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ARTICLE TYPE

Photoelectric Conversion at a $[Ru(bpy)_3]^{2+}$- Based Metallic Triad Anchored on ITO Surface.

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A tri-metallic triad based on a $[Ru(bpy)_3]^{2+}$ moiety connected to Fe(II) and Co(III) bisterpyridine has been grafted on an ITO electrode by a stepwise procedure. Under visible light, in the presence of a sacrificial electron donor, the system produces electric current. The photo-current magnitude is compared to the one generated from a Co(III)-Ru(II) dyad and shows an increase of 40%.

There is a significant challenge in mimicking Nature's extraordinary ability to efficiently transport charges across long distances under solar light. Since the first example of an efficient synthetic system and its incorporation into a lipidic membrane,[1] intense research has been carried out to design molecular triads (D-P-A) displaying this property by covalently attaching an electron donor (D) and acceptor (A) to a photosensitizer (P). Among the different examples of triads, those containing Ru(II) polypyridinic complexes have been frequently studied and proved their efficiency in solution.[2] For instance in a Mn_2^{II} / $[Ru(bpy)_3]^{2+}$ / naphtalenediimide triad (bpy = 2,2' bipyridine) under irradiation, an average charge separation state lifetime of 600 µs was obtained at room temperature.[3] Another example built around a rod-like $[Ru(dqp)_2]^{2+}$ (dqp = 2,6 di(quinoline-8yl)pyridine) covalently linked to benzoquinone and phenothiazine shows a charge separation state yield ≥ 95%.[4] To utilize charge flow under irradiation in molecular devices some photoactive D-P-A have been grafted onto a conducting surface [5-7] and P-A dyad connected between two electrodes.[8] Surprisingly, none of these works are based on a $[Ru(bpy)_3]^{2+}$ photosensitizer. Moreover, in these systems the donor, the acceptor or both entities are preferentially organic fragments although transition metal complexes can offer oxidized or reduced systems with better stability and with multiple redox or spin states suitable for applications in molecular electronic devices or catalysis. This work describes the easy construction of the first molecular triad built with a $[Ru(bpy)_3]^{2+}$ photosensitive unit on an ITO surface, A and D being two different metallic complexes. To obtain a well-organized triad, we followed a stepwise approach based on terpyridine coordination assembly. This layer-by-layer methodology makes possible the formation of heteroleptic complexes of labile systems such as first row transition metal complexes.[9-13] Our strategy to construct a linear triad on a surface and overcome the formation of statistical isomers of $[Ru(bpy)_3]^{2+}$, has been to anchor two terpyridine sites on the same, symmetrically-substituted bipyridine (Figure 1).

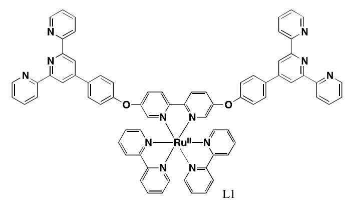
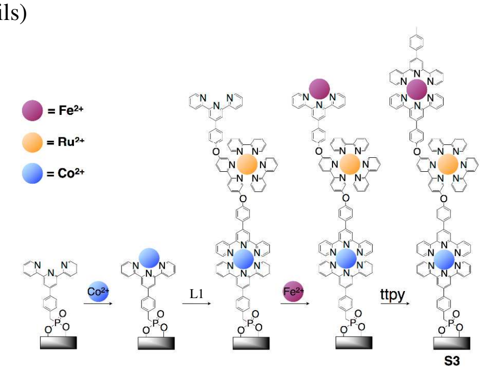


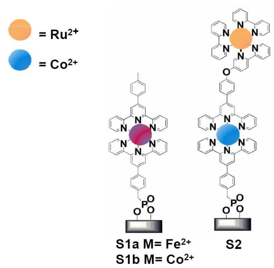
Figure 1. Structure of the photoactive ditopic metallo-ligand L1.

