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Photoswitchable Luminescence of Rhenium(I) Tricarbonyl Diimines

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The synthesis, characterization, and X-ray crystal structures of [Re(diimine)$(CO)_3$(dpe)](PF_6) (dpe = 1,2-di(4-pyridyl)-ethylene) compounds are reported. The cis-dpe complexes exhibit yellow luminescence after UV excitation, whereas the trans-dpe counterparts are nonluminescent. The luminescence quantum yields of the cis-dpe complexes are strongly dependent on the identity of the diimine ligand. Irradiation (350 nm) of the trans-dpe complexes induces trans → cis dpe-ligand isomerization with quantum yields on the order of 0.2, and this process leads to an on-switching of yellow luminescence. After long 350-nm irradiation times, a steady state composed of roughly 70% cis- and 30% trans-dpe complexes is reached. The reverse cis → trans photoisomerization reaction is induced by irradiating the cis-dpe complexes at 250 nm, switching off the yellow luminescence. For 250-nm excitation, photodecomposition of the [Re(diimine)$(CO)_3$(dpe)]$^+$ complexes competes efficiently with photoisomerization.

I. Introduction

High density information storage is becoming an increasingly important technological objective. Molecular data storage systems that have been investigated in recent years include simple yes/no switches as well as molecules that perform logic operations.[1−3] The external stimuli that trigger these switching processes are most commonly change of pH, variation of redox potential, and irradiation with visible or UV light.

In the course of our work on rhenium(I) tricarbonyl diimines,[4] we examined several systems that function as photoswitches.[5,6] The photoswitchable complexes contain a stilbene-like ligand, 1,2-di-(4-pyridyl)ethylene (dpe), which undergoes reversible trans → cis photoisomerization upon UV excitation, thereby turning the yellow Re(I) emission either on (c) or off (t). In much of the previous work on [Re(I)(diimine)$(CO)_3$X]$^+$ complexes (X is a photoisomerizable ligand),[5] including Iha's report on X = dpe,[6] only the more stable trans-X forms were isolated and properly characterized. Luminescence off-switching, although an essential process in terms of data storage, has not been studied extensively for systems of this type.

We report the synthesis, characterization, and X-ray crystal structures of both [Re(diimine)$(CO)_3$(trans-dpe)]$^+$ and [Re(diimine)$(CO)_3$(cis-dpe)]$^+$ complexes, as well as details of the photoinduced isomerization processes responsible for luminescence on- and off-switching.

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II. Experimental Section

A. Materials. 2,2′-Bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), 1,10-phenanthroline (phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), pentacarbonylchlororhenium(I), *trans*-1,2-di(4-pyridyl)ethylene (t-dpe), 1,2-di(4-pyridyl)ethane (dp-ethane), trifluoromethanesulfonic acid, benzil, and ammonium hexafluorophosphate were used as received from Sigma Aldrich. All solvents used for synthesis were reagent grade. High purity solvents from Burdick & Jackson were used for optical spectroscopic measurements.

B. Syntheses of cis-dpe and Re(I) Complexes. B.1. cis-dpe. A solution of trans-dpe (0.05 M) and benzil (0.5 M) in CH_2Cl_2 was irradiated [75 W Xe lamp (Oriel)] for 4 h under N_2 atmosphere.[7] The benzil sensitizer was removed from dpe by column chromatography on alumina using CH_2Cl_2 as the eluant. The dpe was eluted using a 10% CH_3OH/90% CH_2Cl_2 mixture. This procedure yields dpe in a cis/trans ratio > 50:1 as confirmed by ^{1}H NMR experiments. ^{1}H NMR ($CDCl_3$) data for c-dpe: δ 8.51 (dd, 4H), 7.08 (dd, 4H), 6.71 (s, 2H).

B.2. Re(I) Complexes. The *fac*-[ReL(CO)$_3$Cl] (L = diimine) complexes were prepared according to a literature procedure.[8] They were converted to *fac*-[ReL(CO)$_3$(CF_3SO_3)] following a standard method.[9] The latter complexes were reacted with excess dpe or dp-ethane in methanol to yield *fac*-[ReL(CO)$_3$(dpe/dp-ethane)]$^+$ ions, which were isolated as PF_6^- salts and purified as described previously.[6] The overall yield with respect to the Re(CO)$_5$Cl starting material was between 50 and 60%.

Re(bpy)(CO)$_3$(t-dpe)PF$_6$ (1a). ESI-MS *m*/*z*: 609 (M$^+$). IR (NaCl): ν(CO) = 1916, 1924, 2032 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.23 (d, 2H, 5.7 Hz), 8.59 (d, 2H, 6.0 Hz), 8.38 (d, 2H, 9.1 Hz), 8.28 (d, 2H, 7.8 Hz), 8.24 (t, 2H, 6.6 Hz), 7.80 (t, 2H, 6.6 Hz), 7.70 (d, 2H, 6.0 Hz), 7.46 (A of AB, 1H, 16.5 Hz), 7.44 (d, 2H, 5.7 Hz), 7.39 (B of AB, 1H, 16.5 Hz).

