

Supporting information for:

Photon Upconversion Facilitated Molecular Solar Energy Storage

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- S2 Experimentals
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Experimental Section

General synthesis and characterization: FvRu₂ was synthesized in accordance to literature procedures.⁷ All other chemicals and solvents were purchased from Aldrich or Acros and used without further purification. Absorption and emission spectra were obtained on a Cary 5000 spectrometer (Varian) and Spex Fluorolog 3 spectrofluorometer (JY Horiba), respectively. Proton NMR was used to analyze the photochemical conversion of FvRu₂ and was recorded on a 400 MHz Varian spectrometer.

Upconversion quantum yield: The upconversion quantum yield was calculated in similar fashion as in reference⁶. 9-10-diphenylanthracene (DPA, 1.7 mM) and palladium(II)octaethylporphyrin (PdOEP, 0.6 mM) dissolved in toluene was carefully deaerated by argon bubbling and transferred to a cuvette via cannula. The emission of DPA (front face mode) was monitored after excitation of PdOEP (527 nm) and direct excitation of DPA (339 nm), and the spectrofluorometers internal reference photo diode was used to compensate for variations in light intensities at the different wavelengths.

Device: The fused silica chips used in the microfluidic device were fabricated by Litcon AB in accordance to a provided mask (Fig. S1). The channel in the chip is 60 μm high, 3.5 mm wide and has an area of about 400 mm². The internal volume of the chip (25 μl) was determined by monitoring the time it took for a liquid to flow through the chip at a certain flow rate. A metal-halide lamp (Osram Powerstar HQI-R) provided white light at a color temperature of 4200 K, and a measured irradiation intensity of 15.2 W. The focused area of the lamp was about the size of the area of the glass chip. The device consisting of a glass filter (cut on wavelength = 495 nm; Newport) and two glass chips (Figure 2) was immersed in a temperature regulated water tank (30 °C, Figure S2). The TTA photon upconversion fluid consisted of DPA (15 mM) and PdOEP(0.9 mM) dissolved in toluene, and was deaerated prior to experiments by bubbling of Argon for 1 h. The upconversion solution was slowly streamed through the glass chip by the aid of gravity throughout the experiment. FvRu₂ (1.7 mM) dissolved in toluene-*d*₈ was streamed through the device with the flow speed controlled by a syringe pump (KDS100, KD Scientific), and the residence time was calculated by dividing the volume of the chip (25 μl) with the flow speed set by the syringe pump. The total volume of the system (including tubing) was 300 μl, and for each new data point 400 μl of FvRu₂ solution was first flown through the system prior to collection of 550 μl used for NMR analysis.



Figure S1. The negative used for etching the microfluidic glass chips. Four glass chips were made using one glass wafer.

