated into two groups, on the basis of their

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[28] Meier, H.; Zertani, R.; Noller, K.; Oelkrug, D.; Krabichler, G. *Chem. Ber.* **1986**, *119*, 1716.

[29] The detailed photophysical studies of L1 and other stilbene-like molecules will be reported elsewhere.

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emission lifetimes and quantum yields. Group A consists of complexes linked by ligand L1, and group B consists of complexes linked by ligand L2. Group A complexes show only very weak emission in room-temperature CH_3CN solution, and no emission was detected in the case of complexes **4** and **24**. The typical emission quantum yields for group A complexes are less than 1×10^{-3}, and the lifetimes range between 4.9 and 20.5 ns. On the other hand, group B complexes exhibit relatively strong (quantum yields greater than 2×10^{-2}) and structureless emission in room-temperature CH_3CN solution, except for complex **25**, which shows no detectable emission under the same experimental conditions. The emission lifetimes of group B complexes are in the range of hundreds of nanoseconds. It is clear that the emission features from group B complexes are ^{3}MLCT in nature on the basis of their long lifetimes, structureless emission spectral profiles, and relatively high quantum yields. However, as noted above, two ^{3}MLCT excited states exist in group B complexes and the lowest energy transition can be either to the diimine ligands or to the bridging ligand, L2.

It is pertinent to ask which actually is the lowest lying ^{3}MLCT excited state in the group B complexes. Complexes **26** and **27**, where the only low-lying emitting excited state is the Re ($d\pi$) to π^* (bridging ligand) charge transfer state, were synthesized in order to determine the answer to this question. The photophysical data of complexes **26** and **27** collected in Table 3 show that the emission is at higher energy than for the other complexes and, thus, the lowest emitting excited states in the rest of the group B complexes are clearly of Re ($d\pi$) to diimine (π^*) charge-transfer character. In addition, the variation of the emission maximum with different diimine ligands confirms that the lowest excited state is diimine ligand based ^{3}MLCT. The meta connection of the substituted pyridyl groups in L1 and L2 interrupts the extended conjugation of the π system, resulting in the bridging ligand π^* orbital being at higher energy.[30]

Assuming that the MLCT intersystem crossing efficiency is unity, then Φ_{em} and τ for group B complexes can be expressed as eqs 1 and 2.

$$\Phi_{em} = k_r/(k_r + k_{nr}) \qquad (1)$$

$$\tau = (k_r + k_{nr})^{-1} \qquad (2)$$

The calculated k_r and k_{nr} values are also collected in Table 3. As expected, all the k_r values are very close, ca. $1 \times 10^4 - 1 \times 10^5$ s^{-1}, for the series of *fac*-(diimine)-$Re^I(CO)_3L$ complexes and in agreement with related Re(I)−diimine chromophores.[31]

An analysis of the determined nonradiative rate constants vs excited-state energies of group B complexes is presented in Figure 1. A linear relationship in the plot between the $\ln(k_{nr})$ vs E_{em} values is observed, which confirms that the excited state decay is essentially governed by the energy gap law.[17a] In essence, the energy gap law states that the nonradiative decay rate constants decrease exponentially with an increasing energy gap between the ground and emitting excited states.[17a,32] The slopes obtained from linear least-squares fits for bpy and phen derivatives are −12.03 and −10.24 eV^{-1}, respectively. These values are comparable to those for other $[fac\text{-(diimine)Re(CO)}_3L]^+$ complexes[17a] and higher than the values derived from Ru^{II}− and Os^{II}−bpy (or phen) derivatives.[32c] It is noted that the primary vibrational acceptor modes in these Re(I) complexes are at higher frequencies, due to the CO vibrational modes (1926−2036 cm^{-1} for group B complexes), than for the Ru(II)− and Os(II)−bpy (or phen) derivatives, which have lower frequency diimine vibrational modes (~1350 cm^{-1}), and this may be the reason for the differences in the rates of nonradiative decay of the ^{3}MLCT excited states.[17a,33] Moreover, the weak emission from group A complexes implies that there are additional nonradiative deactivation processes occurring in them.