Re(bpy)(CO)$_3$(c-dpe)PF$_6$ (1b). ^{1}H NMR (CD_3CN): δ 9.17 (d, 2H, 5.4 Hz), 8.44 (d, 2H, 6.0 Hz), 8.40 (d, 2H, 6.0 Hz), 8.27 (t, 2H, 7.8 Hz), 8.03 (d, 2H, 6.6 Hz), 7.80 (t, 2H, 6.3 Hz), 7.13 (d, 2H, 6.0 Hz), 7.01 (d, 2H, 6.6 Hz), 6.85 (A of AB, 1H, 12.6 Hz), 6.63 (B of AB, 1H, 12.6 Hz).

Re(bpy)(CO)$_3$(dp-ethane)PF$_6$ (1c). ESI-MS *m*/*z*: 611 (M$^+$).

Re(Me$_2$bpy)(CO)$_3$(t-dpe)PF$_6$ (2a). ESI-MS *m*/*z*: 637 (M$^+$). IR (NaCl): ν(CO) = 1914, 1926, 2030 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.04 (d, 2H, 6.0 Hz), 8.59 (d, 2H, 6.0 Hz), 8.23 (s, 2H), 8.20 (d, 2H, 6.6 Hz), 7.61 (d, 2H, 5.7 Hz), 7.56 (d, 2H, 6.0 Hz), 7.43 (d, 2H, 7.2 Hz), 7.42 (A of AB, 1H, 16.5 Hz), 7.34 (B of AB, 1H, 16.5 Hz), 2.55 (s, 6H).

Re(Me$_2$bpy)(CO)$_3$(c-dpe)PF$_6$ (2b). ^{1}H NMR (CD_3CN): δ 8.98 (d, 2H, 6.0 Hz), 8.43 (d, 2H, 5.4 Hz), 8.23 (s, 2H), 8.04 (d, 2H, 6.6 Hz), 7.57 (d, 2H, 5.1 Hz), 7.09 (d, 2H, 5.4 Hz), 7.01 (d, 2H, 6.0 Hz), 6.88 (A of AB, 1H, 12.6 Hz), 6.69 (B of AB, 1H, 12.6 Hz), 2.55 (s, 6H).

Re(Me$_2$bpy)(CO)$_3$(dp-ethane)PF$_6$ (2c). ESI-MS *m*/*z*: 639 (M$^+$).

Re(phen)(CO)$_3$(t-dpe)PF$_6$ (3a). ESI-MS *m*/*z*: 633 (M$^+$). IR and ^{1}H NMR spectra as previously reported.[6]

Re(phen)(CO)$_3$(c-dpe)PF$_6$ (3b). ^{1}H NMR (CD_3CN): δ 9.56 (d, 2H, 5.1 Hz), 8.84 (d, 2H, 8.4 Hz), 8.35 (d, 2H, 5.7 Hz), 8.18 (s, 2H), 8.11 (d, 2H, 5.4 Hz), 8.09 (d, 2H, 5.4 Hz), 7.06 (d, 2H, 6.3 Hz), 6.90 (d, 2H, 6.6 Hz), 6.81 (A of AB, 1H, 12.6 Hz), 6.61 (B of AB, 1H, 12.6 Hz).

Re(phen)(CO)$_3$(dp-ethane)PF$_6$ (3c). ESI-MS *m*/*z*: 635 (M$^+$).

Re(Me$_4$phen)(CO)$_3$(t-dpe)PF$_6$ (4a). ESI-MS *m*/*z*: 689 (M$^+$). IR (NaCl): ν(CO) = 1911, 1923, 2030 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.34 (s, 2H), 8.57 (d, 2H, 6.3 Hz), 8.31 (d, 2H, 6.6 Hz), 8.29 (s, 2H), 7.70 (d, 2H, 5.4 Hz), 7.39 (A of AB, 1H, 16.5 Hz), 7.34 (B of AB, 1H, 16.5 Hz), 7.33 (d, 2H, 5.4 Hz), 2.82 (s, 6H), 2.69 (s, 6H).

