An Os^{II}-Ni^{II}-Pd^{II} Trimetallic Complex as an Electro-Switchable-Photoinduced-Electron-Transfer Device

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Abstract: A trimetallic complex bearing a sequence of redox-active metal coordination sites (Os^{II}-Ni^{II}-Pd^{II} **1**) and an analogous bimetallic complex (Os^{II}-Ni^{II} **2**) function as electro-switchable-photoinduced-electron-transfer (ESPET) molecular devices, in which the Os^{II} center is the light-harvesting component, the Pd^{II} site is the electron acceptor, and the Ni^{II} site serves as the electroswitchable intervening spacer. The Ni^{II} center can be reduced selectively, permitting regulation of the photoinduced-electron-transfer from the excited Os^{II} site to the Pd^{II}. In their oxidized forms, both **1** and **2** show transient biexponential emission decays in which the short-lived component is assigned to oxidative quenching of $*Os^{II}$ by Ni^{II} and the long-lived (minor) component to the unquenched $*Os^{II}$ site. In the electroreduced form, the bimetallic complex **2** shows suppressed oxidative quenching by the Ni^{II} site and an extended localized emission lifetime. In the trimetallic complex, the electroreduction enables direct oxidative quenching by the Pd^{II} site. The direct oxidation by Ni^{II} was significantly reduced (from 90% to 50%) and the lifetime of the excited Os^{II} site was extended.

Keywords: electron transfer · molecular devices · molecular switches · osmium · P ligands

Introduction

In recent years, the search for molecular-scale devices for information processing has been intensive.[1–4] The ability to switch a molecular unit ON and OFF is a key component of an efficient molecular device, since it allows modulation of the physical response of such a device by external physical or chemical triggers. Light-driven molecular switches have been used in photoisomerizable molecules,[2, 5] supramolecular systems,[1, 3] photoresponsive polymers,[6] and in the photoactivation of enzymes.[7, 8]

Molecular switches were also achieved by utilizing chemical triggers for controlling the emission properties and the structures of supramolecular systems.[3, 4, 9, 10, 11] For example, Wasielewski et al.[12] have recently demonstrated a new approach to forming a molecular switch by employing a photogenerated intramolecular electric field (from a D_1^+–A_1^- ion pair) to influence charge separation in a second donor–acceptor (D_2–A_2) pair. Wagner et al.[13] have shown that the redox state of a Mg-porphyrin unit can switch the direction of photoinduced energy flow and the emission intensity observed within a multiporphyrin array. Goulle et al.[14] have achieved an electro-photoswitch in the luminescence of a $Ru^{II}(bpy)_3$ unit covalently attached to a quinone. Recently Otsuki et al.[15] presented a means for electroswitching the emission of a bis-Ru^{II} complex by reducing the azo linker connecting the two metal centers. Polynuclear metal complexes have also been investigated as potential components of such molecular devices[16–23] because of their electron- and energy-transfer properties.

Herein we present a molecular device, based on a polynuclear metal complex, that functions as an electro-switchable-photoinduced-electron-transfer (ESPET) device. The operational principle of this molecular device is outlined in Scheme 1, in which S is the light-harvesting component, A is the electron acceptor, and E is an intervening electro-switchable component that possesses stable oxidation and reduction states, E_{ox} and E_{red}, respectively. Photoexcitation of S produces an easily oxidizable state, and electron transfer to either E_{ox} or A is permissible. However, if the reduction potential of the couple E_{ox}/E_{red} is less negative than the A/A^- couple and the spacer is geometrically closer to S*, the oxidation of S* by E_{ox} would be favored (route 1, Scheme 1). The geometric proximity of these two components will rapidly lead to the thermodynamically favored reaction, that is, charge recombination (route 2, Scheme 1). That route would reconvert the molecular device into the OFF state. However, electroreduction of E_{ox} to E_{red} will create a new molecular functionality. When E is in its reduced state, electron transfer from S* to A can take place, either in one or two steps to produce S^+-E_{red}-A^- (route 3, Scheme 1). This redox pair might be stable and long-lived, thanks to the geometric separation of the charged sites and the difficulty in generating the further reduced state E^-_{red} (route 4, Scheme 1). Charge separation will

