

Supplementary information

for

Photocatalyst Z-scheme system composed of a linear conjugated polymer and BiVO₄ for overall water splitting under visible light

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1. Experimental

Reagents and solvents were purchased from commercial suppliers (Manchester Organics, Sigma-Aldrich, Kanto Chemical, Wako Pure Chemical Industries, and Tanaka Kikinzoku) and used without further purification. FT-IR spectra were recorded on a Bruker Tensor 27 with an ATR attachment at room temperature. UV-Visible spectra of the polymers were recorded on a Shimadzu UV-2550 UV-Vis spectrometer as powders in the solid state. Photoluminescence spectra of the polymer powders were measured with a Shimadzu RF-5301PC fluorescence spectrometer at room temperature. Photoluminescence spectra of the polymer powders were measured with a Shimadzu RF-5301PC fluorescence spectrometer at room temperature. Time-correlated single photon counting (TCSPC) experiments were performed on an Edinburgh Instruments LS980-D2S2-STM spectrometer equipped with picosecond pulsed LED excitation sources and a R928 detector, with a stop count rate below 5%. An EPL-375 diode ($\lambda = 370.5$ nm, instrument response 100 ps, fwhm) was used. Suspensions were prepared by ultrasonating the polymer in water. The instrument response was measured with colloidal silica (LUDOX® HS-40, Sigma-Aldrich) at the excitation wavelength. Decay times were fitted in the FAST software using suggested lifetime estimates. PXRD measurements were performed on a PANalytical X'Pert PRO MPD, with a Cu X-ray source, used in high throughput transmission mode with $K\alpha$ focusing mirror and PIXCEL 1D detector. Static light scattering measurements were performed on a Malvern Mastersizer 3000 Particle Sizer. Sample was dispersed in water by 10 minutes of ultrasonication and the resultant suspensions were injected into a stirred Hydro SV quartz cell, containing more water, to give a laser obscuration of 5 – 12%. Particle sizes were fitted according to Mie theory, using the Malvern 'General Purpose' analysis model, for non-spherical particles. A sample refractive index of 1.59, sample absorbance of 0.1 and solvent refractive index of 1.333 were used for fitting. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on an ICP-OES Agilent 5110 with equipped with a collision/reaction cell after a microwave digest of the materials in nitric acid (67-69%, trace metal analysis grade) in a microwave. The solutions were diluted with water before the measurement and the instrument was calibrated with Pd and Ru standards in aqueous solution and Y-89 as the internal standard. Electron spin resonance (ESR) spectra were recorded at room temperature on an ESR spectrometer (ADANI; SPINSCAN) with a microwave frequency of 9.4 GHz.

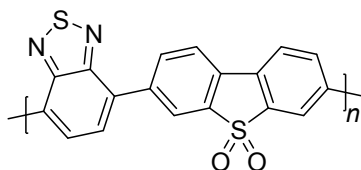
Synthesis of P10-160 ppm Pd

A flask was charged with the 3,7-dibromodibenzo[*b,d*]thiophene sulfone (748 mg, 2 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene sulfone (936 mg, 2 mmol), *N,N*-dimethylformamide (120 mL), an aqueous solution of K_2CO_3 (21.6 mL, 2.0 M), and $[Pd(PPh_3)_4]$ (1 mg, 0.045 mol%). The mixture was degassed by bubbling with N_2 for 30 minutes and heated to 150 °C for 2 days. The mixture was cooled to room temperature and poured into water. The precipitate was collected by filtration and washed with H_2O and methanol. Further purification of the polymers was carried out by Soxhlet extraction with chloroform to remove any low-molecular weight by-products. The product was dried under reduced pressure and obtained as a yellow powder (535 mg, 62%). Pd content: 160 ppm.

Ru Deposition P10-30 ppm Pd

Ru co-catalysts were loaded on P10-low Pd by photodeposition. In the photodeposition method, P10-low Pd powders were dispersed in an aqueous methanol solution (10 vol. %, 120 mL) containing $RuCl_4 \cdot 1.29H_2O$ (37.5 mM, 198 μ L). The co-catalyst-loaded photocatalysts were collected by filtration, washed with water, and then dried at room temperature in air. Pd content: 30 ppm, Ru content: 0.25%.

Synthesis of P74



A flask was charged with the 4,7-dibromo-2,1,3-benzothiadiazole (748 mg, 2 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene sulfone (936 mg, 2 mmol), *N,N*-dimethylformamide (120 mL), an aqueous solution of K_2CO_3 (21.6 mL, 2.0 M), and $[Pd(PPh_3)_4]$ (40 mg, 1.8 mol%). The mixture was degassed by bubbling with N_2 for 30 minutes and heated to 150 °C for 2 days. The mixture was cooled to room temperature and poured into water. The precipitate was collected by filtration and washed with H_2O and methanol. Further purification of the polymers was carried out by Soxhlet extraction with chloroform to remove any low-molecular weight by-products. The product was dried under reduced pressure and obtained as a red powder (535 mg, 62%). Anal. Calcd for $(C_{18}H_8N_2O_2S_2)_n$: C, 62.06; H, 2.31; N, 8.04; S, 18.40%; Found C, 57; H, 3; N, 7; S, 16%.

