Supporting Information

# Organic linkage controls the photophysical properties of covalent photosensitizer-polyoxometalate hydrogen evolution dyads

Yusen Luo,<sup>a,b,†</sup> Salam Maloul,<sup>c,†</sup> Patrick Endres,<sup>d,e</sup> Stefanie Schönweiz,<sup>c</sup> Chris Ritchie,<sup>f</sup> Maria Wächtler,<sup>a,b</sup> Andreas Winter,<sup>d,e</sup> Ulrich S. Schubert,<sup>d,e</sup> Carsten Streb\*<sup>c</sup> and Benjamin Dietzek\*<sup>a,b,e</sup>

<sup>a</sup>Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany

<sup>b</sup>Department Functional Interface, Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Strasse 9, 07745 Jena, Germany

<sup>c</sup>Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

<sup>d</sup>Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 07743 Jena, Germany

<sup>e</sup>Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany

<sup>f</sup>School of Chemistry, Monash University, Clayton, Vic. 3800, Australia

<sup>+</sup>Both authors contributed equally to the manuscript

\*Corresponding authors: carsten.streb@uni-ulm.de

benjamin.dietzek@leibniz-ipht.de

# **Experimental details**

**Gas chromatography**: Hydrogen evolution was measured by headspace GC on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: molecular sieve 5A, 75 m × 0.53 mm, oven temperature 70 °C, flow rate 25 mL min<sup>-1</sup>, detector temperature 200 °C) using Argon as carrier gas.

In a typical HER experiment, the Schlenk tube ( $21 \text{ cm}^3$ ) was filled with the PS-POM catalyst (0.8 mL, 0.1 mM), dry DMF (6.0 mL), sacrificial donor (triethyl amine, 1.11 mL, 1 M) and a proton source (acetic acid, 0.09 mL, 0.2 M). Thus, a total volume of 8 mL solution was used. The concentration in each parenthesis refers to the final concertation after mixing. The 80 TONs correspond to ca. 6.4  $\mu$ mol H<sub>2</sub> and ca. 12.8  $\mu$ mol AcOH has been used.

**X-ray diffraction of 2:** Single-crystal X-ray diffraction studies were performed at the Australian Synchrotron at beamline MX1 on an ADSC Quantum 210r diffractometer using monochromated radiation,  $\lambda = 0.71073$  Å. Structure solution and refinement was carried out using the SHELXL package *via* Olex2. Structures were solved by a combination of direct methods and difference Fourier syntheses and refined against *F2* by the full-matrix least-squares technique. Crystal data, data collection parameters and refinement statistics are listed in Table S1. Note that due to the small crystal size, diffraction data was only collected to a resolution of 1.0 Å. These data were submitted to the Cambridge Crystallographic Data Center, reference no CCDC 2009438.

**Spectroscopic characterization**: Steady-state UV/Vis absorption spectra were recorded in a quartz cell with 1 mm path length (for fs transient absorption experiment, JASCO V-670 spectrophotometer) and with 1 cm path length (for ns transient absorption experiment, Cary 5000 UV-Vis spectrometer, Varian, USA). For all time-resolved experiments, the stability of samples was ensured by recording the steady-state UV/Vis absorption spectra before and after every measurement. The steady-state emission spectra were recorded in a quartz cell with 1 cm path length on a FLS980 spectrofluorimeter (Edinburgh). All the spectroscopic characterization was performed at room temperature.

Resonance Raman spectroscopy. Resonance Raman (RR) spectra were recorded through excitation by a 405 nm diode laser (TopMode-405-HP, Toptica, Germany) and detected by an IsoPlane 160 spectrometer (Princeton Instruments, USA) with an entrance slit width of 0.05 mm, a focal length of 750 mm, and grating 2400 grooves/mm. The excitation energy was attenuated to around 8 mW. The Raman signals were recorded by a thermoelectrically cooled PIXIS eXcelon camera (Princeton Instruments, USA). The Raman spectra were initially baseline corrected and normalized with respect to a solvent band, *i.e.* to the signal at 1404 cm<sup>-1</sup> for DMF.