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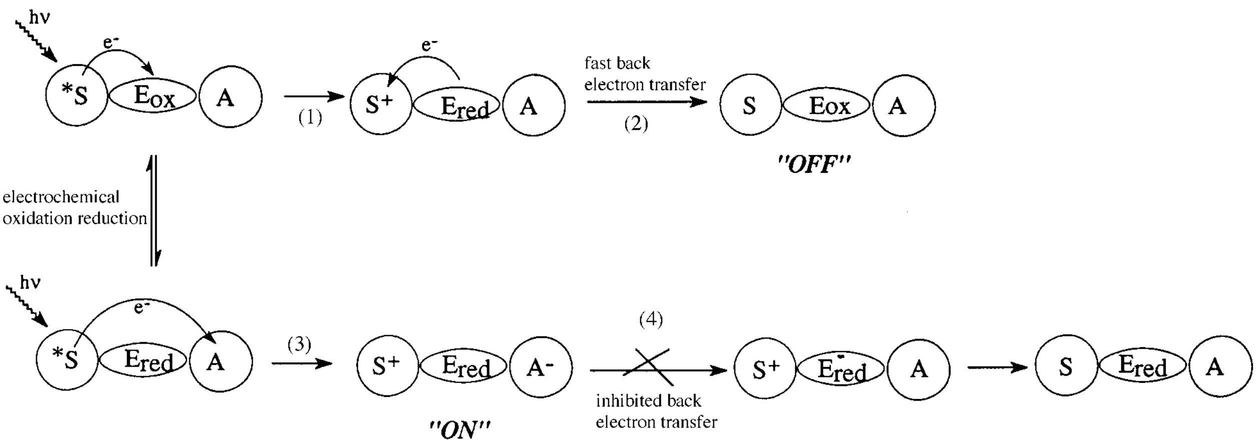
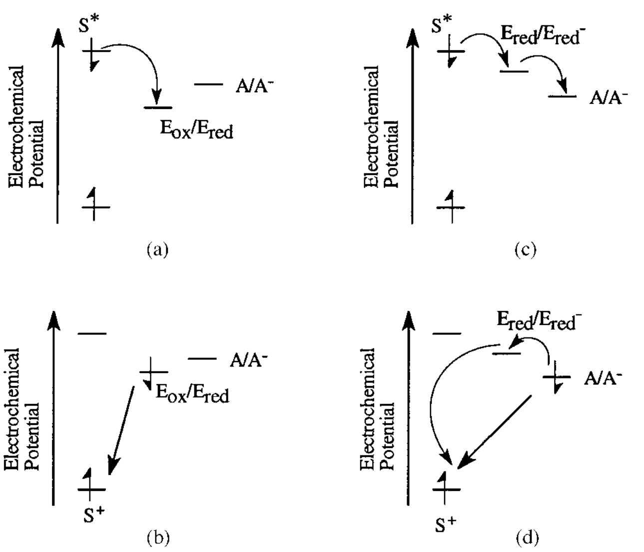


Scheme 1. The operational principle governing an electro-switchable-photoinduced-electron-transfer (ESPET) device. See text for details.



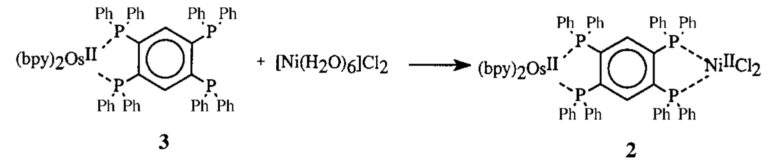
Scheme 2. Energetic ordering for favorable photoinduced electron transfer to produce S$^+$-E$_{red}$-A in (a) and to produce S$^+$-E$_{red}$-A$^-$in (c). Charge recombination is rapid in S$^+$-E$_{red}$-A (b), but slow in S$^+$-E$_{red}$-A$^-$(d) because of the inaccessibility of E$_{red}$ to A$^-$.

thus form the ON state of the supramolecule. The required energetic ordering for each of the components of this device is shown in Scheme 2.