This ditopic metallo-ligand (see SI for synthetic procedure and characterization) is the photo-active spacer between the donor and the acceptor moieties. We chose to link the two coordination sites by an ether bond for ease of synthesis, to ensure a weak electronic coupling and to obtain a relative rigidity. Substitution on the 5,5' position of the 2,2'-bipyridine increases the distance between the donor and the acceptor site [14] in comparison to the more common 4,4' modification that we previously proposed.[15] On the other hand, this substitution conserves well the photophysical properties of the $[Ru(bpy)_3]^{2+}$ subunit.[16] (see SI for details)



Scheme 1. Stepwise assembly of the trimetallic triad on ITO (S3). For clarity, charges have been omitted. (ttpy = 4'-*p*tolyl-2,2':6',2"-terpyridine)

The assembly of the triad on the electrode has been carried out stepwise (Scheme 1), taking advantage of the strong self-assembling interaction between phosphonates with ITO and between terpyridine ligands with first row transition metals. In a first step, the surface is grafted with a phosphonate-substituted terpyridine. This modified surface is then dipped in an ethanolic solution of $Co(BF_4)_2$ at room temperature. After thorough rinsing, the surface is again dipped in a solution containing the photosensitizing moiety (**L1**) that self-assembles on the pending metallic center, building the acceptor-photosensitizer part of the triad (see further in the text). The free terpyridine exposed to the outer solution can then be involved in a coordination process with a metallic center, namely Fe^{2+}. After rinsing, the system is capped with a final 4'-*p*tolyl-2,2':6',2"-terpyridine producing a bis-terpyridine complex acting as the electron donor unit (see SI for construction details). For comparison purposes, we also prepared mono and dinuclear system grafted on ITO (Scheme 2). The construction of the dyad (**S2**) was carried out using a mono-functionalized analog of complex **L1** denoted **L2** (see SI for synthetic procedure and characterization).



Scheme 2. Structure of the mono and dinuclear systems. Charges have been omitted for clarity.

All systems were characterized by cyclic voltammetry in acetonitrile + 0.1 M tetrabutylammonium perchlorate (TBAP). The oxidation potentials are collected in Table 1. The ether linkage between units allows each complex to behave independently. For all systems the potential of the redox process assigned to a given metallic center remains unchanged throughout the series. For **S3** (Figure 2), the first reversible peak, around - 0.1 V, is characteristic of the Co^{III}/Co^{II} couple. Then, at higher potentials, a reversible monoelectronic peak at 0.75 V assesses the presence of the $[Fe(tpy)_2]^{2+}$ fragment while the oxidation of Ru^{II} into Ru^{III} is observed slightly below 1 V. The linear relationship between the intensity of the peaks and the scan rate clearly indicates that the processes observed occur on a grafted surface (Figure 2). The same cyclic voltammogram was obtained after a period of two weeks, showing the stability of the assembly.

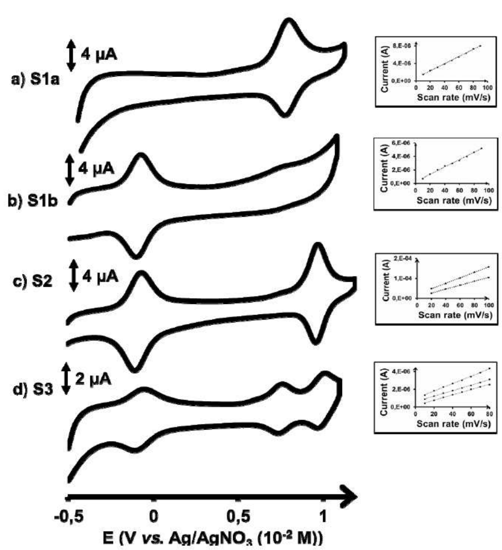


Figure 2. Cyclic voltammogram of the modified electrodes in a CH_3CN+0.1M TBAP scan rate = 20 mV/s. Right: plot of current intensity under oxidation peak *vs*. scan rate.