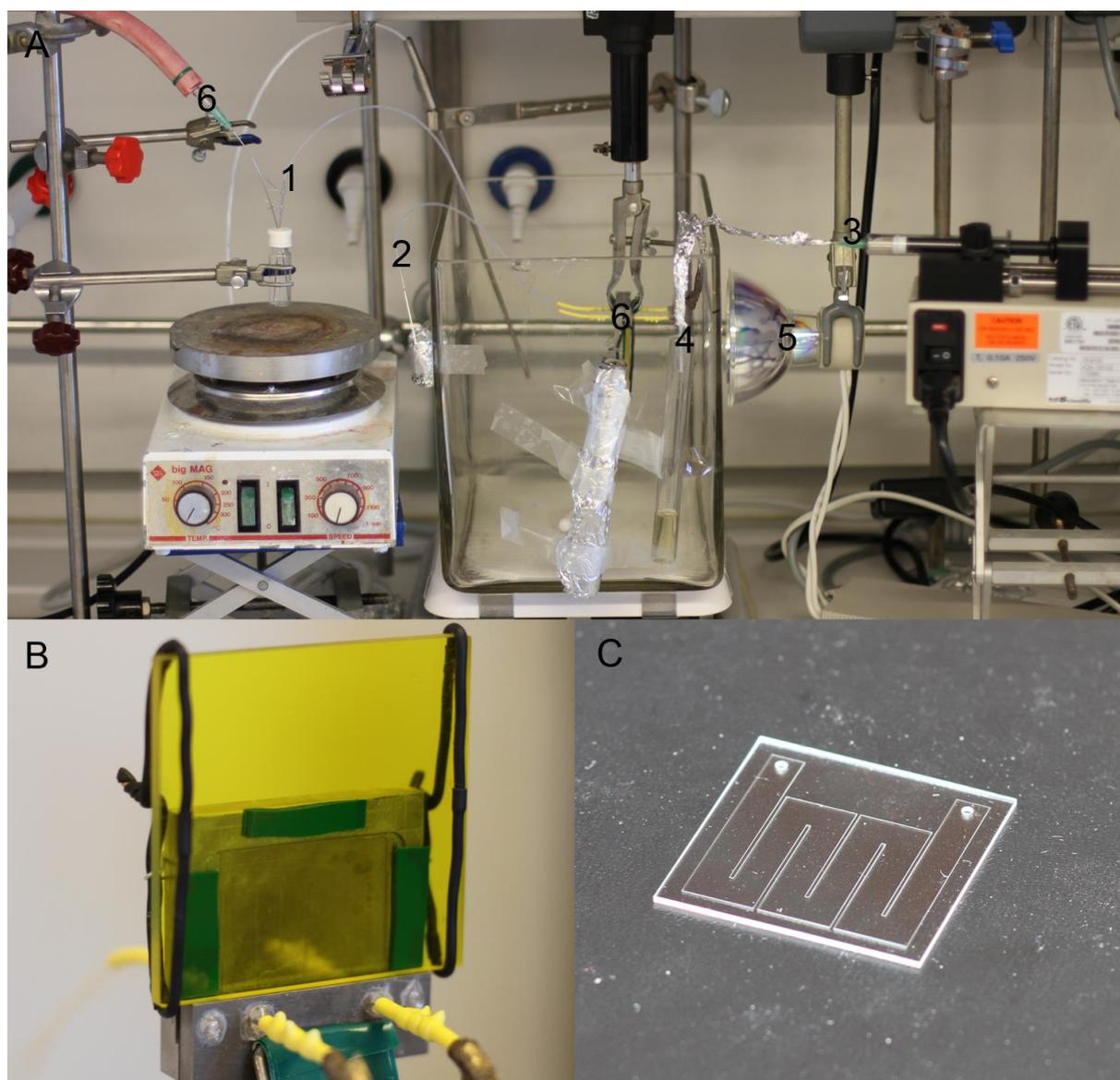


Figure S2. A picture showing the setup used in the study. A) The complete setup consisting of : (1) TTA photon upconversion solution inlet and (2) outlet, (3) syringe and syringe pump for pumping the solar fuel into the device, (4) solar fuel outlet, (5) lamp, and (6) the microfluidic device. B) The device consisting of glass filter and two microfluidic glass chips. C) The microfluidic glass chip.