Photocatalytic Experiments

Water splitting experiments were carried out using BiVO_4 (0.05 g) and P10 (0.05-0.004 g) in aqueous solutions containing the mediator (120 mL) after dispersion using ultrasonication. A top-irradiation cell with a Pyrex window was used after degassing by applying vacuum and purging with argon. The set-up was brought back to reduced pressure (70 torr) and irradiated with a 300 W Xe arc light source (PerkinElmer; CERMAX PE300BF) or a solar simulator (Yamashita Denso; YSS-80QA, 100 mW cm^{-2}). Amounts of evolved hydrogen and oxygen were determined using an online gas chromatograph (Shimadzu; GC-8A, MS-5Å column, TCD, Ar carrier).

Deuterium Labelling Experiments

FeCl_2 (5.1 mg) was dissolved in D_2O (20 mL), the pH value was adjusted to 2.7 using deuterated sulfuric acid (D_2SO_4). P10 (20 mg) was dispersed in this solution by ultrasonication before degassing thoroughly by argon bubbling for 30 minutes. The mixture was placed in a quartz vessel and sealed in a reactor under nitrogen. The sample was illuminated with a 300 W Newport Xe light source (Model: 6258, Ozone free) for the time specified at a fixed distance under atmospheric pressure. The Xe light source was cooled by water circulating through a metal jacket. Gas samples from the 1.3 mL headspace of the reactor were analyzed at the time periods specified by a customized HPR-70 batch sampling system from Hiden Analytical using a HAL3F/301 triple filter Mass Spectrometer with a Faraday detector for analysis.

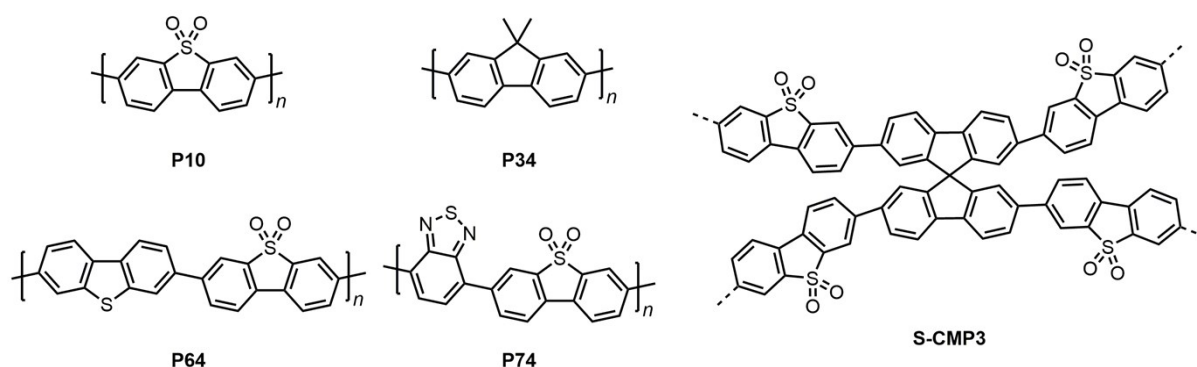


Figure S-1. Structures of the polymer photocatalysts used in this study.

2. Photocatalyst Characterization

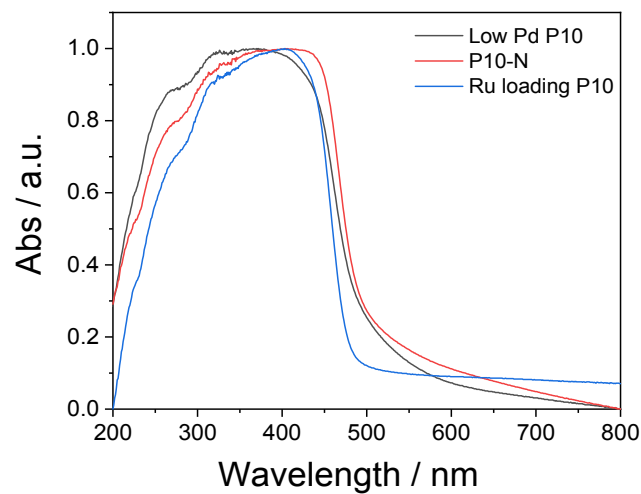


Figure S-2. UV-Vis absorption spectra of **P10-160 ppm Pd**, **P10**, and **Ru deposition P10-30 ppm Pd** measured as powders in the solid-state.