Re(Me$_4$phen)(CO)$_3$(c-dpe)PF$_6$ (4b). ^{1}H NMR (CD_3CN): δ 9.28 (s, 2H), 8.36 (d, 2H, 3.6 Hz), 8.29 (s, 2H), 8.11 (d, 2H, 5.4 Hz), 7.02 (d, 2H, 3.9 Hz), 6.89 (d, 2H, 5.7 Hz), 6.83 (A of AB, 1H, 12.9 Hz), 6.60 (B of AB, 1H, J = 12.9 Hz), 2.82 (s, 6H), 2.69 (s, 6H).

Re(Me$_4$phen)(CO)$_3$(dp-ethane)PF$_6$ (4c). ESI-MS *m*/*z*: 691 (M$^+$).

C. Spectroscopic Measurements. Mass spectra were obtained from the Caltech Mass Spectrometry Laboratory. IR spectra were recorded on a Perkin-Elmer Paragon 1000 infrared spectrometer. ^{1}H NMR spectra were measured on a Varian 300 MHz instrument. An Agilent Chemstation was used for absorption measurements, and emission spectra were recorded on a Spex Fluorolog-2 spectrofluorometer. The latter instrument was also employed for monochromatic photolysis. Excitation for the luminescence lifetime experiments employed 8 ns pulses (at a repetition rate of 10 Hz) from a frequency-tripled Nd^{3+}:YAG laser (Quanta Ray Pro, Spectra Physics). The luminescence was dispersed through a monochromator (Instruments SA DH-10) onto a photomultiplier tube (PMT) (Hamamatsu R928). The PMT current was amplified and recorded with a transient digitizer (Tektronix).

D. X-ray Structure Determination. [Re(phen)(CO)$_3$(t-dpe)]BF$_4$ (**3a**) and [Re(phen)(CO)$_3$(c-dpe)]BF$_4$ (**3b**) were crystallized as yellow plates by slow diffusion of diethyl ether into acetonitrile solutions at room temperature. Higher quality crystals were obtained using this method when using BF_4^- rather than PF_6^- salts.[10] The diffraction experiments were carried out at 100 K using a Bruker SMART 1000 diffractometer and Mo Kα radiation (λ = 0.71073 Å). The SHELX-97 program was used for structure solution and refinement.[11] The Re atoms and the non-H atoms in its first coordination sphere were located from a Patterson map, while all other non-H-atoms were found by Fourier map calculations. The structure was refined by least-squares refinement of F^2 against all reflections. H-atoms were placed at calculated positions (**3a**) or refined isotropically (**3b**). The crystal data and structure refinement parameters for **3a** and **3b** are summarized in Table 1.[12]

III. Results and Discussion

A. Crystal Structures. In crystals of [Re(phen)(CO)$_3$(c-dpe)]BF$_4$, the cations form dimers in which the central rings of the phen-ligand are π-stacked. No π-stacking occurs in

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(10) The PF_6^-salt of **3a**, grown by slow diffusion of hexane into a dichloromethane solution, crystallizes in a C-centered monoclinic cell with a = 33.656 Å, b = 10.916 Å, c = 25.953 Å, β = 119.4°, V = 8309 Å^3, and Z = 8. The structure is seriously disordered in both space groups C_s and $C2/c$.
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Table 1. Summary of Crystal Data Information and Collection/Refinement Parameters for $[Re(phen)(CO)_3(t\text{-}/c\text{-}dpe)]BF_4$ (**3a** and **3b**)

dpe-isomer	trans (**3a**)	cis (**3b**)
formula	$[C_{27}H_{18}N_4O_3Re]^{+}$-$[BF_4]\cdot CH_3CN$	$[C_{27}H_{19}N_4O_3Re]^{2+}$-$[BF_4]_2\cdot C_2H_5OC_2H_5$
fw [g·mol^{-1}]	760.52	881.40
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	10.2385(2)	11.2246(2)
b [Å]	15.6636(3)	12.0663(2)
c [Å]	17.3841(4)	13.6308(3)
α [deg]	90	111.490(1)
β [deg]	100.573(1)	94.164(1)
γ [deg]	90	101.640(1)
V [Å^3]	2740.58(10)	1660.59(5)
Z	4	2
D_{calcd} [g·cm^{-3}]	1.843	1.763
wavelength	Mo Kα	Mo Kα
T [K]	100	100
scan mode	*ω* and *ϕ*	*ω*
μ [mm^{-1}]	4.50	3.75
abs correction	none	face-indexed
θ-range [deg]	1.76−38.30	1.63−38.35
index ranges [*h*, *k*, *l*]	−17 → 17 −26 → 27 −29 → 29	−18 → 19 −20 → 20 −23 → 23
reflns collected	68604	43636
no. indep reflns	14443	16184
refinement method	least-squares on F^2	least-squares on F^2
final *R* indices [no. reflns]	10052	13475
no. refined params	426	565
treatment of H-atoms	riding	unrestrained
R [$F^2 > 2\sigma(F^2)$]	0.0325	0.0350
R (all data)	0.0601	0.0474
GOF	1.15	1.32
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e ·Å^3]	2.07, −1.74	2.95, −1.79

