Supplementary Material for

A heptanuclear light-harvesting metal-based antenna dendrimer with six Ru(II)-based chromophores directly powering a single Os(II)based energy trap

<u>E</u>manuele La Mazza, Fausto Puntoriero, Francesco Nastasi, Baptiste Laramée-Milette, Garry S. Hanan and Sebastiano Campagna.

Index

Materials and Methods	2
Synthesis	3
NMR characterization (including Figure S1 and S2)	3
TOF-SIMS spectrum (Figure S3)	6
Supplementary redox data (includes Figure S4)	7
Excitation spectrum of 1 (includes Fig. S5)	6
Energy transfer in 1. Additional information	8
Complete kinetics of transient absorption spectra, with Figure S6	9
References to Supplementary Information	10

Materials and methods

UV/Vis absorption spectra were taken on a Jasco V-560 spectrophotometer. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax 2 spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier. The spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. For the luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used. As excitation sources, a Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and/or the nitrogen discharge (pulse width 2 ns at 337 nm) were employed. Emission quantum yields for deaerated solutions were determined using the optically diluted method.^{S1}As luminescence quantum yield standards, we used [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine).^{S2}

Time-resolved transient absorption experiments were performed using a pump-probe setup based on the Spectra-Physics MAI-TAI Ti:sapphire system as the laser source and the Ultrafast Systems Helios spectrometer as the detector. The output of laser beam was split to generate pump and probe beam pulses with a beam splitter (85 and 15%). The pump pulse (400 nm, 1-2 μ J) was generated with a Spectra-Physics 800 FP OPA and was focused onto the sample cuvette. The probe beam was delayed with a computer controlled motion controller and then focused into a 2-mm sapphire plate to generate a white light continuum (spectral range 450–800 nm). The white light is then overlapped with the pump beam in a 2-mm quartz cuvette containing the sample. The effective time resolution was ca. 200 fs, and the temporal chirp over the white-light 450–750 nm range ca. 150 fs; the temporal window of the optical delay stage was 0–3200 ps. Please note that all the transient spectra shown in the present paper are chirp corrected. The chirp correction was done by using the pump-induced absorption signals themselves in the same conditions (same cuvette, solvent, temperature, stirring frequency...) used for each single experiment. The time-resolved data were analyzed with the Ultrafast Systems Surface Explorer Pro software.

Electrochemical measurements were carried out in the dry and argon-purged stated acetonitrile, at r.t. with a Autolab multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm², Amel) electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using the redox couple ferrocene/ferrocinium as internal reference (395 mV vs. SCE in acetonitrile). The concentration in analyte was about 0.5 mM, unless otherwise stated. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates between 50 and 500 mV/s and were stated in each case. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of

the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons reported in the main text was established using the areas of the peaks in differential pulse voltammetry (DPV).

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 15%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; luminescence quantum yields, 20%; transient absorption decay and rise rates, 10%; redox potentials, 20 mV.

Synthesis

[{Ru(bpy)₂]₂(µ-L)](PF₆)₄. The dinuclear Ru(II) precursor was prepared as previously reported.^{S3}