Electrochemistry and Spectroelectrochemistry. Cyclic voltammetry (CV) and spectro-electrochemistry (SEC) measurements were performed in a home-built three-electrode thin-layer cell with a path length of 1 mm. The three-electrode system consists of a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. CV and potential-controlled monitoring were performed using a computer-controlled potentiostat (VersaSTAT 3, Princeton Applied Research). All potentials given in the manuscript refer to the ferrocene/ferrocenium couple as internal standard. The corresponding UV-Vis spectra were recorded on a single-beam spectrometer (Avantes, Avalight-DH-S-BAL).

Time-resolved spectroscopy. Femtosecond (fs) transient absorption spectra were collected by using a previously reported home-built pump-probe laser system which is based on an amplified Ti: Sapphire

oscillator (Libra, Coherent Inc.).<sup>1-3</sup> All compounds were excited by pump pulse centered at 400 nm produced by the second harmonic generation of the laser fundamental (800 nm, ~110 fs, 1 kHz) with a BBO crystal. The power of the pump beam was kept at 0.4 mW and the beam diameter of the pump was 170  $\mu$ m at the sample position. This corresponds to  $0.7 \times 10^{20}$  photons m<sup>-2</sup> per pulse. A white light supercontinnum generated by focusing a fraction of the fundamental in a rotating CaF<sub>2</sub> plate is used to probe the samples in a wide spectral range (340 to 750 nm). The probe beam is delayed in time with respect to the pump beam by means of an optical delay line and the polarization between probe and pump is set at the magic angle (54.7°). Each solution (optical density ca. 0.25 at the excitation wavelength) was kept in a 1 mm quartz cuvette. Transient absorption data were displayed after chirp correction. The transient absorption data was analyzed by a global multi-exponential fit after exclusion of a temporal window of 200 fs around time-zero in order to avoid contributions of the coherent-artifact region to the data analysis. Furthermore, a spectral band of 20 nm around the pump-wavelength is omitted from the data analysis due to pump-scatter in this spectral range.

Nanosecond (ns) transient absorption spectra<sup>3</sup> were collected to study the long-lived species in the fs transient absorption data. The pump pulses centered at 410 nm were produced by a Continuum OPO Plus which is pumped by an continuum surelite Nd:YAG laser system (pulse duration 5 ns, repetition rate 10 Hz). The probe light is provided by a 75 W xenon arc lamp. Spherical concave mirrors are used to focus the probe beam into the samples and then send the beam to the monochromator (Acton, Princeton Instruments) and detected by a photomultiplier tube (Hamamatsu R928). The signal is amplified and processed by a commercially available detection system (Pascher Instruments AB). For all measurements, the power of the pump beam was kept at 0.35 mJ. ns TA spectra were recorded by using a bandpass (325 to 385 nm) and a long pass filter (435 nm) to eliminate the pump scattering. Time-resolved emission spectra were collected with the use of a long pass filter (435 nm) as well. Each sample was freshly prepared and the optical density (ca. 0.35) at the excitation wavelengths 410 nm was kept the same. All measurements were performed in 1 cm path length fluorescence cuvettes. Oxygen-free solutions were obtained by five freeze-pump-thaw cycles.

## Stability of 1 and 2



**Figure S1.** UV/Vis absorption spectra of **1** and **2** before (black) and after (red) the fs TA measurement. The inset in each figure shows the contribution of POM-absorption (structure is incorporated) to each dyad. This was obtained *via* subtracting the normalized (at 400 nm where POM does not absorb) UV/Vis absorption spectrum of **1** (and **2**) by that of **Ir** reference. Apparently, the simulated absorption spectrum of POM unit (blue line) shows a spectral shape deviation from the experimental result (grey line). This indicates a certain electronic interaction between Ir photosensitizer and POM unit in **1** and **2** at the ground state.

The simulated UV/Vis absorption spectrum of POM unit shows a shape deviation from the experimental one. It indicates a certain electronic interaction between Ir photosensitizer and POM unit in **1** and **2** at the ground state. Thus, the bond breakage between Ir photosensitizer and POM unit in **1** and **2** during the TA experiments would lead to spectral changes. However, as shown in Figure S1, identical absorption spectra of **1** and **2** before and after the TA measurements are revealed. This points to a good stability of the samples.