the crystal structure of the respective trans-dpe complex. In both structures, the BF_4^- anions are disordered, and 1 equiv of solvent per cation is included: acetonitrile in the trans-structure and diethyl ether in the cis-structure. The coordination geometry of the cation is approximately octahedral with facial arrangement of the linearly coordinated carbonyl ligands. Drawings of the cations, including the numbering schemes, are shown in Figure 1. Although both **3a** and **3b** were prepared under identical chemical conditions, in the former N4 is unprotonated, whereas in the latter it is protonated. The geometries around the rhenium atoms are in good agreement with a number of related structures.[13] All bond lengths and angles in the phen-ligands are normal. In both structures, the C21 ethylene carbon atom is nearly coplanar with the N3-pyridyl moiety of the dpe-ligand. Consequently, the dihedral angle between the two pyridyl rings of the dpe-ligand is essentially given by the C21−C22−C23−C24 torsion angle. In the trans-dpe structure, this angle is 15.5°, whereas in the cis-dpe complex it is 51.0°. This compares to 1.6° and 53.0° in the free trans- and cis-dpe ligands.[14]

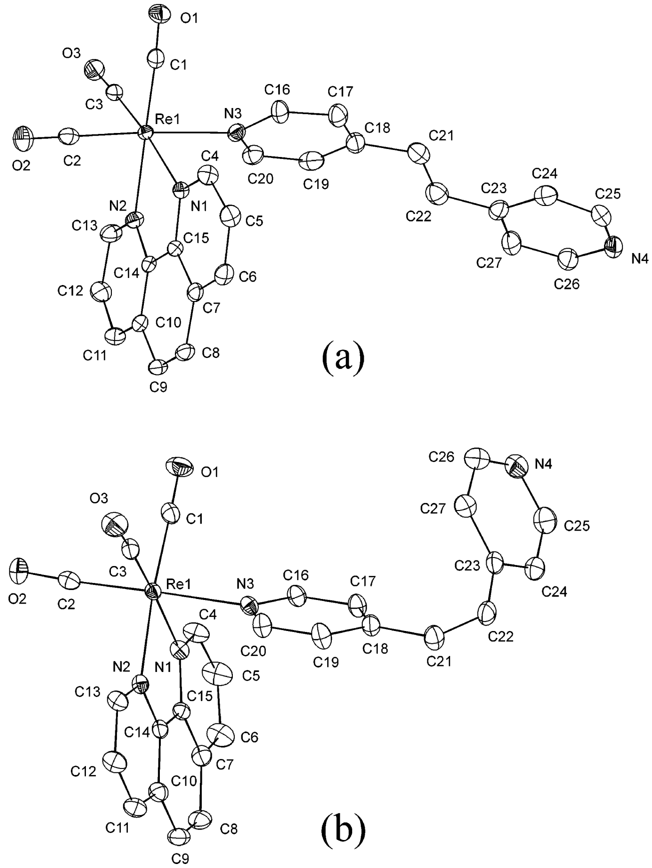

Figure 1. Cations of **3a** (a) and **3b** (b). Displacement ellipsoids are drawn to the 50% probability level. H-atoms are omitted for clarity.

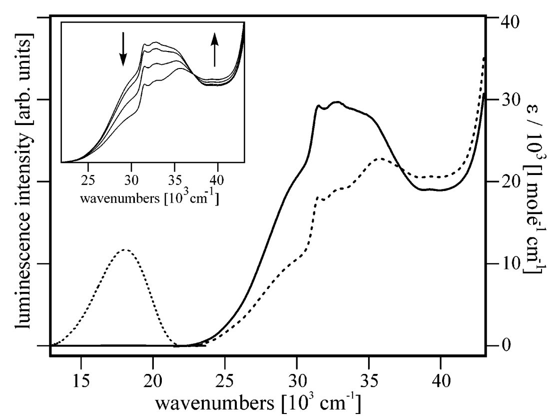

Figure 2. Absorption and emission spectra of CH_2Cl_2 solutions of **2a** (—) and **2b** (- - -). Inset: Absorption spectra of a degassed CH_2Cl_2 solution of **2a** after irradiation at 350 nm for 0, 10, 30, and 90 min.