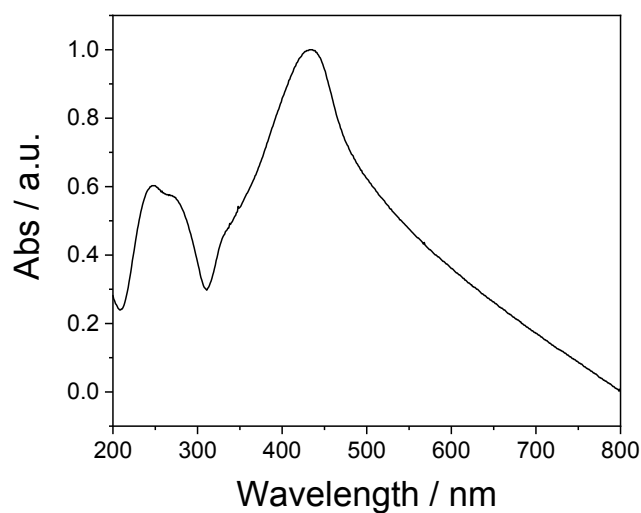


Figure S-3. UV-Vis absorption spectra of **P10** measured as suspension in water.

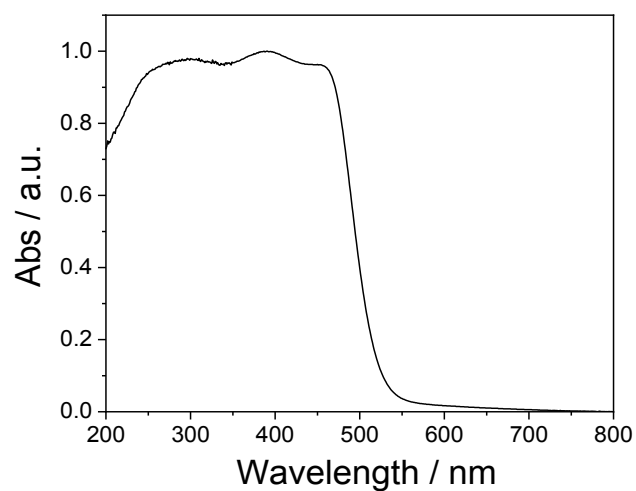


Figure S-4. UV-Vis absorption spectra of **BiVO₄** measured as a powder in the solid-state.

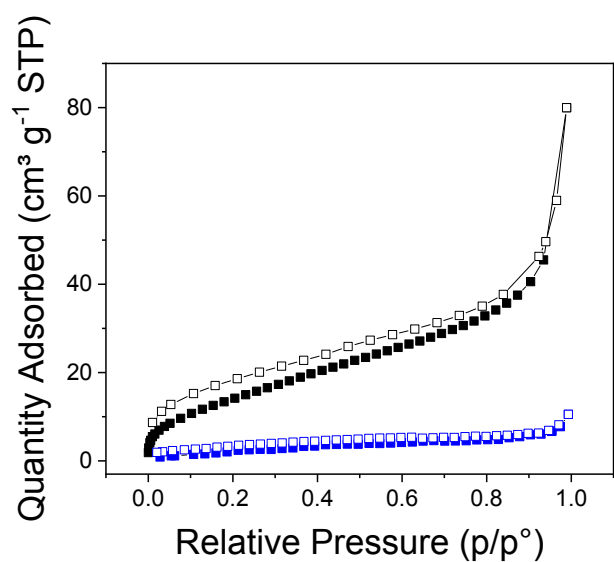


Figure S-5. Nitrogen sorption isotherm for **P10** (black) and **BiVO₄** (blue) measured at 77.3 K and up to 1 bar (desorption curves shown as open symbols).

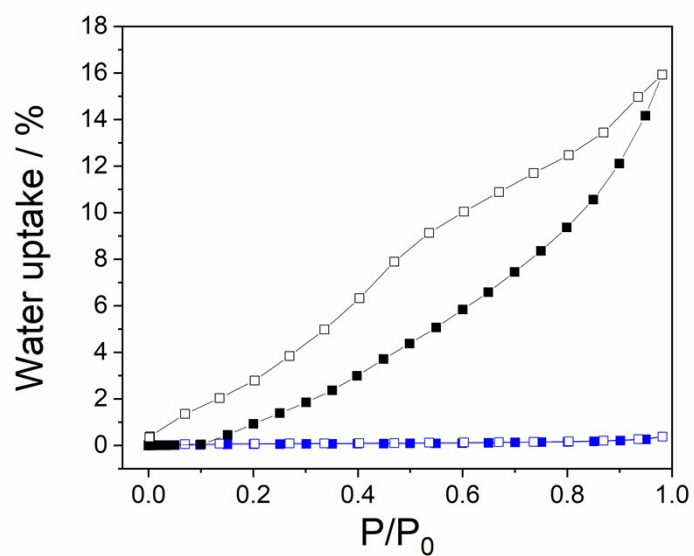


Figure S-6. Water uptake measurements for **P10** (black) and **BiVO₄** (blue) at 20.0 °C and up to 23.393 mbar.

