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Photoswitchable trinuclear transition-metal complexes. Intramolecular triplet–triplet energy transfer from *fac*-(diimine)Re^{I}(CO)$_3$ chromophores to a stilbene-like bridging ligand†

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A series of novel trinuclear metal complexes containing *fac*-(diimine)Re^{I}(CO)$_3$ chromophores and a stilbene-like bridging ligand have been synthesized and in CH$_3$CN exhibit photoswitchable luminescence arising from photoinduced intramolecular energy transfer from the *fac*-(diimine)-Re(CO)$_3$ chromophores to the bridging ligand.

Recently, molecular systems containing multiple electron or energy transfer donor–acceptors have been widely studied for potential applications as optical switches or gates in which the emission from these molecular systems can be switched on or off by external stimuli or environmental changes such as light or pH.[1] Polynuclear transition-metal complexes containing *fac*-(diimine)Re^{I}(CO)$_3$ chromophores have been used for extensive studies of photoinduced intramolecular energy transfer and electron transfer.[2] Earlier studies on ligand-bridged dimeric systems have illustrated that the bridging ligand π*-electron system has a profound effect on the spectroscopic, photochemical, and redox behavior of these complexes.[2,3]

The light-driven *cis*–*trans* isomerization processes of stilbenes and compounds containing stilbene units have undergone active investigation both through fundamental studies and practical applications.[4] The *cis*- or *trans*-stilbenes and their analogues are good triplet energy acceptors for exploring photosensitization and energy transfer processes.[5,6] We herein report the photophysics and photochemistry of trinuclear metal complexes containing *fac*-(diimine)Re^{I}(CO)$_3$ chromophores bridged by a stilbene-like tridentate ligand. The results show that following excitation into the Re (dπ) → diimine (π*) MLCT manifold, efficient triplet–triplet energy transfer from the ^{3}MLCT state to the bridging ligand occurs and this results in *trans*–*cis* isomerization of the bridging ligand. The structures of the bridging ligands and complexes studied here are shown in Scheme 1.

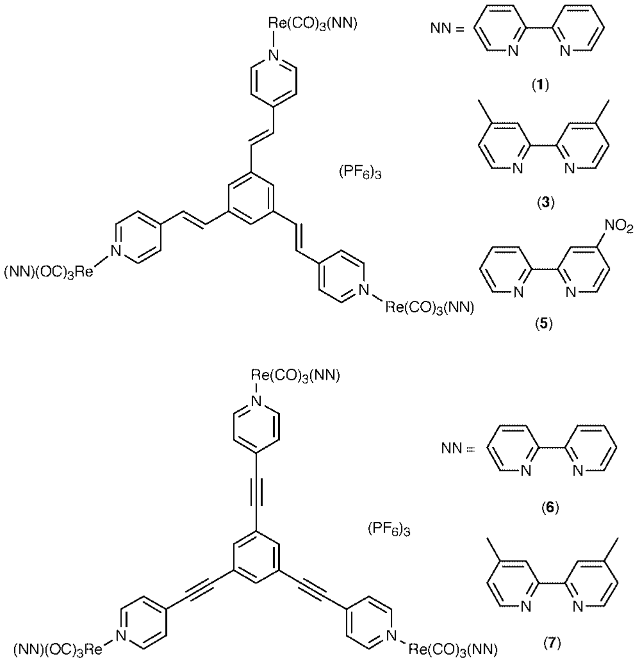
Complexes [(NN)Re(CO)$_3$]$_3$(μ-TEEPB)(PF$_6$)$_3$, where NN = bpy, 4,4′-Me$_2$bpy or 4-NO$_2$bpy, and TEEPB = 1,3,5-tris(2-ethenyl-4-pyridyl)benzene, were synthesized by refluxing a 3:1 molar ratio of [(NN)Re(CO)$_3$(CH$_3$CN)]PF$_6$ and TEEPB in THF solution and then standard workup procedures.[2c,7] All new complexes have been characterized by infrared spectra, ^{1}H, ^{13}C NMR and elemental analysis.‡

Photophysical parameters obtained from compounds **1**–**7** are summarized in Table 1. The absorption spectra of all these compounds feature a series of ligand localized π → π* and metal (dπ) to ligand (π*) charge transfer (MLCT) bands. Unlike most metal complexes containing the *fac*-(diimine)Re^{I}(CO)$_3$ unit, which are typically highly luminescent in solution,[2,3,6] compounds **1** and **3** show only weak luminescence (Φ_{em} < 0.0015) in room temperature CH$_3$CN solution. The quenching appears to occur *via* intramolecular sensitization of the π → π* transition localized on the olefin link of the bridging ligand accompanied by a *trans*–*cis* isomerization process.