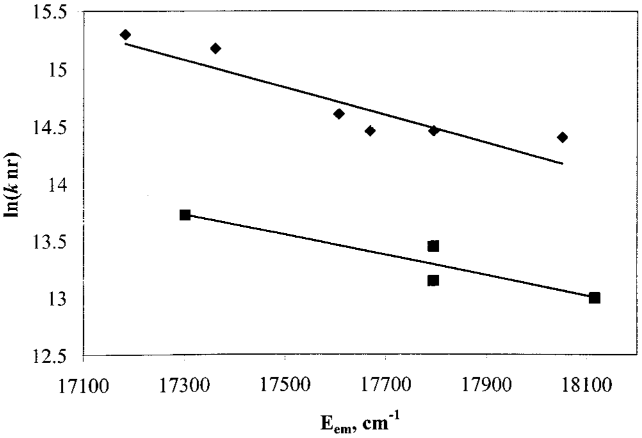

Figure 1. Plot of ln k_{nr} vs E_{em} for the group B complexes: (◆) bpy and its derivatives; (■) phen and its derivatives.

Photoinduced Isomerization. When group A complexes were irradiated at 366 nm, their MLCT bands started to bleach and the intensities of the ligand-localized $\pi \rightarrow \pi^*$ bands slightly increased with a clear isosbestic point. Concomitantly, the emission intensities increased during the irradiation. Similar absorption spectral changes were also observed for the free ligand L1 upon irradiation at 313 nm. The UV−visible difference absorption spectra of complex **1** in CH_3CN as a function of photolysis time and the changes on the corresponding emission spectra are presented in Figure 2. After prolonged irradiation, the lifetimes of group A complexes also increased to the point where they become the same magnitude as group B complexes: ca. hundreds of nanoseconds. Controlled photolysis experiments performed in CD_3CN and monitored by ^{1}H NMR showed the formation of several cis isomers of L1. The amount of *cis,cis,cis*-L1-bridged complex present in solution is typically in the range of 75−95% after 36 h of photolysis. The spectral changes are fully reversible after heating the solution at 60 °C for 5 h, and the emission quantum yields from the complexes drop back down to less than 1×10^{-3} after heating. The irradiation−emission pro-

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(30) (a) Höger, S.; Meckenstock, A.-D.; Müller, S. *Chem. Eur. J.* **1998**, *4*, 2423. (b) Sun, S.-S.; Lees, A. J. *Organometallics* **2001**, *20*, 2353.

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(32) (a) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. (b) Freed, K.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (c) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

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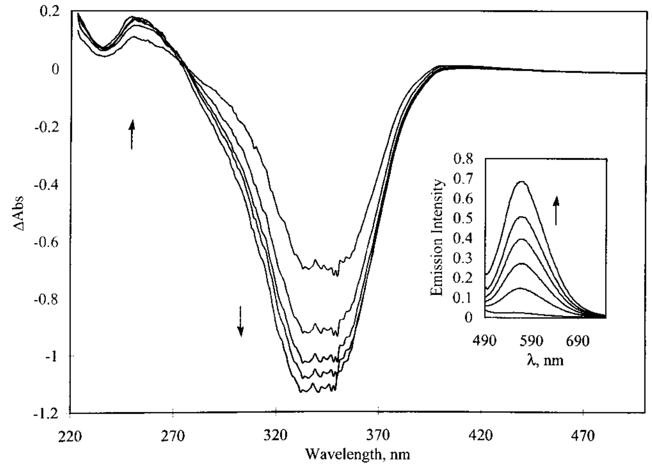

Figure 2. UV−visible difference absorption spectra ($\Delta_{Abs} = A_t - A_{t=0}$) of $[(bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ in CH_3CN at 293 K as a function of photolysis time (λ = 366 nm; 1, 2, 3, 4, and 6 h). The inset shows the emission spectra before and after the photolysis. The direction of the arrows show increasing photolysis time.