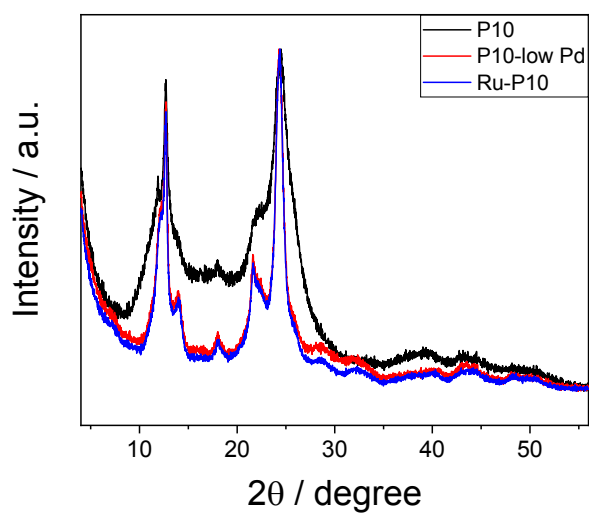


Figure S-7. pXRD patterns for **P10** (black line), **P10-160 ppm Pd** (red line), and **Ru Deposition P10-30 ppm Pd** (blue line).

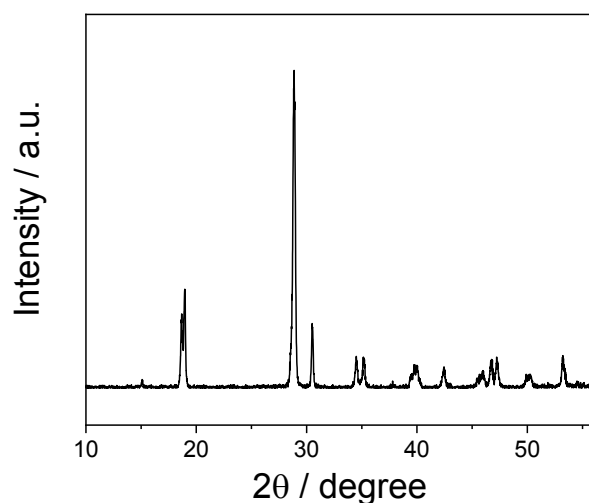


Figure S-8. pXRD pattern of **BiVO₄** (monoclinic scheelite phase).

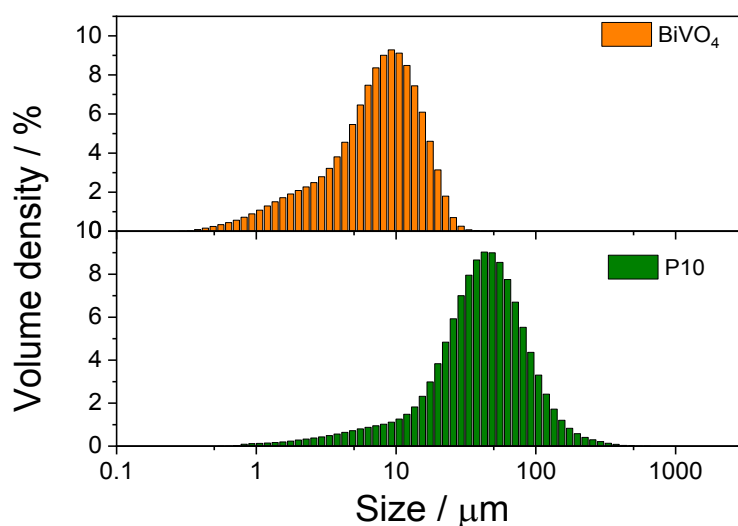


Figure S-9. Volume density distributions of **P10** and **BiVO₄** in H₂O (pH 2.7).

Table S-1. Particle sizes by static light scattering.

Polymer	$D_{,50}^{[a]}$	$D[4,3]^{[b]}$	$D[3,2]^{[c]}$
	/ μm	/ μm	/ μm
BiVO₄	7.65	8.45	4.41
P10	41.4	60.5	20.9

[a] 50th percentile of particle size volume distribution; [b] Volume mean diameter; [c] Surface area mean diameter (Sauter mean diameter);