[Os{(\mu-L)[Ru(bpy)₂]₂}](PF₆)₁₄ (1). A 50 mL round-bottomed flask was charged with 9.29 mg (0.00476 mmol) of {[Ru(bpy)₂]₂(μ -L)}(PF₆)₄, 0.77 mg (0.00159 mmol) of K₂OsCl₆ and 1.5 mL of ethylen glycole. The reaction mixture was left stirring under reflux for 48 h, under a N₂ atmosphere. After this time, at room temperature, 5 mL of a saturated solution of Na₂S₂O₈ were added. The resulting slurry was filtered over a glass frit. The solid was treated with water several times and at the end with Et₂O. The dried solid was dissolved in the minimum amount (few drops) of acetonitrile and treated with an excess of EtOH and NH₄PF₆. The solid recovered by filtration was washed at least 10 times with ethanol. A further purification was made by flash chromatography on Sephadex G15. The pure sample was recovered by precipitation in Et₂O, as a violet solid. (yield 84%). ¹H NMR (CD₃CN, 300 MHz, 298 K): δ (ppm) 9.66 (m, 9H), 8.98 -8.69 (m, 16H), 8.68 (s, 9H), 8.53–8.51 (m, 24H), 8.16–8.04 (m, 34 H), 7.90–7.60 (m, 33H), 7.58–7.27 (m, 34H). TOF-SIMS: [M(PF₆)₁₃]⁺ = 6188.3368 (theoretical = 6188.3334). Elemental analysis Calc. for C₂₁₉H₁₅₉N₅₁OsRu₆P₁₄F₈₄: C, 41.62; H, 2.67; N, 11.25; Elemental analysis Found: C, 41.55; H, 2.53; N, 11.28.

NMR characterization

The analysis of the ¹H NMR of the heptanuclear species indicates that the correct number of proton resonances are found in the aromatic region of the spectrum (see Figure S1). Because of the complexity of the system (the molecule exists in a number of isomers so contributing to broad the signals), detailed assignments of the peaks were not possible. By comparison with the spectrum registered for the precursor species **Ru2L** (see Figure S2, bottom panel), the singlets found above 9.5-9.7 ppm can be assigned to the proton located near the triazine core (labelled as "a" in Figure S2). Two singlets, corresponding to the coordinated and non-coordinated 2,2'-bipyridyl arms, are

found in the case of the **Ru2L** compound. However, as shown in the top panel of Figure S2, only one broad signal is found near 9.6 ppm in the case of the heptanuclear species, since, in that case, the protons of each arms are quite similar each other. Moreover, the signals labelled b and c, presents in the dinuclear species, are not present in the spectrum of the heptanuclear compound, so indicating that all the bpys are coordinated to metal centers. The same behavior have been observed for **Ru2L** and a related trinuclear species (although in a different deuterated solvent) previously published, please see ref S3.



Figure S1. ¹H NMR spectrum of **1** in CD₃CN, range 0-12 ppm (top). In the bottom, the range 7-10 is expanded, and peak integration is shown.



Figure S2. ¹H NMR spectra of 1 (top) and of the precursor $[{Ru(bpy)_2}_2(\mu-L)](PF_6)_4$ (bottom) in CD₃CN.

TOF-SIMS Spectrum



Figure S3. TOF-SIMS spectrum of **1** (range 5700 – 6300).

Supplementary Redox data



Figure S4. Ciclic Voltammogram of 1 in acetonitrile, [1]= 0.5 mM, scan rate: 200 mV/s, supporting electrolyte [TBAPF₆]= 0.1 M.



Excitation spectrum of 1

Figure S5. Absorption (blue line) and excitation (red line, dashed) spectra of **1** in acetonitrile. For the excitation spectrum, emission wavelength is 800 nm.

Energy transfer in 1

The calculated rate constant for Förster energy transfer k_{en}^F, in 1 is based on equation S1.^{S4}

$$k_{en}^{F} = 8.8 \times 10^{-25} \frac{K^{2} \Phi}{n^{4} r_{AB}^{6} \tau} J_{F}$$

In eq. S1, K is an orientation factor which accounts for the directional nature of the dipole-dipole interaction (from statistics considerations, assumed as 0.66), Φ and τ are the luminescence quantum yield and lifetime of the donor, respectively, n is the solvent refractive index, r_{AB} is the distance (in Å) between donor and acceptor, estimated to be 13 Å, from computer modelization. The spectral overlap J_F is given by equation S2.