Table 4. Quantum Efficiencies of Isomerization (Φ_{iso}) in CH_3CN at 293 K

compd	Φ_{iso}
L1	5.24×10^{-2}
$[(bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**1**)	1.35×10^{-2}
$[(4,4'\text{-}Me_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**3**)	1.53×10^{-2}
$[(4,4'\text{-}Ph_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(OTf)_3$ (**6**)	1.22×10^{-2}
$[(4,4'\text{-}tBu_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**8**)	9.29×10^{-3}
$[(5,5'\text{-}Me_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**10**)	8.55×10^{-3}
$[(6,6'\text{-}Me_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**12**)	8.84×10^{-3}
$[(6\text{-}Mebpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**14**)	1.32×10^{-2}
$[(phen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**16**)	1.76×10^{-2}
$[(4\text{-}Mephen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**18**)	2.42×10^{-2}
$[(4,7\text{-}Ph_2phen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**20**)	5.87×10^{-3}
$[(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**22**)	7.81×10^{-3}

cess followed by the heating−no emission step can be repeated several times without any sign of complex decomposition.

It is well-known that *trans*-stilbene and its derivatives possess low-lying triplet $\pi\pi^*$ excited states. These low-lying triplet $\pi\pi^*$ excited states have been proved to be easily accessed by sensitization reactions. Several papers have reported that transition-metal chromophores possessing ^{3}MLCT excited states are efficient $^3\pi\pi^*$ sensitizers for *trans*-stilbene and its derivatives.[4c,10a,b,d−g] Thus, the low quantum yields and short lifetimes of group A complexes are attributed to the presence of a low-lying $\pi \rightarrow \pi^*$ transition localized on the ethylene link of L1.[34] Excitation into the ^{3}MLCT states is followed by intramolecular sensitization of the $\pi \rightarrow \pi^*$ transition localized on the ethylene link of L1. Subsequently, the excited-state energy deactivates via a trans−cis isomerization of the ethylene units[4c,10a,b,d−g] and ^{3}MLCT luminescence, therefore, reappears for the *cis*-L1-bridged complexes. Apparently, the energy transfer rates in complexes **5** and **26** are too slow to compete with the rapid nonradiative decays from the low-energy ^{3}MLCT excited states to the ground states. Table 4 summarizes the quantum efficiencies of the photoisomerization for group A complexes and free ligand L1. The quantum efficiencies of isomerization of *trans*-L1 in the complexes are slightly lower than the isomerization quantum efficiency of free *trans*-L1, and there is no clear correlation between the quantum efficiencies and the energy levels of the ^{3}MLCT excited states.

Scheme 1 summarizes the excited-state energy transfer and isomerization processes occurring in this system and includes the results of some previous studies on the photochemistry and photophysics of stilbene and its derivatives.[4c,35] Here, ^{3}(p-L1)* represents the twisted (perpendicular) triplet excited state of L1 and K represents the equilibrium constant between the *trans*-L1 triplet excited state and the twisted triplet excited state of L1.

Assuming that the MLCT intersystem crossing efficiency is unity, radiative (k_r) and nonradiative (k_{nr}) decay to the ground state and energy transfer (k_{ENT}) to $^3\pi\pi^*$ localized on L1 are the only deactivation processes for the ^{3}MLCT excited state, and the decay from the ^{3}L1 excited state is much faster than the reverse energy transfer process (k_{-ENT}), then Φ_{em} and τ for group A complexes can be expressed as eqs 3 and 4.[4c,36]

$$\Phi_{em} = k_r/(k_r + k_{nr} + k_{ENT}) \tag{3}$$

$$\tau = (k_r + k_{nr} + k_{ENT})^{-1} \tag{4}$$

The energy transfer rate constant, k_{ENT}, and the efficiency for generating the $^3\pi\pi^*$ excited state localized on L1, Φ_{ENT}, at 293 K can be determined by eqs 5 and 6 with the corresponding group B complexes serving as model compounds.