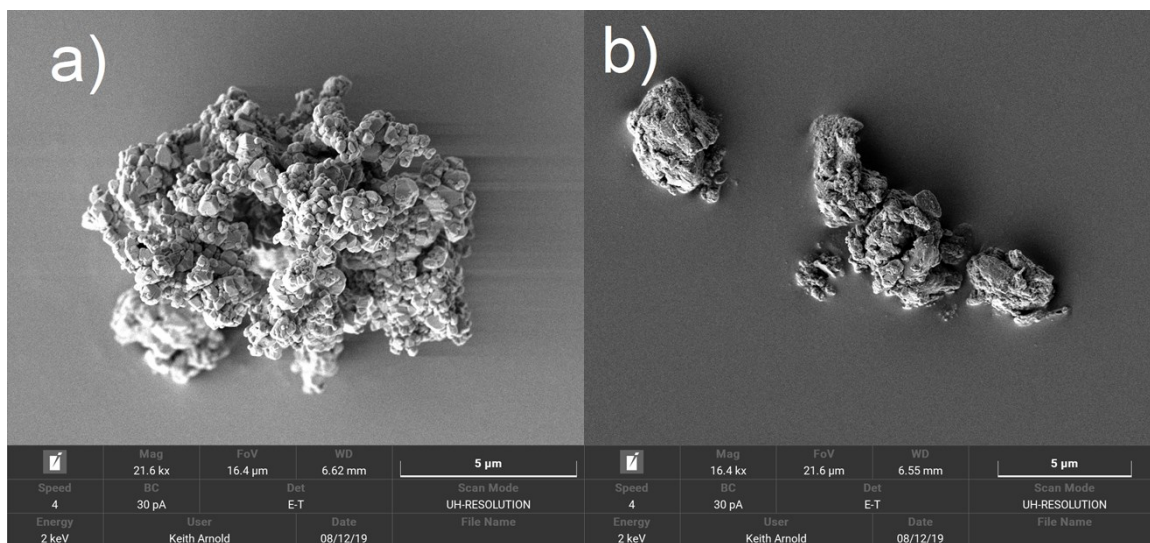


Figure S-10. SEM images of a) BiVO_4 and b) P10.

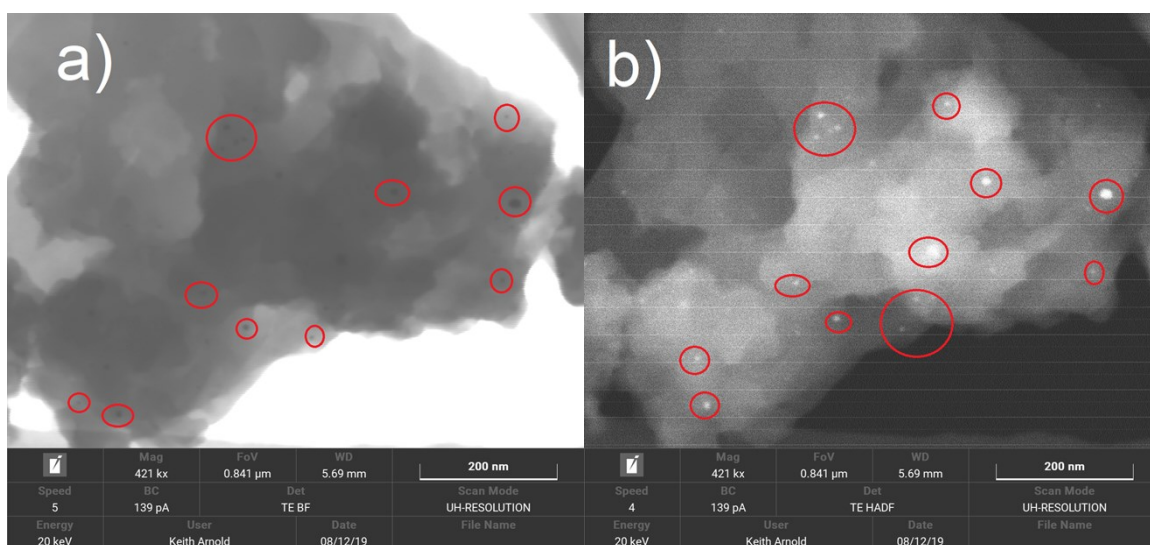


Figure S-11. TEM images of P10 using (a) bright field STEM mode and (b) HAADF STEM mode (Red circles highlight Pd particles).

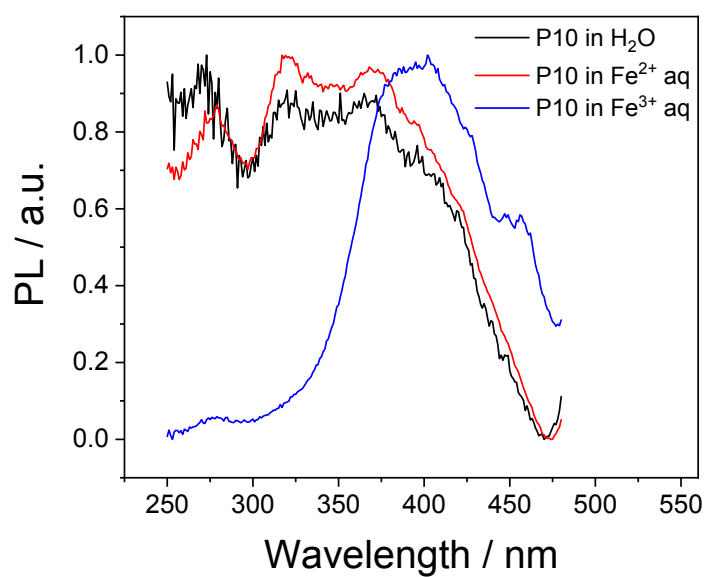


Figure S-12. Excitation spectra of **P10** suspensions measured in different solutions.