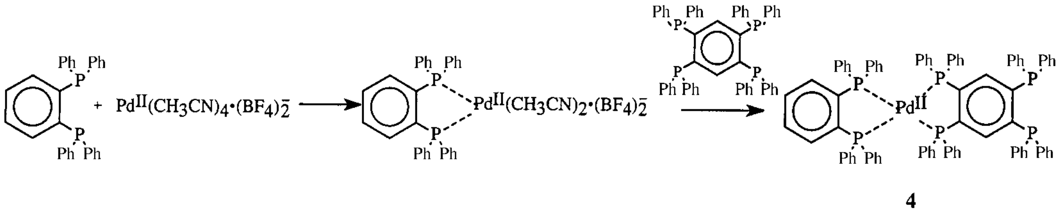
We show herein a demonstration of the concept embodied in Scheme 1 by employing a trimetallic complex with electrochemical potentials ordered as required by Scheme 2. To our knowledge, this study represents, for the first time, a clear indication that electrochemical switching of the redox state of a spacer intervening between a donor–acceptor pair can dictate the type of the observable charge separation and the lifetime of the resulting ion pair.

Results and Discussion

Preparation of the metalated complexes: Trimetallic complex **1**, bearing Os^{II}, Ni^{II}, and Pd^{II} at sequential metal coordination sites, and an analogous bimetallic complex **2** with only the first two metals were prepared by standard means. The bimetallic complex **2** is prepared by metalation of a previously described complex **3** [Eq. (1)].[23] Upon treatment of **2** with monome-



(1)



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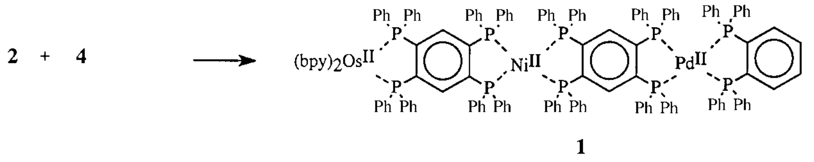
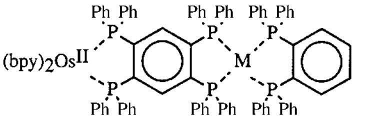


(3)

tallic complex **4**, which was attained by a previously described route [Eq. (2)],[25] complex **1** is obtained in 44% yield [Eq. (3)].

Absorption spectra and redox potentials: The trimetallic complex **1** contains the three required sites for the proposed ESPET device arranged in the correct potential gradient. The Os^{II} center serves as the light-harvesting component, the Pd^{II} site as the electron acceptor, and the Ni^{II} site as the electroswitchable couple. Previous studies in our group[23] have measured the electrochemical potentials for monometallic reference compounds **5a** and **5b**. From the cyclic voltammetric peak positions of **1**–**4** and the onset of light absorption by the Os^{II} complex **3**, the redox potentials (vs. Ag/AgCl) of the relevant pairs were calculated: Os^{II}/Os^{III} = 1.36 V, *Os^{III}/*Os^{II} = −0.69 V, Ni^{II}/Ni^{I} = −0.18 V, Ni^{I}/Ni^{0} = −0.45 V, and Pd^{II}/Pd^{0} = −0.6 V.



5a : M=Ni^{II}

5b : M=Pd^{II}

The absorption spectra of **1**, **2** and **3** are shown in Figure 1. Complex **1** exhibits an absorption maximum at 480 nm assigned to an MLCT state of Os^{II} → bpy,[24] the shoulder at 380 nm assigned to an MLCT state of Os^{II} → tppb,[24] and an additional strong absorption at 360 nm, assigned to a LMCT state of tppb → Pd^{II}.[25] The absorption spectrum of **2** is similar except that its absorption at 360 nm is weaker.