$$k_{ENT} = \tau^{-1} - \tau_{model}^{-1} \tag{5}$$

$$\Phi_{ENT} = k_{ENT}/(k_r + k_{nr} + k_{ENT}) \tag{6}$$

Table 5 lists calculated values for k_{ENT} and Φ_{ENT}. The high energy-transfer rate constants and near-unity values of Φ_{ENT} account for the predominant quenching of the emission from the ^{3}MLCT excited states in group A complexes. While the k_{ENT} and Φ_{ENT} values are generally correlated to the energy levels of the ^{3}MLCT excited states in the complexes, i.e. the higher k_{ENT} and greater Φ_{ENT} values are associated with higher energy ^{3}MLCT levels, there is no apparent correlation between the quantum efficiencies of isomerization of *trans*-L1 in the complexes and the energy levels of the ^{3}MLCT excited states. In contrast, the isomerization quantum efficiency of the free *trans*-L1 is higher and this is attributed to either a low equilibrium constant (*K*) or faster deactivation from the ^{3}(p-L1) excited state to the ground state with (*trans*-L1) configuration (ie. $k_2 \geq k_1$).

The energy gap between the ^{3}MLCT donor and $^3\pi\pi^*$ acceptor is calculated according to $\Delta E_{ENT} = E_T - E_{MLCT}$, where E_T is the triplet $\pi\pi^*$ energy of L1 and E_{MLCT} is the energy of the triplet MLCT excited state of the metal-complex chromophores. However, we were unable

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[34] (a) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 2725. (b) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389.

[35] Görner, H.; Kuhn, H. J. *Adv. Photochem.* **1995**, *19*, 1 and references therein.

[36] We also assumed here that the solution comprises only cis,-cis,cis isomer after photolysis. In fact, on the basis of controlled photolysis experiments performed in CD_3CN and monitored by ^{1}H NMR, the amount of cis,cis,cis isomer presence in solution is typically in the range between 75 and 95%. Thus, the calculated efficiencies of energy transfer represent only the upper limits.

Scheme 1

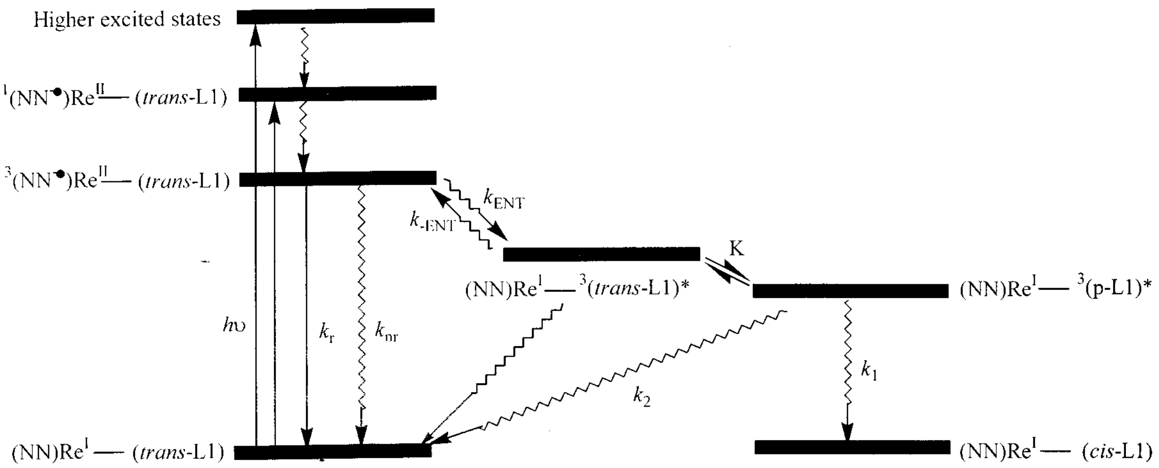

Table 5. Calculated Physical Parameters for Triplet–Triplet Energy Transfer Processes