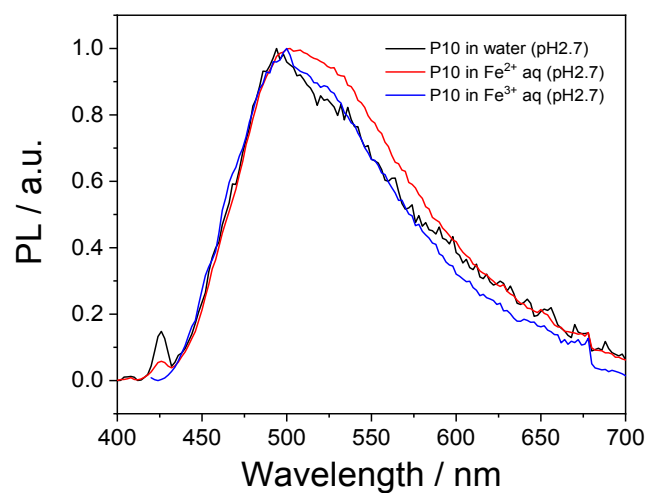


Figure S-13. Emission spectra of **P10** suspensions measured in different solutions.

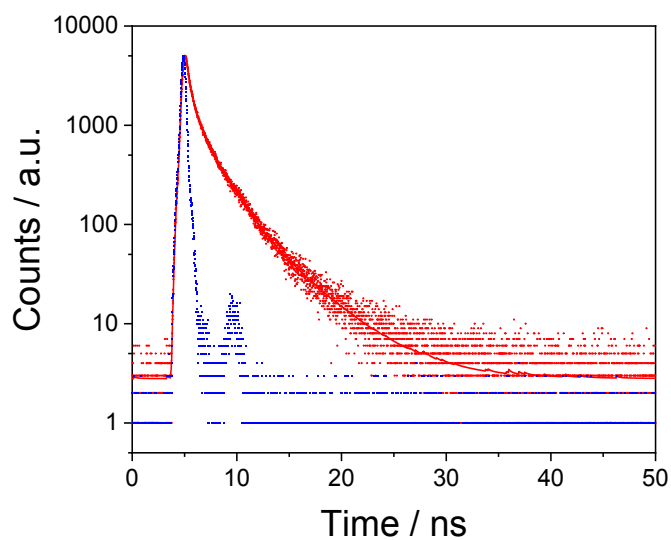


Figure S-14. Fluorescence life-time decays of **P10** in water (pH 2.7, red dots), fit line (red line), instrument response (blue dots).

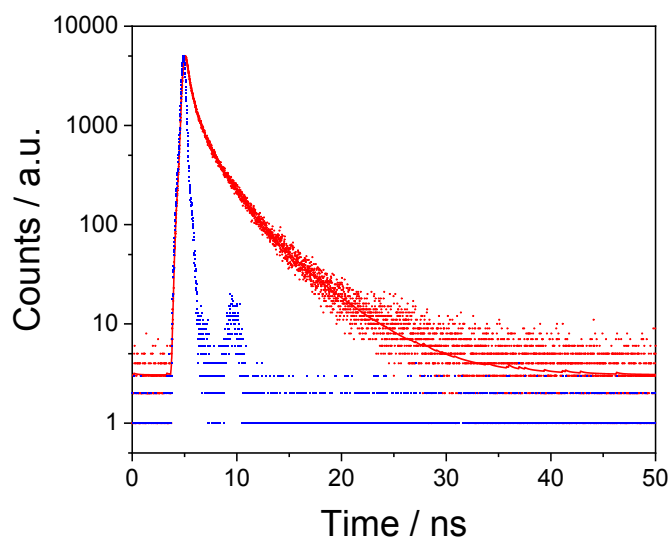


Figure S-15. Fluorescence life-time decays of **P10** in aqueous FeCl_2 (2 mmol L^{-1} , pH 2.7, red dots), fit line (red line), instrument response (blue dots).

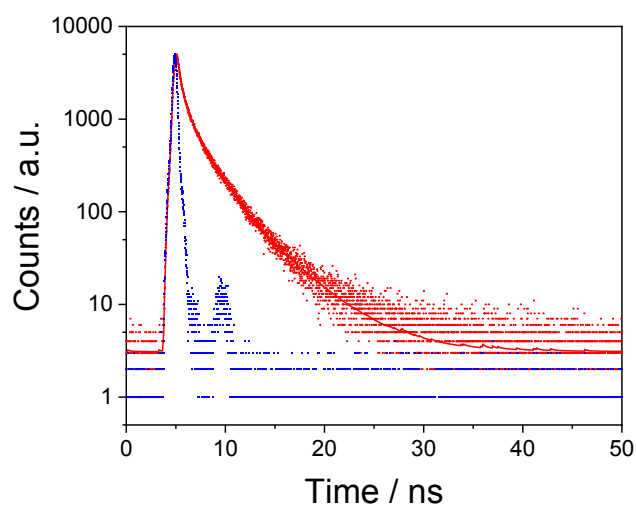


Figure S-16. Fluorescence life-time decays of **P10** in aqueous FeCl_3 (2 mmol L^{-1} , pH 2.7, red dots) in suspension, fit line (red line), instrument response (blue dots).

Table S-2. Estimated fluorescence lifetimes of **P10** suspensions in different solutions.