(S1)

(S2)

$$J_{F} = \frac{\int F(\overline{v})\varepsilon(\overline{v})/\overline{v}^{4}d\overline{v}}{\int F(\overline{v})d\overline{v}}$$

In this equation, F(v) is the luminescence spectrum of the donor (the trinuclear Ru(II) species taken as model, described in the main text)), and $\varepsilon(v)$ is the absorption spectrum of the acceptor (essentially, the spectrum of **1**, since only the Os(II) core absorbs at relevant wavelengths), on an energy scale (cm⁻¹).

By using the experimental data, the calculated rate constant is $1.0 \times 10^{10} \text{ s}^{-1}$. This value is almost one order of magniture smaller than the experimetal result, that is $9.1 \times 10^{10} \text{ s}^{-1}$. As a consequence, the Förster mechanism is excluded as the main mechanism for energy transfer in **1**. the main mechanism is therefore assumed to be the Dexter electron exchange energy transfer.^{S5} Assuming as valid the Landau-Zener and Fermi golden rules derived from a semi-quantum mechanical approach (inherently non-adiabatic), equations S3 and S4 have to be considered, in which v_{en} is the electronic factor and H_{AB} is the energy transfer matrix element for energy transfer between the subunits A and B.^{S6}

$$k_{en} = v_{en} \exp(-\Delta G^{\neq} / RT)$$
(S3)

$$v_{\rm en} = (2\pi \,\mathrm{H_{AB}}^2 \,/\,\mathrm{h}) \,(1/4\pi\lambda\mathrm{RT})^{1/2} \tag{S4}$$

R and T have the usual values (8.617 x 10⁻⁵ eV K⁻¹ atom⁻¹ and 298 K, respectively), and λ and ΔG^{\neq} are the reorganization energy and the activation energy, respectively, expressed in equations S5 and

S6.^{S7}

$$\lambda = \left(\frac{1}{\mu} - \frac{1}{\varepsilon}\right) \left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{r_{AB}}\right)$$
(S5)

$$\Delta G^{\neq} = (\Delta G^{\circ} + \lambda)^2 / 4\lambda \tag{S6}$$

In eqs S5 and S6, μ and ϵ are the optical and static dielectric constants, respectively, r_A and r_B are the radii of the donor (A) and of the acceptor (B), r_{AB} is the donor-acceptor distance, and ΔG° is the driving force of the energy transfer process.

In the present case, r_A and r_B are both 3.5 Å, r_{AB} is 13 Å (from computer-based calculations), so that λ is 0.343 eV, and ΔG^{\neq} is 0.013 eV. Therefore, v_{en} is 1.5 x 10¹¹ and H_{AB} is 0.00105 eV, equivalent to 8.5 cm⁻¹.

Complete kinetics of transient absorption spectra

In the main text, **Figure 4** (inset) shows the kinetics at early times of transient decay of **1**. Here **Figure S5** shows the complete (up to the upper limit of the equipment, 3 .3 ns) kinetics.



Figure S6. Transient absorption decay of **1** at representative wavelengths (see Figure 4 in the main text for transient absorption spectra). Solvent: acetonitrile; excitation wavelength, 400 nm.

References to Supplementary Information

- S1 J. N. Demas and G. A. Crosby, J. Phys. Chem., 1971, 75, 991.
- S2 N. Nakamaru, Bull. Chem. Soc. Jpn., 1982, 55, 2697.
- S3 B. Laramée-Milette, F. Lussier, I. Ciofini and G. S. Hanan, *Dalton Trans.*, 2015, 44, 11551.
- S4 Th. H. Förster, *Discuss. Faraday Soc.* 1959, 27, 7.
- S5 (a) V. Balzani, P. Ceroni and A. Juris, *Photochemistry and Photophysics*, Wiley-VCH, 2013. (b) D. L. Dexter, *J. Chem. Phys.*, 1953, 21, 836.
- S6 (a) V. Balzani, F. Bolletta and F. Scandola, J. Am. Chem. Soc. 1980, 102, 2552. (b) F.
 Scandola and V. Balzani, J. Chem. Educ. 1983, 60, 814.
- S7 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, 811, 265.