B. Optical Absorption. The solid and dashed lines in the right part of Figure 2 are the room-temperature absorption spectra of **2a** and **2b**, respectively, in CH_2Cl_2 solution.[15] The

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absorption bands above 30000 cm^{-1} are assigned to Me_2-bpy and t-/c-dpe intraligand (IL) electronic transitions. The lowest absorption feature, which is observed between 23000 and 31000 cm^{-1} as a shoulder on the higher energy bands, occurs in the normal energy range for MLCT excitations in $[ReL(CO)_3X]^{0/+}$ complexes, where L is an α-diimine ligand and X can be varied from simple ions such as Cl^- to organic ligands.[8,16] However, the oscillator strength of the above band is almost a factor of 5 higher than typically observed for Re(I) MLCT transitions. The absorption associated with the lowest spin-allowed transition of protonated t-dpe peaks at 31500 cm^{-1};[6] thus, in each of our Re(I) complexes, this feature overlaps the MLCT system. In addition, owing to their proximity, the MLCT and dpe IL states are strongly mixed, thereby enhancing the oscillator strength of the MLCT transition.[17]

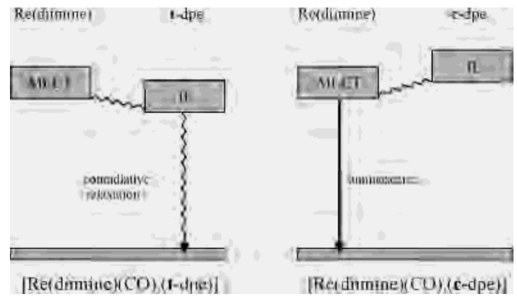
In **2b** the extinction between 23000 and 37000 cm^{-1} is lower than in **2a**, and between 37000 and 40000 cm^{-1} the opposite is true (Figure 2), owing to the different IL transition energies of trans- and cis-dpe. In *cis*-stilbenes and -stilbazoles the $\pi \rightarrow \pi^*$ transitions are generally at higher energies than in their trans-isomers, due to a twisting of the two benzene/pyridine moieties relative to each other in the cis-isomers (the trans-isomers are essentially planar, section III.A).[18] In free cis-dpe, the lowest-energy spin-allowed $\pi \rightarrow \pi^*$ transition is blue-shifted by 4000 cm^{-1} relative to trans-dpe.[19] In Re(I)-ligated dpe the change in the pyridyl torsion angle between the trans and cis-isomer is roughly 30% smaller than for the free ligand (complexes **3a** and **3b** in section III.A). Consequently, the dpe $\pi \rightarrow \pi^*$ energy differences between our cis- and trans-dpe complexes are somewhat smaller than 4000 cm^{-1}. These differences in optical absorption spectra, namely, stronger low energy absorptions in the t-dpe complexes and higher extinctions around 40000 cm^{-1} in the c-dpe analogues, which are observed for all four $[ReL(CO)_3(dpe)]^+$ systems reported here, are of crucial importance for the interpretation of our photoinduced isomerization experiments.

C. Emission Properties. The left part of Figure 2 shows the emission spectra obtained after 350-nm excitation of **2a** (—) and **2b** (- - -), respectively, in CH_2Cl_2 solution at room temperature. No luminescence was detected from **2a** under these experimental conditions. Complex **2b**, by contrast, exhibits a broad and unstructured luminescence centered at 17920 cm^{-1}, with a lifetime in degassed CH_2Cl_2 solution of 0.57 μs (Table 2). The position, band shape, and lifetime of this luminescence are consistent with expectation for MLCT emission. The emission properties of **2a**/**2b** are representative of all other dpe-complexes reported here: the t-dpe complexes are uniformly nonluminescent, whereas the c-dpe analogues exhibit yellow MLCT emission with lifetimes ranging from 0.52 to 2.04 μs (Table 2). Transient IR measurements on **3a** and **3b** by Iha and Meyer have shown that the lowest-lying excited state is dpe-localized in the trans-dpe complex.[20] For uncomplexed dpe, radiative decay is negligible.[21] About 90% of the photoexcited dpe molecules return to the ground state via (nonradiative) multiphonon relaxation, whereas the remaining 10% undergo photoinduced trans ↔ cis isomerization. Also, in the trans-dpe complexes, nonradiative relaxation is the dominant excited-state decay process (left part of Scheme 1). On the other hand, for the $[ReL(CO)_3(c\text{-}dpe)]^+$ complexes, the lowest energy dpe IL excited state is blue shifted by about 10% (section III.B) relative to that of the t-dpe complexes (right part of Scheme 1), and thus, the lowest excited state has less dpe IL (more MLCT) character, thereby allowing radiative decay to compete with nonradiative relaxation processes.