Polymer	τ_1	B_1	τ_2	B_2	τ_3	B_3	χ^2	τ_{AVG}
	/ ns	/ %	/ ns	/ %	/ ns	/ %		/ ns
P10 in water	0.285	34.7	1.575	43.5	4.383	21.8	1.32	1.74
P10 in FeCl_2 aq	0.31	34.2	1.548	42.4	4.651	23.5	1.29	1.85
P10 in FeCl_3 aq	0.27	33.4	1.524	42.4	4.227	24.2	1.39	1.76

[a] Fluorescence life-times for **P10** in different solution suspension obtained from fitting time-correlated single photon counting decays to a sum of three exponentials, which yield τ_1 , τ_2 , and τ_3 according to

$$\sum_{i=1}^n (A + B_i \exp(-t/\tau_i)).$$

τ_{AVG} is the weighted average lifetime calculated as $\sum_{i=1}^n B_i \tau_i$.

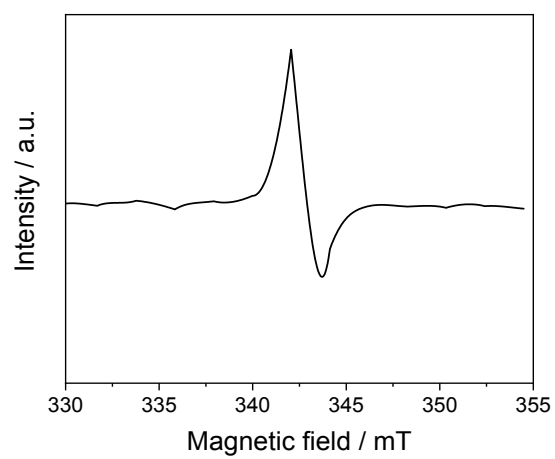


Figure S-17. ESR of **P10** at a) room temperature

3. High-throughput Screening

Polymers (5 mg) or metal oxide (5 mg) were added into sample vials ($V = 12.5$ mL) and purged with nitrogen in a Sweigher Chemspeed Technologies robot for 6 hours. The liquid transfer head (handled by the autoarm) was used to transfer redox mediator aqueous solution (2 mg mL^{-1}) via the liquid handling system under inert conditions from stock jars inside the system into the sample vials. The capper/crimper tool then capped/crimped the vials automatically under inert conditions. All sample vials were ultrasonicated in an ultrasonic bath for 5 minutes before removing the vials and illuminating them with a solar simulator (AM1.5G, Class AAA, IEC/JIS/ASTM, 1440 W Xe, 12×12 in., MODEL:94123A) for the time specified while constantly being redispersed with a rocker/roller device. Gaseous products were analyzed on an Agilent HS-GC injecting a sample from the headspace via a transfer line (temperature 90 °C) onto a molecular sieve 5 \AA column (temperature: 45 °C) with He as the carrier gas at a flow rate of 30 mL min^{-1} . Hydrogen was detected with a pulsed discharge detector referencing against standard gas with a known concentration of hydrogen. Hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations. No hydrogen evolution was observed from redox mediator solutions under solar simulator illumination in absence of a photocatalyst.

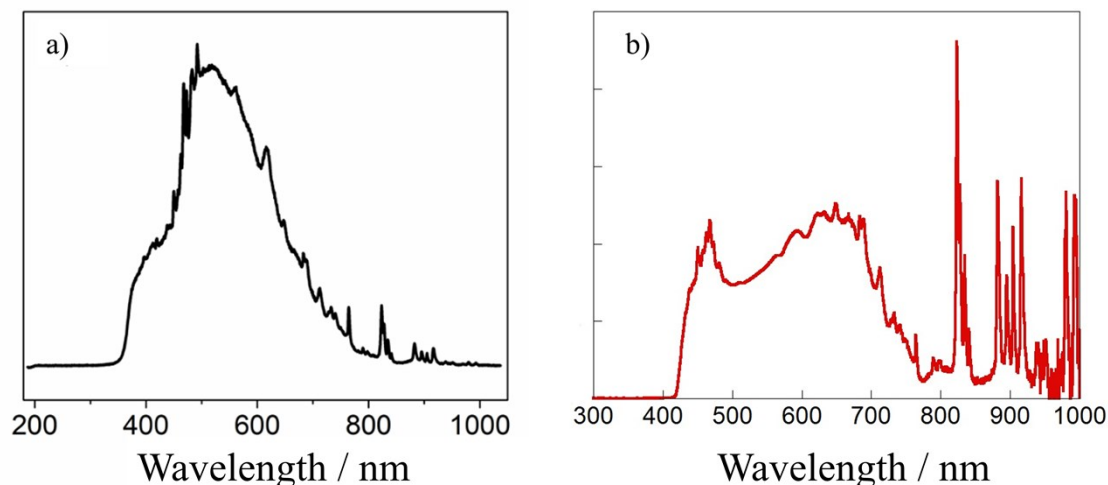


Figure S-18. Spectral output of a) Solar simulator (AM1.5G, Class AAA, IEC/JIS/ASTM, 1440 W Xenon, 12×12 in., MODEL: 94123A); b) 300 W Xe arc light source (PerkinElmer; CERMAX PE300BF) equipped with a $\lambda > 420$ nm cut-off filter.