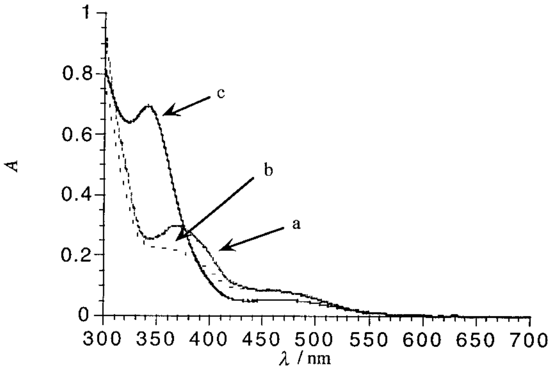
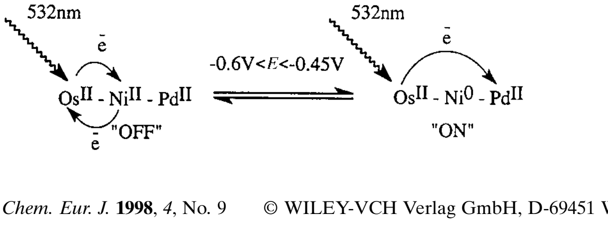


Figure 1. Absorption spectra of (40 μM) solutions in degassed [nBu$_4$N]PF$_6$/acetonitrile: a) **3**; b) **2**; c) **1**.

From the electrochemical data and the energy of the excited state of the Os^{II} site, the free energy (ΔG) involved for electron transfers from the excited Os^{II} to the Ni^{II} and Pd^{II} sites and in the charge recombination in **1** can be calculated (Scheme 3). The Ni^{II} site can be selectively reduced electrochemically to Ni^{0} in the potential range from −0.60 V to −0.45 V to the ON state, whereas its oxidized state (as Ni^{II}) will function as the OFF state [Eq. (4)].



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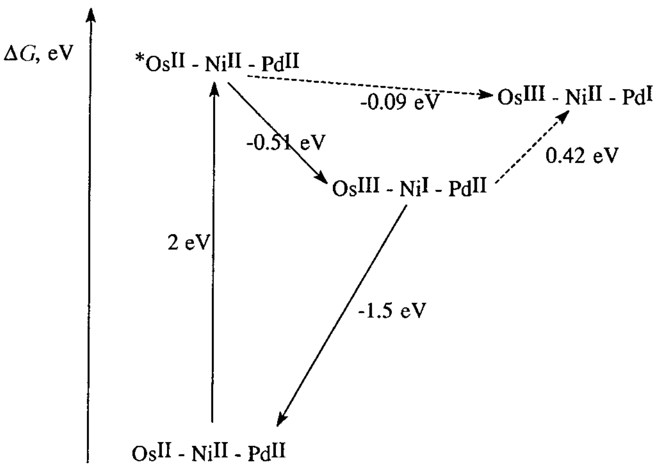

Scheme 3. ΔG changes in **1** that accompany the electron transfer reaction.

Excited-state interactions in the oxidized state: The emission spectra of **1**, **2**, and **3** are shown in Figure 2. The presence of the Ni^{II} and Pd^{II} sites in **1** and the presence of the Ni^{II} site in **2** cause strong emission quenching of the excited Os^{II} site. The emission quantum yields decreased from $\phi_3 = 0.049$ for **3** to $\phi = 0.003$ for both **1** and **2**. The quenching implies strong intramolecular interaction between the Os^{II} excited state and the acceptor sites in the trimetallic and the bimetallic complexes.

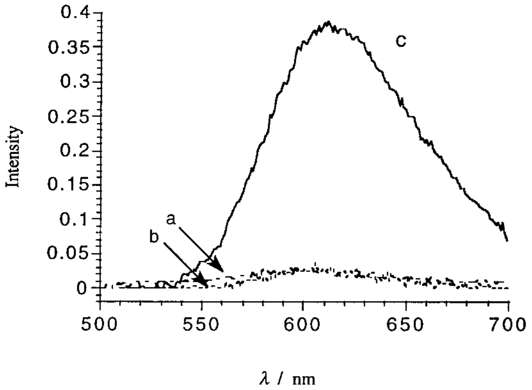

Figure 2. Fluorescence spectra of (0.3 mM) solutions in degassed [nBu$_4$N]PF$_6$/acetonitrile: a) **1**; b) **2**; c) **3**.