Table 2. Luminescence Band Maximum Energies E_{max}, Luminescence Quantum Yields ϕ_{lum}, and Luminescence Lifetimes τ of the $[ReL(CO)_3(X)]^+$ Complexes in Room Temperature (Degassed) CH_2Cl_2 Solutions

		X = cis-dpe			X = dp-ethane		
no.	L	E_{max} (cm^{-1})	ϕ_{lum}	τ (ns)	E_{max} (cm^{-1})	ϕ_{lum}	τ (ns)
1b/c	bpy	17600	0.007	550	17750	0.044	610
2b/c	Me_2bpy	17920	0.008	570	18100	0.049	740
3b/c	phen	18120	0.012	2040	18200	0.061	3080
4b/c	Me_4phen	19050	0.002	520	19400	0.075	12500

Scheme 1



The luminescence quantum yields of the $[ReL(CO)_3(c\text{-}dpe)]^+$ complexes in degassed CH_2Cl_2 have been determined by comparison with the known luminescence yield from $[Re(bpy)(CO)_3(py)]^+$ (py = pyridine).[8] The luminescence quantum yields for all of our $[ReL(CO)_3(c\text{-}dpe)]^+$ complexes are systematically lower by at least a factor of 6 when compared to $[ReL(CO)_3(dp\text{-}ethane)]^+$ analogues (Table 2). The lowest dp-ethane IL excited states are at substantially higher energies than those of dpe, with the result that the corresponding $ReL(CO)_3(dp\text{-}ethane)^+$ states have much greater MLCT character. In addition, photoinduced isomerization processes are not

(15) All optical spectroscopic measurements were performed on unprotonated samples.

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(19) In stilbene, this blue shift amounts to 4500 cm^{-1}; see: Glynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

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possible in these cases, and thus, the luminescence quantum yields are higher.

For both $[ReL(CO)_3(c\text{-dpe})]^+$ and $[ReL(CO)_3(dp\text{-ethane})]^+$ complexes, the energy of the emission band maximum increases with L as follows: bpy < Me_2bpy < phen < Me_4-phen (Table 2). For $[ReL(CO)_3(dp\text{-ethane})]^+$, this increase is accompanied by an increase in the luminescence quantum yields and lifetimes, as is well documented for several MLCT emitters.[8,22] Studies of a large number of $[Re(bpy)(CO)_3X]^+$ complexes have revealed good correlations between the nonradiative MLCT excited-state decay rate constant k_{nr} and the MLCT emission energy: k_{nr} decreases as the emission energy increases. Accordingly, the increase of the luminescence quantum yield along the above series of $[ReL(CO)_3(dp\text{-ethane})]^+$ complexes follows the normal pattern, as does the corresponding increase along the $[ReL(CO)_3(c\text{-dpe})]^+$ series with L varying from bpy to Me_2bpy to phen (Table 2). Upon changing from L = phen to Me_4phen, however, there is a factor of 6 decrease in the luminescence quantum yield despite a 930 cm^{-1} increase in the emission band maximum energy. In addition, the luminescence lifetime decreases by a factor of 3.9 when going from **3b** to **4b** (Table 2). We offer the following explanation: owing to the 930 cm^{-1} blue shift of the MLCT in **4b** relative to **3b**, the energetic separation between the MLCT state and the lowest energy c-dpe IL state decreases substantially, leading to stronger mixing between the two states and more efficient nonradiative relaxation. Thus, the luminescence quantum yield reaches an upper limit of 0.012 in $[ReL(CO)_3(c\text{-dpe})]^+$ complexes (the value obtained for L = phen).

D. Photoinduced Isomerization. Irradiation of a degassed CH_2Cl_2 solution of **2a** at 350 nm leads to changes in its absorption spectrum (inset of Figure 2). While the extinction below 37000 cm^{-1} decreases, it increases between 37000 and 45000 cm^{-1} (see the arrows). The spectrum obtained after long irradiation times closely resembles the absorption spectrum of **2b** (compare the dashed line in Figure 2). We conclude that UV irradiation induces dpe trans → cis isomerization in **2a**. Confirmation comes from ^1H NMR experiments: the top and bottom traces in Figure 3 show the aromatic region of the ^1H NMR spectra of **2a** and **2b**, respectively. The two most relevant differences between these two spectra are an upfield shift of essentially all resonance signals and a decrease of the ethylene-proton coupling from 16 to 12 Hz on going from **2a** to **2b** (see section II). Traces b−d in Figure 3 are the ^1H NMR spectra of CD_2Cl_2 solutions of **2a** obtained after 350-nm irradiation of these solutions for (b) 10 min, (c) 30 min, and (d) 90 min. These three NMR spectra are superpositions of those of pure **2a** and **2b**, i.e., the respective solutions contain a mixture of both trans- and cis-dpe complexes. With increasing irradiation times, more of the cis-complex is formed at the expense of its trans-dpe counterpart. After about 90 min, a steady state is reached in which there are no further changes in either the ^1H NMR or the optical absorption spectrum. Trace d shows the ^1H NMR spectrum of a solution in this steady state. It contains 28% **2a** and 72% **2b**.