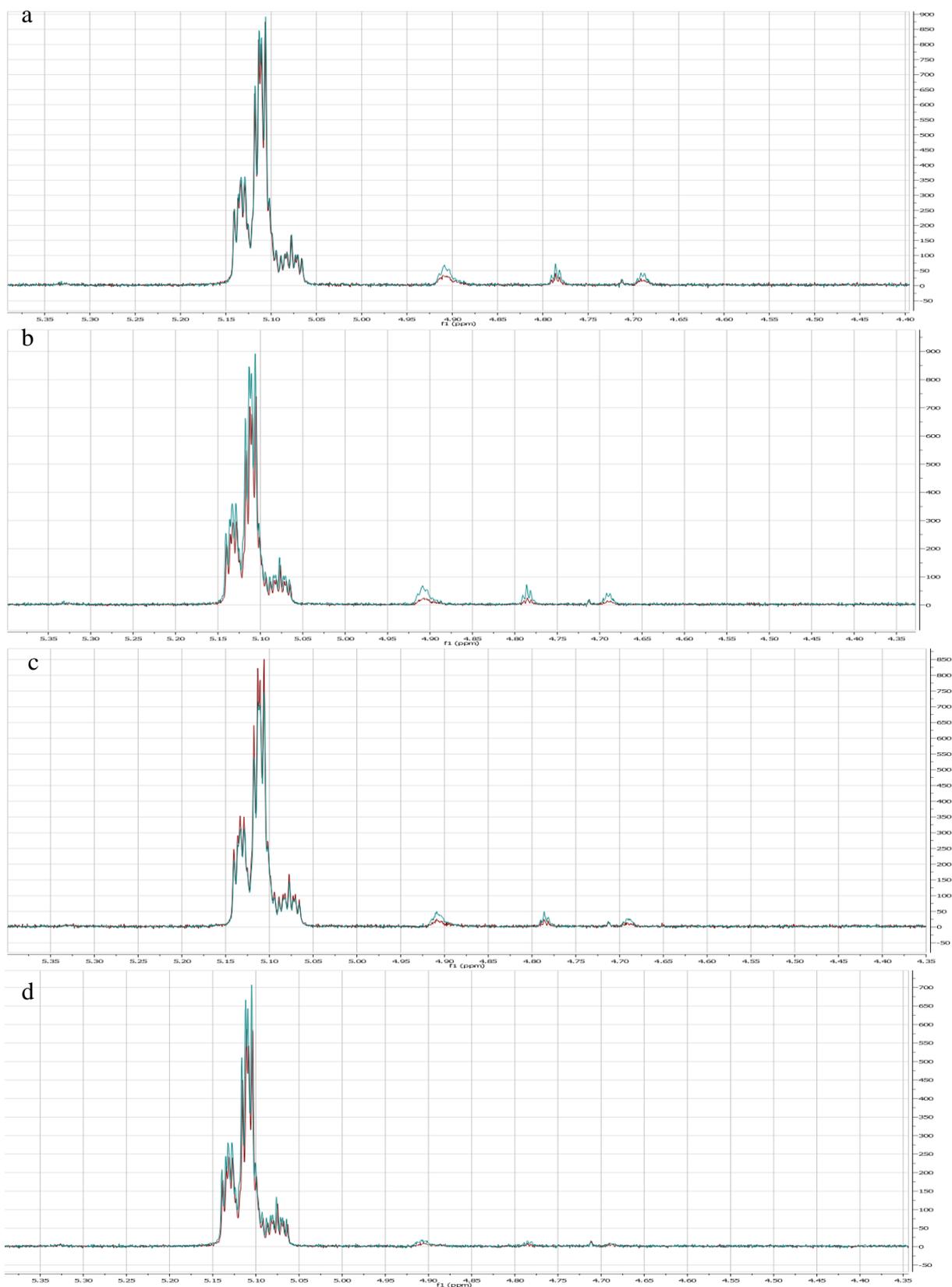


Figure S3. NMR spectra of the ruthenium complex after light exposure in presence (blue) and absence (red) of upconversion. The molar ratio of the low (peak at 5.10 ppm) and high (peak at 4.90 ppm) energy forms were determined by integration and the different residence times used was 0.28 (a), 0.19 (b), 0.13 (c) and 0.06 min (d).

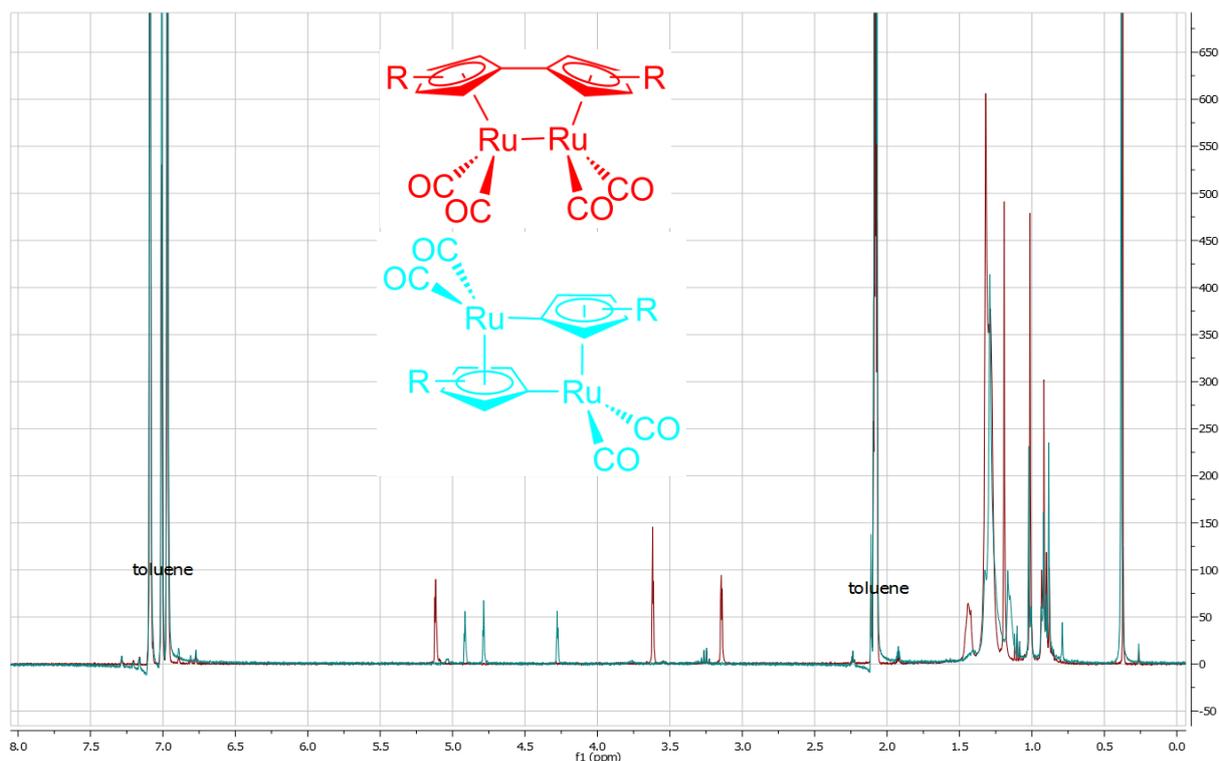


Figure S4. Full NMR spectra of the low (red) and high (blue) energy isomers.