Table 1. Oxidation potentials $E_{1/2}$ (ΔEp mV) of **S1**, **S2** and **S3** in V *vs*. $Ag/AgNO_3$ 10^{-2} M, scan rate: 20 mV/s in CH_3CN + 0.1 M TBAP.

	$E_{CoIII/II}$, V	$E_{FeIII/II}$, V	$E_{RuIII/II}$, V
S1a		0.75 (20)	
S1b	-0.08 (55)		
S2	- 0.08 (40)		0.97 (10)
S3	- 0.09 (40)	0.75 (30)	0.98 (44)

For **S3** the surface coverage value Γ [17] obtained by integration under the cobalt oxidation peak (1.1 10^{-11} mol.cm^{-2}) is almost similar to the value obtained under the iron peak (0.8 10^{-11} mol.cm^{-2}). It shows that the stepwise construction is efficient, leading mainly to a trimetallic triad with a limited amount of the simple Ru^{II}/Co^{II} dyad immobilized on surface. For **S2** and **S1a,b** the surface coverage values are higher (between 4 and 3 10^{-11} mol.cm^{-2}). The difference is attributed to the larger structure of ligand **L1** which does not allow the full coverage of the pending cobalt-terpyridine initially modified surface.

Upon visible light irradiation, the modified electrodes **S2** and **S3** to which we apply a bias (0.12 V) are able to generate current in the presence of triethanolamine (TEOA) (1 M in CH_3CN) as sacrificial electron donor. The value of the bias has been selected to keep the cobalt ion in its oxidation state III, thus making it a good electron acceptor towards the excited state of $[Ru(bpy)_3]^{2+}$.[18] Figure 3 shows the typical response as the excitation light is turned on and off.

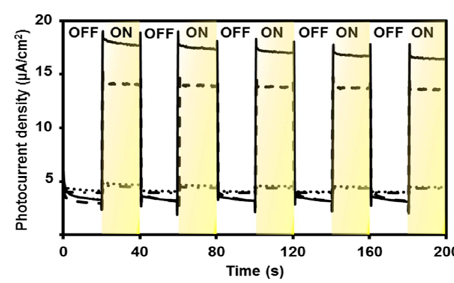
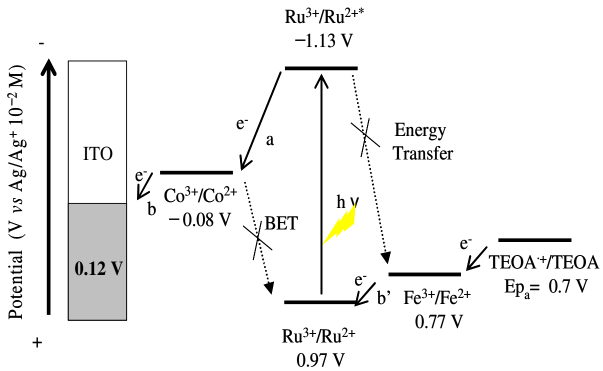


Figure 3. Photocurrent density of **S3** (full line), **S2** (dashed line) and **S1a,b** (dotted line) *vs* time. Irradiation periods are highlighted in yellow.

For **S3** an anodic photocurrent magnitude of 14 µA.cm^{-2} is quickly reached. The irradiation process was repeated over 2 h providing reproducible photocurrent response proving the mechanical and photophysical stability of the film (See SI). It should be noted that the photolysis in the absence of TEOA or the irradiation of **S1a,b** in presence of TEOA causes only negligible photocurrent. The photocurrent originating from irradiation of **S3** is 40% higher than **S2** (10 µA.cm^{-2}). Despite the energy transfer (En.T.) process between Ru(II)* and Fe(II) subunits which reduce the excited state lifetime of Ru(II)*,[19] **S3** is still able to generate a large amount of current. In **S3**, the En. T is short-circuited by an electron transfer process from Ru(II)* to the Co(III) subunit. Moreover, the Fe(II) subunit reacts efficiently with the photogenerated Ru(III) species to compete with the back electron transfer (BET) reaction between Co(II) and Ru(III) species. The incident photon-to-electron conversion efficiency (IPCE) [20] at 455 nm is estimated to 0.031% for **S3** and 0.013% for **S2**.