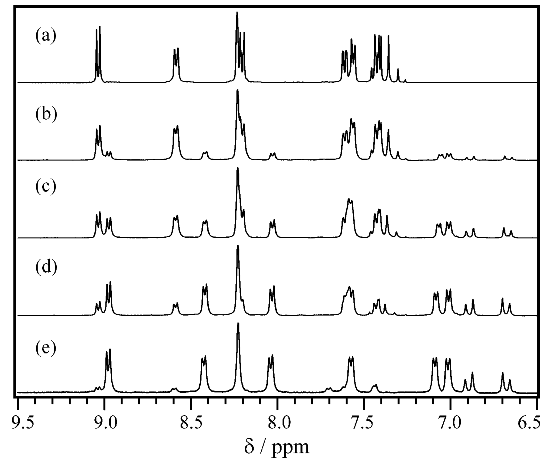

Figure 3. Traces a−d: ^1H NMR spectral changes of a CD_2Cl_2 solution of **2a** during irradiation at 350 nm. Irradiation times were 0, 10, 30, and 90 min. Trace e: ^1H NMR spectrum of a CD_2Cl_2 solution of **2b**.

Table 3. Steady State Concentration Ratios c_{cis}/c_{trans} Reached after Irradiation at 350 nm, Extinction Coefficients ϵ at λ = 350 nm (in M^{-1} cm^{-1}), and trans → cis ($\phi_{t\to c}$) and cis → trans ($\phi_{c\to t}$) Isomerization Quantum Yields for 350 nm Irradiation of the Various $[ReL(CO)_3(t\text{-}/c\text{-dpe})]^+$ Complexes

no.	L	c_{cis}/c_{trans}	ϵ_t	ϵ_c	$\phi_{t\to c}/\phi_{c\to t}$	$\phi_{t\to c}$	$\phi_{c\to t}$
1	bpy	2.50	15100	7350	1.2	0.21	0.18
2	Me_2bpy	2.56	15900	8250	1.3	0.23	0.18
3	phen	2.17	16500	8900	1.2	0.22	0.18
4	Me_4phen	2.22	15250	9000	1.3	0.21	0.16

An analogous trans → cis dpe photoisomerization process is observed after 350-nm irradiation of complexes **1a**, **3a**, and **4a**. The steady state concentration ratios of cis-dpe versus trans-dpe complexes c_{cis}/c_{trans} are set out in Table 3. For the bpy complexes, this ratio is around 2.5, whereas for the phen complexes it is roughly 2.2. Equation 1 relates c_{cis}/c_{trans} to the ratio of the quantum yields ϕ for the trans → cis (t → c) and cis → trans (c → t) photoisomerizations[23,24]

$$\frac{c_{cis}}{c_{trans}} = \frac{\epsilon_t}{\epsilon_c} \cdot \frac{\phi_{t\to c}}{\phi_{c\to t}} \tag{1}$$

where ϵ_t and ϵ_c are the extinction coefficients for the trans- and cis-forms, respectively, at the irradiation wavelength. The ϵ_t and ϵ_c values at 350 nm for the dpe complexes are given in Table 3. Using eq 1, we calculate $\phi_{t\to c}/\phi_{c\to t}$ ratios of 1.2−1.3 for all our systems (Table 3). Thus, the relative trans → cis and cis → trans isomerization quantum yields are nearly unaffected by changing the α-diimine ligand. The slightly higher steady state c_{cis}/c_{trans} concentration ratios achieved for the phen complexes relative to the bpy complexes result from higher ϵ_t/ϵ_c ratios at 350 nm for the former. The $\phi_{t\to c}/\phi_{c\to t}$ ratios for our $[ReL(CO)_3(dpe)]^+$ complexes are very close to the value of 1.4 obtained for free stilbene.[23]

The absolute value of the initial trans → cis dpe ligand isomerization quantum yield $\phi_{t\to c}$ in **2a** can be determined

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(24) Note that this equation is only valid for low absorbance values.