$$[(\mathrm{NN})\mathrm{Re}^{\mathrm{I}}(\mathrm{CO})_3]_3(\mu\text{-}t\text{-TEEPB}) \xrightarrow{h\nu} [^3(\mathrm{NN}^{\bullet -})\mathrm{Re}^{\mathrm{II}}(\mathrm{CO})_3]_3{}^{*}(\mu\text{-}t\text{-TEEPB}) \underset{k_{-\mathrm{ENT}}}{\overset{k_{\mathrm{ENT}}}{\rightleftharpoons}}$$

$$[(\mathrm{NN})\mathrm{Re}^{\mathrm{I}}(\mathrm{CO})_3]_3{}^3(\mu\text{-}t\text{-TEEPB})^{*} \xrightarrow[\text{isomerization}]{trans-cis} [(\mathrm{NN})\mathrm{Re}^{\mathrm{I}}(\mathrm{CO})_3]_3(\mu\text{-}c\text{-TEEPB})$$

This is supported by steady-state photolysis experiments. Fig. 1 shows the difference absorption spectrum of compound **1** in CH$_3$CN solution as a function of photolysis time. Photolysis into the MLCT band at 366 nm bleaches the ππ* absorption of the bridging ligand at *ca.* 280–370 nm and induces small increases at *ca.* 200–270 nm. A similar bleaching effect at *ca.* 280–330 nm was also observed for free TEEPB photolyzed at 313 nm. Furthermore, changes observed in the emission are very substantial and the emission quantum yield is 18 times greater for **1** (see inset in Fig. 1) and 21 times greater for **3** after 7 h of photolysis at 366 nm compared to the original spectra. The UV–VIS spectral changes and large increase in the luminescence intensity for **1** and **3** are consistent with the *trans*–*cis* isomerization of the bridging ligand, TEEPB,§[6a,b,8] and highly efficient energy transfer (*vide infra*). The energy transfer from the ^{3}MLCT state to the higher energy triplet excited state



Scheme 1

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† Spectral and analytical data for **1**, **3**, **5**, **6** and **7** are available from the RSC web site, see http://www.rsc.org/suppdata/cc/a9/a908074k/

Table 1 Photophysical properties of TEEPB and compounds **1–7**[a]

Compound	Absorption spectra λ_{max}/nm ($10^{-3}\ \varepsilon$/M^{-1} cm^{-1})	Emission						
		λ_{max}/nm	$10^2\Phi_{em}$[b]	τ/ns	k_r/s^{-1}	k_{nr}/s^{-1}	k_{ENT}/s^{-1}[c]	Φ_{ENT}[d]
1 $[(bpy)Re(CO)_3]_3(\mu$-*t*-TEEPB$)(PF_6)_3$	341 (85), 320 (88), 280 (48), 239 (49)	574	0.14	15.1	9.3×10^4	3.1×10^6	6.3×10^7	0.94
2 $[(bpy)Re(CO)_3]_3(\mu$-*c*-TEEPB$)(PF_6)_3$[e]		568	2.57	166	1.5×10^5	5.9×10^6		
3 $[(4,4'-Me_2bpy)Re(CO)_3]_3(\mu$-*t*-TEEPB$)(PF_6)_3$	341 (94), 318 (86), 280 (50), 240 (55)	562	0.099	10.2	9.9×10^4	1.9×10^6	9.8×10^7	0.98
4 $[(4,4'-Me_2bpy)Re(CO)_3]_3(\mu$-*c*-TEEPB$)(PF_6)_3$[e]		556	2.13	187	1.1×10^5	5.2×10^6		
5 $[(4-NO_2bpy)Re(CO)_3]_3(\mu$-*t*-TEEPB$)(PF_6)_3$	402 (sh, 21), 336 (90), 285 (sh, 57), 238 (60)	[f]						
6 $[(bpy)Re(CO)_3]_3(\mu$-TEPB$)(PF_6)_3$	342 (sh, 47), 319 (88), 301 (94), 283 (84), 251 (66)	576	3.03	246	1.2×10^5	3.9×10^6		
7 $[(4,4'-Me_2bpy)Re(CO)_3]_3(\mu$-TEPB$)(PF_6)_3$	326 (sh, 75), 316 (95), 304 (94), 288 (79), 251 (71)	566	6.11	507	1.2×10^5	1.9×10^6		

[a] The excitation wavelengths are 380 nm. [b] The emission quantum yields were determined using $[(bpy)Re(CO)_3(4\text{-Etpy})](PF_6)$ ($\Phi_{em}^{CH_3CN} = 0.027$) as reference.[2d] [c] Triplet–triplet energy transfer rate constant: see text for detail. [d] Quantum yield for generating ^{3}TEEPB excited state: see text for detail. [e] Generated by photolysis at 366 nm for 36 h. The k_r and k_{nr} values are calculated based on 100% *cis*-TEEPB presence in solution. [f] No emission detected.