Scheme 3. Proposed mechanism of the electron transfer across the triad **S3**.

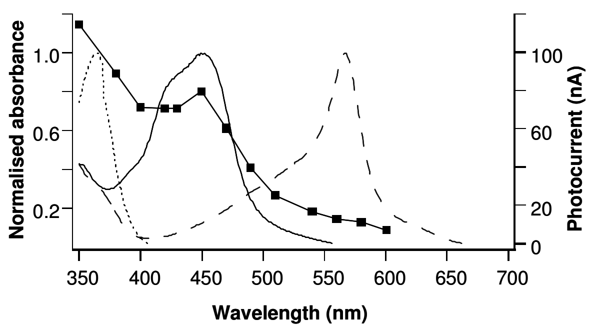


Figure 4. Photoaction spectrum (•) of **S3** along with the UV/vis spectra of triad's building block: $[Ru(bpy)_3]^{2+}$ (full line), $[Fe(ttpy)_2]^{2+}$ (dashed line) and $[Co(ttpy)_2]^{3+}$ (dotted line).

The mechanism we propose for electron transfer process at the triad is depicted in Scheme 3. As illustrated in Figure 4, the photocurrent results only from absorption of light by the $[Ru(bpy)_3]^{2+}$ subunit of the assembly. The mechanism is based on the assumption that intramolecular electron transfer as well as electron injection to the electrode are faster than intermolecular electron transfer. After absorption of light, En. T between Ru(II)* and Fe(II) is efficiently short-circuited by an electron transfer process toward the Co(III) subunit as proven by the resulting photocurrent generation (step a). Further experiments would be necessary to elucidate the sequential pathway of electron transfer between step b and b' (Scheme 3). However, the photocurrent intensity of **S3** is higher than **S2** which allows us to presume that the electron transfer between Ru(III) and Fe(II) reduces the efficiency of the electron recombination between Ru(III) and Co(II).

In conclusion, we designed a bis-terpyridine ditopic ligand bearing a $[Ru(bpy)_3]^{2+}$ moiety and used it in a stepwise construction with Co(III) and Fe(II) centers. In such a triad the energy transfer between Ru(II)* and Fe(II) is advantageously short-circuited by an electron transfer process resulting in an efficient photon to electron conversion. To our knowledge, this is the first example of the use of $[Ru(bpy)_3]^{2+}$ in a grafted photoinduced charge-separation system. The stepwise construction proved to be an efficient way to assemble a tri-metallic D-P-A triad on ITO. This strategy can easily be transposed to other metallic centers notably those exhibiting redox catalytic properties to photoinduce chemical reactions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental part, Synthesis, Grafting procedures, Photophysics, Cyclic voltammogram of **L1**, **L2**, and **S3**. See DOI: 10.1039/b000000x/

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16 Luminescence quantum yield (ϕ) and lifetime (τ) of **L1** was estimated to ϕ=0.037 and τ=265 ns in deoxygenated CH_3CN.

17 Γ = Q/nFA, where Q is the charge required to oxidize the metallic center determined from the area under the oxidation peak of $M^{2+/3+}$, n the number of electrons transferred (n = 1), F the Faraday's constant and A the area of the electrode.

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20 IPCE=1240 × j/(W_{in} × λ_{ex}.), where j is the photocurrent density ($A.cm^{-2}$), W_{in} the incident intensity ($W.cm^{-2}$) and λ_{ex}. the excitation wavelength (nm).

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