compd	ΔE_{ENT}, kJ/mol[a]	k_{ENT}, s^{-1} [b]	Φ_{eff}[c]
$[(bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**1**)	−31.4	6.3×10^7	0.94
$[(4,4'\text{-}Me_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**3**)	−35.8	9.8×10^7	0.98
$[(4,4'\text{-}Ph_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(OTf)_3$ (**6**)	−26.5	6.0×10^7	0.93
$[(4,4'\text{-}tBu_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**8**)	−35.8	1.2×10^8	0.98
$[(5,5'\text{-}Me_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**10**)	−34.3	8.1×10^7	0.98
$[(6,6'\text{-}Me_2bpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**12**)	−38.9	9.9×10^7	0.98
$[(6\text{-}Mebpy)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**14**)	−33.6	5.9×10^7	0.96
$[(phen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**16**)	−35.8	5.6×10^7	0.99
$[(4\text{-}Mephen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**18**)	−39.7	1.8×10^8	~1.00
$[(4,7\text{-}Ph_2phen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**20**)	−29.9	4.8×10^7	0.98
$[(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)Re(CO)_3]_3(\mu\text{-}t\text{-}L1)(PF_6)_3$ (**22**)	−35.8	2.0×10^8	~1.00

[a] $\Delta E_{\mathrm{ENT}} = E_{\mathrm{T}} - E_{\mathrm{MLCT}}$. See text for details. [b] Triplet–triplet energy-transfer rate constant. [c] Quantum yield for generating the $^3\pi\pi^*$ excited state localized on L1.

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to observe the phosphorescence from L1, even from a 77 K glass of 2-methyltetrahydrofuran with addition of ethyl iodide. Hence, the triplet energy of *trans*-1-methyl-4-(4-nitrostyryl)pyridinium iodide in butyronitrile is used as an approximation of E_{T} (197 kJ/mol).[37] The E_{MLCT} values are estimated by taking the average of the emission band onset and the emission band energy.[4c] The calculated ΔE_{ENT} values are also included in Table 5. A precise value of the triplet energy of *cis*-L1 is, again, not available from our experimental data; however, its lower limit can be estimated to be 244 kJ/mol on the basis of the ^{3}MLCT energy level of complex **26**, which still exhibits the photoisomerization. In general, the higher energy-transfer rate constant is observed for the system with the larger driving force. In addition, the phen series exhibits a slightly more efficient energy transfer process than the bpy series. The less distorted ^{3}MLCT excited states for the phenanthroline series compared to those for the bipyridine series[38] may facilitate more efficient energy transfer.

Conclusion

We have demonstrated here that the trinuclear *fac*-(diimine)Re(CO)$_3$ complexes bridged by the stilbene-like ligand L1 exhibit a clear photoswitching property. The *fac*-(diimine)Re(CO)$_3$ chromophores are very efficient triplet sensitizers for a triplet energy acceptor such as L1. The energy transfer process from the ^{3}MLCT excited state to the lowest $^3\pi\pi^*$ excited state localized on L1 has been shown to be very fast and efficient. Subsequent trans to cis isomerization of the olefin double bonds shifts the $^3\pi\pi^*$ excited state localized on L1 to a higher level than the ^{3}MLCT excited state, and thus, the luminescence from the ^{3}MLCT excited state reappears. On the other hand, the *fac*-(diimine)Re(CO)$_3$ complexes bridged by the rigid L2 ligand exhibit typical strong ^{3}MLCT luminescence and long lifetimes in room-temperature solution and their excited-state decays are predominantly governed by the energy gap law.

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Supporting Information Available: A figure showing a representative cyclic voltammogram of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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