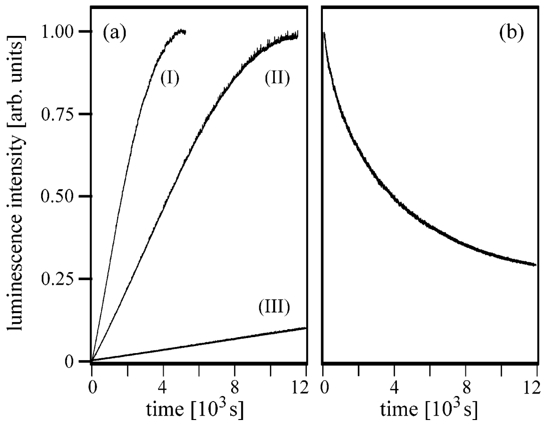

Figure 4. (a) Luminescence intensity of a CH_2Cl_2 solution of **2a** as a function of 350-nm irradiation time using three different excitation photon fluxes: (I) 1.8×10^{16}, (II) 7.2×10^{15}, and (III) 0.6×10^{15} photons/s. (b) Luminescence intensity of a CH_2Cl_2 solution of **2b** as a function of 250-nm irradiation time.

from spectrum b in Figure 3. The solution used for this ^{1}H NMR measurement was irradiated at 350 nm for 600 s, and 4.1 μmol of **2b** were formed during this time. The photon flux I_0 of the irradiation source, as determined by ferrioxalate actinometry,[25] was $I_0 = 1.8 \times 10^{16}$ photons/s. Thus, $\phi_{t\rightarrow c} = 0.23$ for **2a**, and virtually identical values were found for the other $[ReL(CO)_3(t\text{-dpe})]^+$ complexes reported here (Table 3). These $\phi_{t\rightarrow c}$ values are in accord with those reported for **3a** by Iha and Meyer;[20] and they are about a factor of 2 lower than those obtained for a series of rhenium(I) complexes containing styrylpyridine-derived ligands.[5] Additionally, our results are in line with those from a previous study of trans → cis photoisomerization in free dpe's and styrylpyridines, where lower $\phi_{t\rightarrow c}$-values for the former molecules were reported.[21]

Importantly, since the $[ReL(CO)_3(t\text{-dpe})]^+$ complexes are nonluminescent, but their $[ReL(CO)_3(c\text{-dpe})]^+$ counterparts are emissive when irradiated in the UV, trans → cis photoisomerization switches on a yellow light, as shown in the left part of Figure 4 in which the luminescence intensity of a CH_2Cl_2 solution of **2a** is plotted as a function of irradiation time at 350 nm. The three lines correspond to three experiments that were performed using different irradiation intensities. The photon fluxes were (I) 1.8×10^{16}, (II) 7.2×10^{15}, and (III) 0.6×10^{15} photons/s. Normalized to their respective photon flux values, the three sets of data in Figure 4a are superposable. In other words, in this excitation intensity regime, the rate of trans → cis dpe ligand photoisomerization depends linearly on the photon flux of the irradiation source. For $I_0 = 1.8 \times 10^{16}$ photons/s (I), the luminescence intensity increases linearly during the first 2000 s and then levels off at about 4000 s, indicating that a steady state ratio of t- and c-dpe complexes has been reached. The right part of Figure 4 shows the luminescence intensity of a CH_2Cl_2 solution of **2b** as a function of 250-nm irradiation time. A decrease of the luminescence intensity with time is observed, and this is mainly, but not exclusively, due to photoinduced dpe cis → trans isomerization. As shown in Figure 2, **2b** has a higher extinction at 250 nm (40000 cm^{-1}) than **2a**. The ϵ_t/ϵ_c ratio at this wavelength is 0.9. Thus, under the assumption that $\phi_{t\rightarrow c}/\phi_{c\rightarrow t} \approx 1.3$ (as for 350-nm irradiation, Table 3), it follows from eq 1 that the steady state to be reached after long irradiation times is composed of about 45% **2a** and 55% **2b**. In other words, the luminescence cannot be fully switched off, and this is exactly what is observed (Figure 4b). In addition to cis → trans isomerization, 250-nm irradiation also induces photodecomposition of a substantial percentage of the $[ReL(CO)_3(dpe)]^+$ complexes, and the presence of these photoproducts precluded an accurate NMR determination of the **2a**/**2b** steady state concentration ratio. For the same reason, reliable $\phi_{c\rightarrow t}$ values for 250-nm irradiation could not be obtained.

IV. Summary and Conclusions

The $[Re(diimine)(CO)_3(dpe)]^+$ complexes reported here exhibit trans → cis dpe photoisomerization quantum yields on the order of 0.2. Since the trans-dpe complexes are nonluminescent in room temperature solutions, the $[Re(diimine)(CO)_3(dpe)]^+$ systems exhibit very pronounced photoswitchable luminescence properties, even though the luminescence quantum yields of the cis-dpe complexes are limited to values around 0.01. As photoswitches, the major drawback of the $[Re(diimine)(CO)_3(dpe)]^+$ complexes is the off-mode, which can only be induced using irradiation at very short wavelengths, e.g., around 250 nm. Irradiation at this wavelength leads not only to the desired cis → trans back-isomerization of the dpe ligand, but also to photodecomposition.

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Supporting Information Available: Crystal data table and ORTEP plot of cis-dpe. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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