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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(III) 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 $Mn_2^{II}/[Ru(bpy)_3]^{2+}/naphthalenediimide triad (bpy = 2,2')$ 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 \geq 95%.⁴ To utilize charge flow under irradiation in molecular devices some photoactive D-P-A have been grafted onto a conducting surface5-7 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



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

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 wellorganized 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 (Fig. 1).

This ditopic metallo-ligand (see ESI† 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 site¹⁴ 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 ESI† for details).

The assembly of the triad on the electrode has been carried out stepwise (Scheme 1), taking advantage of the strong selfassembling interaction between phosphonates with ITO and

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Fig. 2 Cyclic voltammogram of the modified electrodes in a CH₃CN + 0.1 M TBAP scan rate = 20 mV s^{-1} . Right: plot of current intensity under oxidation peak vs. scan rate.

dently. For all systems the potential of the redox process assigned to a given metallic center remains unchanged throughout the series. For S3 (Fig. 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 (Fig. 2). The same cyclic voltammogram was obtained after a period of two weeks, showing the stability of the assembly.

For S3 the surface coverage value Γ^{17} obtained by integration under the cobalt oxidation peak $(1.1 \times 10^{-11} \text{ mol cm}^{-2})$ is almost similar to the value obtained under the iron peak $(0.8 \times 10^{-11} \text{ mol cm}^{-2})$. 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.



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

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 acceptorphotosensitizer 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 Fe²⁺. After rinsing, the system is capped with a final 4'-ptolyl-2,2':6',2"-terpyridine producing a bis-terpyridine complex acting as the electron donor unit (see ESI[†] 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 monofunctionalized analog of complex L1 denoted L2 (see ESI[†] for synthetic procedure and characterization).

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 indepen-



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



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

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 CH₃CN) 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 $[Ru(bpy)_3]^{2+.18}$ Fig. 3 shows the typical response as the excitation light is turned on and off.

For S3 an anodic photocurrent magnitude of 14 μ A 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 ESI⁺). 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 μ A cm⁻²). Despite the energy transfer (En.T.) process between $Ru(n)^*$ and Fe(n)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 $Ru(\pi)^*$ to the Co(π) subunit. Moreover, the Fe(π) subunit reacts efficiently with the photogenerated Ru(III) species to compete with the back electron transfer (BET) reaction between $Co(\pi)$ and Ru(m) 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.

The mechanism we propose for electron transfer process at the triad is depicted in Scheme 3. As illustrated in Fig. 4,



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



Fig. 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 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 $Ru(\pi)^*$ and $Fe(\pi)$ is efficiently short-circuited by an electron transfer process toward the $Co(\pi)$ 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 $Ru(\pi)$ and $Fe(\pi)$ reduces the efficiency of the electron recombination between $Ru(\pi)$ and $Co(\pi)$.

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(m) and Fe(n) centers. In such a triad the energy transfer between Ru(n)* and Fe(n) 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 trimetallic 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

 (a) T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. F. Lehman, G. Nemeth and A. L. Moore, *Nature*, 1984, **307**, 630; (b) P. Seta, E. Bienvenue, A. L. Moore, P. Mathis, R. V. Bensasson, P. A. Liddell, P. Pessiki, A. Joy, T. A. Moore and D. Gust, *Nature*, 1985, **316**, 653.