The excited-state lifetime of the trimetallic complex **1** and the bimetallic complex **2** were measured by single photon counting. Excitation of the complexes was conducted at 570 nm and emission was measured at 620 nm. Figure 3, curve a, shows the transient decay of the bimetallic complex **2**. The observed decays fit a biexponential curve with lifetimes (Table 1): $\tau_1(\mathbf{2}) = 9(\pm 1)$ ns, $\tau_2(\mathbf{2}) = 250(\pm 10)$ ns, with the spectral weightings of $\xi_1(\mathbf{2}) = 0.96$ and $\xi_2(\mathbf{2}) = 0.04$, respectively.

The transient decay of the trimetallic complex **1** is shown in Figure 4. This decay is also fit by a biexponential curve with similar lifetimes (Table 1): $\tau_1(\mathbf{1}) = 9(\pm 1)$ ns, $\tau_2(\mathbf{1}) = 247(\pm 10)$ ns with the spectral weightings of $\xi_1(\mathbf{1}) = 0.90$ and $\xi_2(\mathbf{1}) = 0.10$, respectively. The short component in each complex is assigned to the direct quenching of the excited

Table 1. Measured lifetimes of **1** and **2** under electroreduction conditions.[a]

	Bimetallic complex **2**				Trimetallic complex **1**					
reduction time [min]	τ_1 [ns]	ξ_1	τ_2 [ns]	ξ_2	τ_1 [ns]	ξ_1	τ_2 [ns]	ξ_2	τ_3 [ns]	ξ_3
0	9(±1)	0.96(±0.05)	250(±10)	0.04(±0.002)	9(±1)	0.90(±0.05)	247(±10)	0.10(±0.01)	-	
30	8.1(±1)	0.74±0.03)	340(±10)	0.26(±0.02)						
90	8.6(±0.9)	0.42(±0.02)	440(±20)	0.58(±0.03))						
150	8.3(±0.9)	0.35(±0.02)	490(±20)	0.65(±0.03))	7.7(±0.9)	0.50(±0.02)	28(±2) ns	0.20(±0.01)	487(±20)	0.3(±0.02)
0[b]	9.1(±1)	0.90(±0.05)	251(±10)	0.10(±0.01)	9.7(±1)	0.79(±0.04)	256(±10)	0.21(±0.01)		

[a] r^2 values for the fitting were from 95–99.2%. [b] Measured after the reduced samples were exposed to air for 24 h .

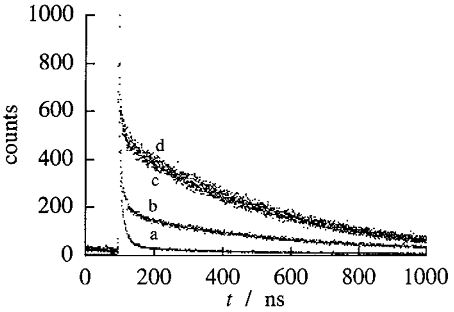

Figure 3. Transient emission of **2** (0.2mM) in degassed 0.1M [nBu$_4$N]PF$_6$/acetonitrile, after electroreduction (−500 mV) for: a) 0 min, b) 30 min, c) 90 min, and d) 150 min.

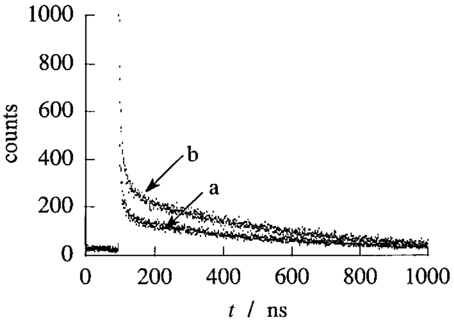

Figure 4. Transient emission of **1** (0.2mM) in degassed 0.1M [nBu$_4$N]PF$_6$/acetonitrile, after electroreduction (−500 mV) for: a) 0 min and b) 150 min.