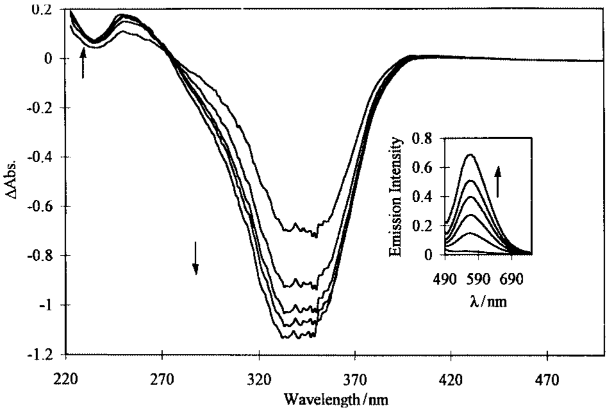

Fig. 1 UV–visible difference absorption spectra ($\Delta_{Abs} = A_t - A_{t=0}$) of $[(bpy)Re(CO)_3]_3(\mu\text{-TEEPB})(PF_6)_3$ in CH_3CN at 293 K as a function of photolysis time ($\lambda = 366$ nm; 0, 1, 2, 3, 4, 6 h). The inset shows the emission spectra before and after the photolysis.

localized on the *cis*-configuration bridging ligand is blocked or, at least, more unfavorable than direct deactivation from the ^{3}MLCT excited state to the ground state.

On the other hand, there is no emission detected from **5**, even after prolonged irradiation at 366 nm for 48 h. The lack of emission from **5** is attributed to the energy gap law, that is, the lower energy ^{3}MLCT excited state results in better vibrational overlap between the ground and excited states and the nonradiative decay increases as vibrational overlap increases.[9] The low energy ^{3}MLCT excited state in **5** also makes the energy transfer process energetically unfavorable.

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 TEEPB are the only deactivation processes for the ^{3}MLCT excited state, and that the decay from the ^{3}TEEPB excited state is much faster than energy transfer, then Φ_{em} and τ for $[(NN)Re(CO)_3]_3(\mu\text{-TEEPB})(PF_6)_3$ can be expressed as : $\Phi_{em} = k_r/(k_r + k_{nr} + k_{ENT})$ and $\tau = (k_r + k_{nr} + k_{ENT})^{-1}$. Calculated photophysical parameters are shown in Table 1. As expected, all the k_r values are very similar, *ca.* 1×10^5 s^{-1}, for the series of *fac*-(diimine)Re^I(CO)$_3$L complexes and in agreement with related Re(I) chromophores.[10] The energy transfer rate constant, k_{ENT}, and the efficiency for generating the ^{3}TEEPB excited state, Φ_{ENT}, at 293 K can be determined based on: $k_{ENT} = \tau^{-1} - \tau_{model}^{-1}$ and $\Phi_{ENT} = k_{ENT}/(k_r + k_{nr} + k_{ENT})$ with **6** and **7** as model compounds and their values are listed in Table 1.

It is not surprising that both the k_{ENT} and Φ_{ENT} values for **3** are larger than the corresponding values for **1**. The higher ^{3}MLCT excited energy in **3** results in a larger energy gap between the triplet donor and acceptor and, thus, a larger driving force that enhances the efficiency of energy transfer process.

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Notes and references

‡ Two structurally similar compounds, $[(NN)Re(CO)_3]_3(\mu\text{-TEPB})(PF_6)_3$ [NN = bpy (**6**) or 4,4′-Me$_2$bpy (**7**) and TEPB = 1,3,5-tris(2-ethynyl-4-pyridyl)benzene] were prepared as model complexes (Scheme 1). Compounds **6** and **7** contain an sp-hybridized carbon link and, thus, avoid photoisomerization deactivation from the ^{3}MLCT excited state.

§ In a control experiment, the photolysis was performed in CD_3CN solution. The ^{1}H NMR spectra of both **1** and **3** showed the appearance of ethylene proton signals with coupling constants, $J_{H\text{–}H} = 12$ Hz ($J_{H\text{–}H} = 16$ Hz before photolysis), which unambiguously confirmed the formation of the *cis*-configuration bridging ligand. On the basis of the integrated areas in the ^{1}H NMR spectra, it was determined that all-*trans*-TEEPB in both **1** and **3** was less than 5% after 36 h of photolysis. The photolysis products are mixtures of *trans-trans-cis*-TEEPB, *trans-cis-cis*-TEEPB, and all-*cis*-TEEPB.

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