- 2 For some recent reviews see: (a) H. Dürr and S. Bossmann, Acc. Chem. Res., 2001, 34, 905; (b) E. Baranoff, J.-P. Collin, L. Flamigni and J.-P. Sauvage, Chem. Soc. Rev., 2004, 33, 147; (c) S. Campagna, F. Puntoriero, F. Natasi, G. Bergamini and V. Balzani, Top. Curr. Chem., 2007, 280, 117; (d) O. S. Wenger, Coord. Chem. Rev., 2009, 253, 1439; (e) L. Hammarström and O. Johansson, Coord. Chem. Rev., 2010, 254, 2546.
- M. Borgstrom, N. Shaikh, O. Johansson, M. Anderlund,
 S. Styring, B. Akermark, A. Magnuson and
 L. Hammarstrom, *J. Am. Chem. Soc.*, 2005, **127**, 17504.
- 4 R. J. Kumar, S. Karlsson, D. Streich, A. Rolandini Jensen, M. Jäger, H.-C. Becker, J. Bergquist, O. Johansson and L. Hammarström, *Chem. – Eur. J.*, 2010, 16, 2830.
- 5 (a) H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki and Y. Sakata, J. Phys. Chem. B, 2000, 104, 2099; (b) H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata and S. Fukuzumi, J. Am. Chem. Soc., 2001, 123, 100; (c) H. Imahori, M. Kimura, K. Hosomizu, T. Sato, T. K. Ahn, S. K. Kim, D. Kim, Y. Nishimura, I. Yamazaki, Y. Araki and S. Fukuzumi, Chem. – Eur. J., 2004, 10, 5111.
- 6 (a) S. Saha, L. E. Johansson, A. H. Flood, H.-R. Tseng,
 J. I. Zink and J. F. Stoddart, *Small*, 2005, 1, 87-90;
 (b) S. Saha, L. E. Johansson, A. H. Flood, H.-R. Tseng,
 J. I. Zink and J. F. Stoddart, *Chem. Eur. J.*, 2005, 11, 6846.
- 7 S. Suzuki, Y. Matsumoto, M. Tsubamoto, R. Sugimura,
 M. Kozaki, K. Kimoto, M. Iwamura, K. Nozaki, N. Senju,
 C. Uragami, H. Hashimoto, Y. Muramatsu, A. Konno and
 K. Okada, *Phys. Chem. Chem. Phys.*, 2013, 15, 8088.
- 8 S. Battacharyya, A. Kibel, G. Kodis, P. A. Liddell, M. Gervaldo, D. Gust and S. Lindsay, *Nano Lett.*, 2011, 11, 2709.

- 9 Y. Liang and R. H. Schmehl, *J. Chem. Soc., Chem. Commun.*, 1995, 1007.
- 10 M. Maskus and H. D. Abruna, *Langmuir*, 1996, **12**, 4455.
- (a) H. Nishihara, K. Kanaizuka, Y. Nishimori and Y. Yamanoi, *Coord. Chem. Rev.*, 2007, 251, 2674;
 (b) Y. Nishimori, H. Maeda, S. Katagiri, J. Sendo, M. Miyachi, R. Sakamoto, Y. Yamanoi and H. Nishihara, *Macromol. Symp.*, 2012, 317, 276;
 (c) H. Maeda, R. Sakamoto and H. Nishihara, *Polymer*, 2013, 54, 4383.
- 12 M. Haga, K. Kobayashi and K. Terada, *Coord. Chem. Rev.*, 2007, **251**, 2688.
- 13 A. Winter, S. Hoeppener, G. R. Newkome and U. S. Schubert, *Adv. Mater.*, 2011, 23, 3484.
- 14 (a) J. Hankache, M. Niemi, H. Lemmetyinen and O. S. Wenger, *J. Phys. Chem. A*, 2012, **116**, 8159;
 (b) J. Hankache, M. Niemi, H. Lemmetyinen and O. S. Wenger, *Inorg. Chem.*, 2012, **51**, 6333.
- 15 B. Galland, D. Limousin, H. Laguitton-Pasquier and A. Deronzier, *Inorg. Chem. Commun.*, 2002, 5, 5.
- 16 Luminescence quantum yield (ϕ) and lifetime (τ) of L1 was estimated to ϕ = 0.037 and τ = 265 ns in deoxygenated CH₃CN.
- 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.
- 18 J. Lombard, R. Boulaouche, D. Amilan Jose, J. Chauvin, M.-N. Collomb and A. Deronzier, *Inorg. Chim. Acta*, 2010, 234.
- 19 J. Lombard, J.-C. Lepretre, J. Chauvin, M.-N. Collomb and A. Deronzier, *Dalton Trans.*, 2008, 658.
- 20 IPCE = $1240 \times j/(W_{\rm in} \times \lambda_{\rm ex.})$, where *j* is the photocurrent density (A cm⁻²), $W_{\rm in}$ the incident intensity (W cm⁻²) and $\lambda_{\rm ex.}$ the excitation wavelength (nm).