Os^{II} center by the Ni^{II} site. The long-lived component (250 ns) is assigned to the natural decay of the Os^{II} site, since the lifetime of the complex **3** is also 250(±10) ns. The long lifetime decays contribute 4% to the observed decay in **2** and 10% in **1**, indicating that the fraction of unquenched Os^{II} complex **3** or the presence of impurity in the final products (because its production by concomitant photodecomposition) is low. Nevertheless, these results show that there is no separate contribution to the quenching process from the Pd^{II} site. That observation is in accord with the original expectations following from thermodynamics; namely, that the excited Os^{II} is quenched by the Ni^{II} site only, and not by interaction with the Pd^{II} site, as a consequence of geometric alignment of the redox-graded metals in the trimetallic complex.

Excited-state interactions in the reduced state: Electroreduction of the complexes was achieved by applying a potential of −500 mV in a standard electrochemical cell with a Pt wire as working electrode, Ag/AgCl as reference electrode, and a Pt wire as counterelectrode separated from the substrate solution by a glass frit. The electroreduction was conducted under a flow of nitrogen saturated with the solvent (CH_3CN). With the reduced complexes, the flash excitation experiments described above were repeated.

Figure 3, curves b, c, and d, show the result of electroreduction of Ni^{II} on the emission lifetime of the bimetallic complex **2**. The short-lived component lifetime (9 ns) is not changed, within experimental error, but its contribution to the biexponential curve is decreased from 96% to 35% after 150 min of electroreduction (Table 1). The long-lived component of the biexponential curve is extended to 490 ns after the electroreduction and its contribution to the excited state decay increases from 4% to 65% (Table 1). Thus, the bulk reduction of Ni^{II} to Ni^0 in **2** avoids the oxidative quenching of the excited Os^{II} center by the Ni^{II} site.

The remaining fraction (35%) of the excited Os^{II} sites that are quenched by the Ni^{II} site can be completely rationalized as a function of incomplete reduction deriving from the limited efficiency of the bulk electroreduction. The longer emission lifetime observed after electroreduction results from the new electronic environment of the excited Os^{II} center. The reduced form of the complex, Os^{II}–Ni^0, contains very high electron density which is reflected in the rigidification of the complex. As a result, the emission lifetime is increased from 250 ns to 490 ns.

Electroreduction of the trimetallic complex **1** produces a similar influence on the emission lifetime. Figure 4, curve b, shows the transient emission observed after electroreduction of the Ni^{II} to Ni^0 for 150 min. This curve fits to a triexponential decay with three independent lifetimes (Table 1), assigned respectively to the oxidative quenching of the excited Os^{II} by the remaining unreduced Ni^{II} sites ($\tau_1 = 7.7 \pm 0.9$ ns), to the newly enabled oxidative quenching of the excited Os^{II} by the Pd^{II} sites ($\tau_2 = 28 \pm 2$ ns), and to the natural decay of the excited Os^{II} complex in its new electronic environment ($\tau_3 = 487 \pm 20$ ns).

After the reduced samples of **1** and **2** had been exposed to air for 24 h and the the emission lifetimes had been remeasured, lifetimes virtually identical to those observed for the oxidized form of the complex (prior to the electroreduction) were measured (Table 1). A small difference in the contribution of the two components to the overall biexponential decay, however, suggests that the electroreduction/oxidation proceeds with partial decomposition of the complexes.

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Transient absorption spectra: The transient absorption spectra of **3** and **1** in its oxidized and reduced form are shown in Figure 5. The absorption spectrum of **3** (Figure 5, curve a) is characterized by a broad absorption from 500 nm to 620 nm.

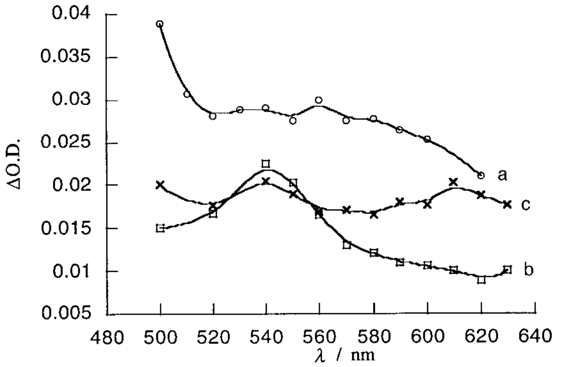

Figure 5. Transient absorption spectra of (0.2 mM) solutions in degassed $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{PF}_6$/acetonitrile: (○) **3**, (□) **1**, (×) **1** after electroreduction (−500 mV, 90 min).