## fs transient absorption spectra of Ir and 2



**Figure S2.** fs transient absorption spectra at selected delay times (left), selected kinetic traces with corresponding fit (middle) and decay-associated spectra (DAS) resulted from the global fit of the fs TA data obtained upon excitation at 400 nm in aerated DMF for **Ir** (a-c) and **2** (d-f).

# UV/Vis spectroelectrochemistry



**Figure S3.** (a) Spectroelectrochemical UV/Vis absorption difference spectra of (a) reduced POM (*i.e.* POM<sup>•-</sup>) and (c) reduced bpy ligand (*i.e.* bpy<sup>•-</sup>) collected in dry DMF. (b) is an enlargement of the absorption difference spectra between 500 and 750 nm in (a). The reduction was performed on **2** and **Ir**, respectively. Potentials are given *vs.*  $Fc^{+/0}$ . The inset in (a) and (c) represents the corresponding CV obtained with a scan rate of 0.05 V/s. The red dot on the CV curve indicates the potential applied for obtaining the UV/Vis absorption difference spectra.

As shown in Figure 1 (also in Figure S1), POM itself does not absorb above 400 nm. The reduction of POM in **2** induces a loss of intensity between 400 and 500 nm (Figure S3a and S3b) belonging to the Ir(III) photosensitizer. This might be caused by an electronic effect that the Ir(III) unit gets closer to the reduced POM due to the rotation of the -C=N- linker.<sup>4</sup>

#### ns transient absorption spectra of Ir and 1



**Figure S4.** ns transient absorption spectra of **1** (a) and **Ir** (d). Time-resolved emission spectra of **1** (b) and **Ir** (e). These data were recorded in aerated DMF upon excitation at 410 nm. (c) and (f) Comparison of the global fit results from the ns TA and time-resolved emission data, respectively.

# Single crystal XRD characterization of 2

CCDC no	2009438
Empirical formula	$C_{92}H_{100}Ir_2MnMo_6N_{11}O_{24}$
Formula weight	2758.80
Temperature / K	100.0
Crystal system	Monoclinic
Space group	C2/c
a / Å	32.266(7)
b / Å	12.878(3)
c / Å	27.879(6)
α / °	90
β/°	108.04(3)
γ/°	90
Volume / Å <sup>3</sup>	5402.1(6)
Z	4
ρ <sub>calc</sub> g / cm <sup>3</sup>	1.664
µ / mm <sup>-1</sup>	3.244
F(000)	5408.0
Index ranges	-32 ≤ h ≤ 32, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27
Reflections collected	40759
Data/restraints/parameters	5761/0/612
Goodness-of-fit on F <sup>2</sup>	1.073
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0393, wR <sub>2</sub> = 0.1008
Final R indexes [all data]	R <sub>1</sub> = 0.0516, wR <sub>2</sub> = 0.1070
Largest diff. peak/hole / e Å-3	1.71/-1.15

# Table S1. Summary of the crystallographic information for 2.



Figure S5. Crystal structure of 2.

#### Purity of sample 1 and 2



Figure S6. Normalized (at each maximum) emission spectra of the samples studied in this work.

According to the steady-state emission spectra (Figure 1 in the main text), **1** and **2** show an emission, which is strongly reduced compared to the **Ir** reference. The integrated emission signal of **1** and **2** amount to 1% and 14% compared to the **Ir** reference, respectively (Figure 1 in the main text). Assuming that samples were contaminated with the unbound Ir photosensitizer, this would point to an upper limit of ca. 1% and 14% of the free Ir complex in **1** and **2**, respectively. However, it seems highly unlikely that the sample of **2** contains such a large fraction of impurity (14% unbound Ir complex) since the sample used in the photophysical measurements was recrystallized and the single-crystal XRD structure has been determined (see Figure S5). For **1**, there is only a tiny emission signal left (ca. 1%). However, the residual emission is slightly blue-shifted (by ca. 14 nm) compared to the emission of the reference compound **Ir** (Figure S6). This shifted emission band proofs a different luminescent species to be present when comparing **1** (for that matter also **2**) to the **Ir** reference. Therefore, we would like to conclude that the initial samples are pure and do not contain unbound Ir complex. The good stability of **1** and **2** during the transient absorption measurements was confirmed and discussed in Figure S1.

# **References**

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