Discussion of possible reabsorption of upconverted photons

As suggested in previous studies¹ there might be an effect of reabsorption of the upconverted photons by the sensitizer. Two mechanisms contribute; non-radiative (FRET) energy transfer between molecules at short distance ($< 50\text{\AA}$) and (trivial) radiative energy transfer effective at “macroscopic” distances. The former contribution could be theoretically estimated through the Förster model² in which the energy transfer efficiency as a function of the donor-acceptor separation distance r is given by

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (1)$$

where the Förster critical distance R_0 is

$$R_0^6 = 0.211(\kappa^2 n^{-4} Q_D J)^{1/6} \text{ (in \AA)}. \quad (2)$$

Here κ^2 is the orientation factor of the donor and acceptor transition moments, in this case set to $2/3$ representing a dynamically randomized orientation distribution, n is the refractive index of the solvent, Q_D is the quantum yield of the donor, and J is the spectral overlap integral of the normalized donor emission spectrum and the acceptor's molar absorptivity spectrum. In a solution of randomly distributed donors and acceptors a characteristic acceptor concentration could be defined as

$$C_0 = \frac{3}{4\pi(R_0 \cdot 10^{-9})^3} \frac{1}{N_A} \quad (3)$$

in molar when R_0 is in Å. With this definition C_0 is the concentration where the energy transfer efficiency is 72%. [2]

For the DPA (donor) – PdOEP (acceptor) system the estimated R_0 is 43 Å which corresponds to $C_0 = 5$ mM, and since the PdOEP concentration in the experiments was only 0.9 mM the non-radiative energy transfer component is expected to be close to negligible. However, this estimation is limited to a non-diffusing donor and acceptor pair and so the actual transfer efficiency might be slightly higher. It is also known that under these conditions, the expected donor emission decay is

$$I_{DA}(t) = I_D^0 \exp \left[-\frac{t}{\tau_D} - 2\gamma \left(\frac{t}{\tau_D} \right)^{1/2} \right] \quad (4)$$

where

$$\gamma = \frac{\sqrt{\pi}}{2} \frac{C}{C_0}. \quad (5)$$

Here C is the acceptor concentration and C_0 is the characteristic acceptor concentration (*vide supra*).² The effect of FRET from DPA to PdOEP was experimentally examined using time-resolved emission³ by determining the fluorescence lifetime of the donor (DPA) with and without 0.9 mM acceptor (PdOEP) in argon bubbled toluene. The obtained lifetimes without and with acceptor present were $\tau_{0D} = 6.7$ ns and $\tau_{DA} = 5.2$ ns, respectively. The donor decay with acceptor present was slightly deviating from mono-exponential in accordance with Equation 4. But since low concentrations of acceptor ($C \ll C_0$) result in small γ (eq. 5) the donor decay (eq. 4) approaches mono-exponential and could therefore be analyzed in this simplified way. If mono-exponential decay is assumed for the donor-acceptor system, the energy transfer efficiency is experimentally estimated to $E = 1 - \tau_{DA}/\tau_{0D} = 22\%$.

In the microfluidic device the optical path lengths are small (60 μm) and this minimizes (trivial) reabsorption. At the concentrations used the estimated maximal PdOEP absorbance in the short wavelength part of the DPA emission (overlapping with the porphyrin Soret band) is below 0.2 and this small reabsorption has not been considered in the analysis.

References

1. P. E. Keivanidis, S. Balushev, G. Lieser, G. Wegner, *ChemPhysChem* **2009**, *10*, 2316–26.
2. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, **2006**.
3. Performed using time-correlated single photon counting (TCSPC). The excitation source was a 10 MHz pulsed laser diode (PicoQuant) at 377nm. Fluorescence was detected at 410±4nm for the DPA reference and at 430±7.5nm for DPA with PdOEP present, using a micro channel plate photomultiplier tube Hamamatsu R3809U-50. Signal was collected in 2048 channels (100 ns time window) with a minimum of 10 000 counts in the top channel in the multichannel analyzer (Lifespec, Edinburgh Analytical Instruments).