Although a quantitative analysis of the kinetic data was difficult because of the small number of repetition pulses at each wavelength, lifetime of the excited state was estimated as 200–250 ns. This result is compatible with the emission lifetime shown to be 250 ns.

Figure 5, curve b, is the transient absorption spectrum of the trimetallic complex **1**. The spectrum is characterized by an absorption maximum at $\lambda = 540$ nm assigned to the intervalence absorption of the formed $\mathrm{Os^{III}}$-$\mathrm{Ni^{I}}$ -$\mathrm{Pd^{II}}$.[26] This result supports our conclusion from the time-resolved emission studies that in the trimetallic complex only the $\mathrm{Ni^{II}}$ site quenches the $\mathrm{Os^{II}}$ excited state, and the $\mathrm{Pd^{II}}$ has no part in the quenching. After electroreduction of the $\mathrm{Ni^{II}}$ site in the trimetallic complex **1**, the absorption spectrum changes (Figure 5, curve c), and two absorption maxima are observed at $\lambda = 540$ nm and $\lambda = 610$ nm. These absorption are assigned to the intervalence absorption of the formed $\mathrm{Os^{III}}$ -$\mathrm{Ni^{I}}$-$\mathrm{Pd^{II}}$ and $\mathrm{Os^{III}}$-$\mathrm{Ni^{0}}$-$\mathrm{Pd^{I}}$.[26] These results are supported by the time-resolved studies that show emission from $\mathrm{Os^{III}}$-$\mathrm{Ni^{I}}$-$\mathrm{Pd^{II}}$ as a result of the oxidative quenching of excited $\mathrm{Os^{II}}$ by the $\mathrm{Ni^{II}}$ in the nonreduced form of the complex that still exists in the solution, and from $\mathrm{Os^{III}}$ -$\mathrm{Ni^{0}}$ -$\mathrm{Pd^{I}}$ as a result of the oxidative quenching of the excited $\mathrm{Os^{II}}$ by the $\mathrm{Pd^{II}}$ in the reduced form of the complex.

In summary, a functional electro-switchable-photoinduced-electron-transfer (ESPET) device has been demonstrated for the trimetallic complex **1** and the bimetallic complex **2**. Electroreduction of a bulk solution of the complex permits a new oxidative quenching route not available prior to electroreduction. Upon partial electroreduction, the bimetallic complex showed a smaller fraction of oxidative quenching by $\mathrm{Ni^{II}}$ (from 96 % to 35 %) and an extended lifetime of the excited $\mathrm{Os^{II}}$ emission (from 250 ns to 490 ns). In the trimetallic complex, partial electroreduction of the $\mathrm{Ni^{II}}$ site enables direct oxidative quenching by the $\mathrm{Pd^{II}}$ site (with a lifetime of 28(±2) ns, $\xi = 0.2$). The direct oxidation by $\mathrm{Ni^{II}}$ was significantly reduced (from 90 % to 50 %) and the lifetime of the excited $\mathrm{Os^{II}}$ site was extended, as for the bimetallic complex under similar conditions, from 250 ns to 490 ns.

Experimental Section

Materials: Tetra(bisphenylphosphino)benzene (tppb)[27] and $(\mathrm{bpy})_2\mathrm{Os^{II}}$-tppb$(\mathrm{PF}_6)_2$ (**3**)[23, 24, 28] were prepared according to literature procedures.

Preparation of $\mathbf{Os^{II}}$-tppb-$\mathbf{Ni^{II}}$ (2):[25, 29] $(\mathrm{bpy})_2\mathrm{Os^{II}}$-tppb$(\mathrm{PF}_6)_2$ (**3**) (60.0 mg, 0.045 mmol) in $\mathrm{CH_2Cl_2}$ (4 mL) was added dropwise to a solution of $[\mathrm{Ni(H_2O)_6}]\mathrm{Cl_2}$ (12 mg, 0.05 mmol) in ethanol (2 mL). The solution was heated to reflux for 30 min under Ar. $\mathrm{CH_2Cl_2}$/methanol (9:1, 40 mL) was added and the resulting clear solution was poured into hexane (100 mL). An orange precipitate (35 mg, 44 % yield) was collected on a glass frit. ^{31}P NMR: $\delta = 55.5$ (s, 1P, Ni-coordinated phosphane); 28.7 (s, 1P, Os-coordinated phosphane); mass spectrum (CI+) for $\mathrm{C_{74}H_{58}N_4P_4Cl_2Os_1Ni_1}$: 1446; calcd 1445.8; elemental analysis for $\mathrm{C_{74}H_{58}N_4P_6F_{12}Cl_2Os_1Ni_1}$: calcd: C 51.09, H 3.33, N 3.33; found: C 45.15, H 3.89, N 3.25. Note that the complexes are quite hygroscopic, so that the CI$^+$ mass spectrum, together with clean NMR spectra, are better indications of purity than the elemental analysis.

Preparation of dppb-$\mathbf{Pd^{II}}$-tppb (4):[25] 1,2-Bis(diphenylphosphino)benzene (Strem Chemical, 100.0 mg, 0.225 mmol) in $\mathrm{CH_2Cl_2}$ (100 mL) was added dropwise to tetrakis(acetonitrile)palladium(II) tetrafluoroborate (Strem Chemical, 100.0 mg, 0.225 mmol) in acetonitrile (10 mL). The solution was stirred under Ar at room temperature for 1 h. The resulting yellow solution was transferred by syringe to an addition funnel under Ar, and then added dropwise to a solution of tppb (200.0 mg, 0.25 mmol) in $\mathrm{CHCl_3/CH_2Cl_2}$ (1:1 20 mL), to afford a green solution. The solvent was removed under reduced pressure and the resulting powder was reprecipitated from $\mathrm{CH_2Cl_2}$/ether (104 mg, 30 % yield). ^{31}P NMR: $\delta = 54.2$ (s, 2P, Pd-coordinated phosphane), −13.3 (s, 1P, free phosphane), mass spectrum (CI+) for $\mathrm{C_{84}H_{66}P_6Pd_1}$:1367; calcd: 1366.4; elemental analysis for $\mathrm{C_{84}H_{66}P_6B_2F_8Pd_1}$: calcd: C 65.45, H 4.28, P 12.07, Pd 6.90; found: C 64.81, H 4.56, P 12.16, Pd 6.24. Note that as with **2**, complex **4** is quite hygroscopic.

Preparation of $\mathbf{Os^{II}}$-tppb-$\mathbf{Ni^{II}}$-tppb-$\mathbf{Pd^{II}}$-dppb (1): A solution of $(\mathrm{bpy})_2\mathrm{Os^{II}}$-tppb-$\mathrm{Ni^{II}Cl_2}$ (**2**), (30 mg, 0.015 mmol) in $\mathrm{CH_2Cl_2/CH_3OH}$ (1:1 30 mL) was mixed with a solution of dppb-$\mathrm{Pd^{II}}$-tppb (**4**) (23 mg, 0.015 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). The resulting solution was stirred for 4 h under Ar at room temperature, during which the solution turned red. The solvent was removed under reduced pressure and the product was reprecipitated from $\mathrm{CH_2Cl_2}$/ether. Orange powder (23 mg, 40 % yield) was collected on a glass frit. ^{31}P NMR: $\delta = 54.8$ (s, 2P, Ni-coordinated phosphane), 48.7 (s, 2P, Pd-coordinated phosphane), 28.8 (s, 1P, Os-coordinated phosphane); mass spectrum (FAB in triethylamine) for $\mathrm{C_{158}H_{124}N_4P_{10}Os_1Ni_1Pd_1}$: 2742; calcd. 2741.3; elemental analysis for $\mathrm{C_{158}H_{124}N_4P_{14}F_{32}B_2Os_1Ni_1Pd_1}$: calcd: C 54.2, H 3.55, N 1.60; found: C 52.0, H 4.01, N 1.10. Note that as with **2**, complex **1** is highly hygroscopic.

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