4. Photocatalysis Experiments

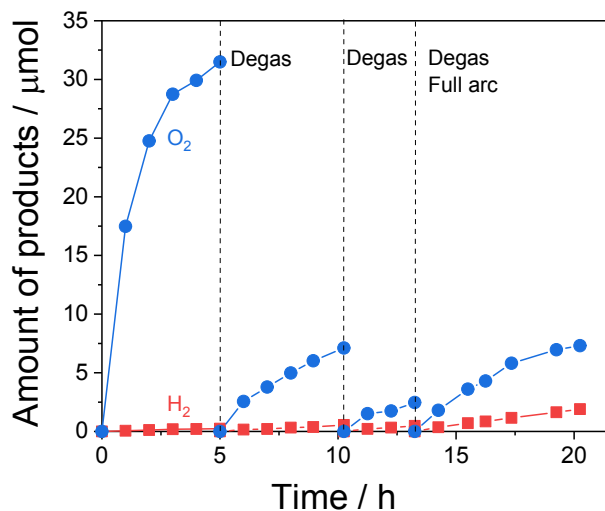


Figure S-19. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **Ru loaded P10-30 ppm Pd** (50 mg) in an aqueous **FeCl₃** solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

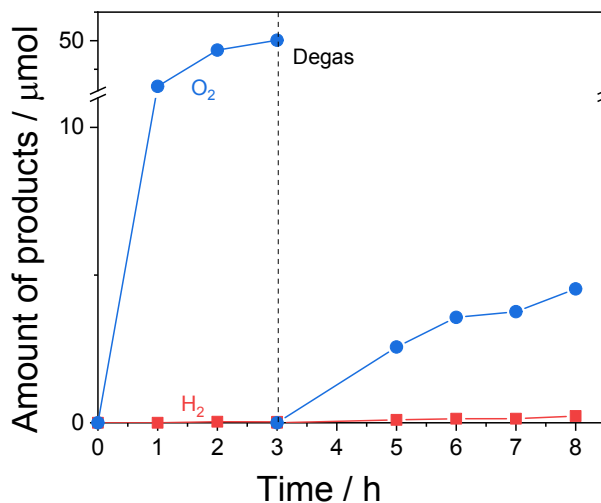


Figure S-20. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10-160 ppm Pd** (50 mg) in an aqueous **FeCl₃** solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

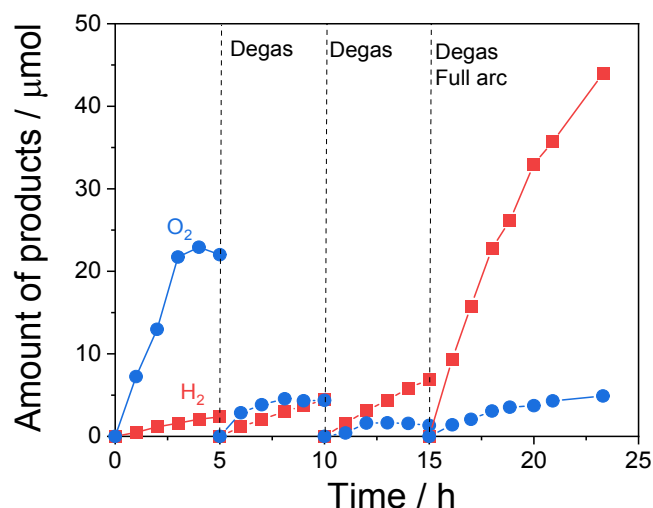


Figure S-21. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (50 mg) in an aqueous **FeCl₃** solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

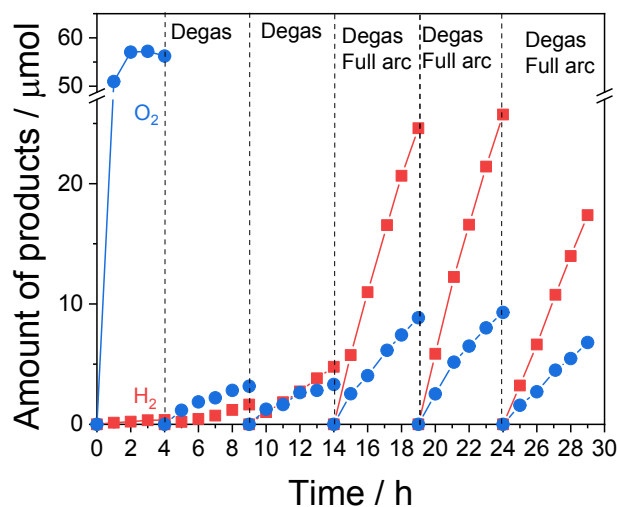


Figure S-22. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (10 mg) in an aqueous **FeCl₃** solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

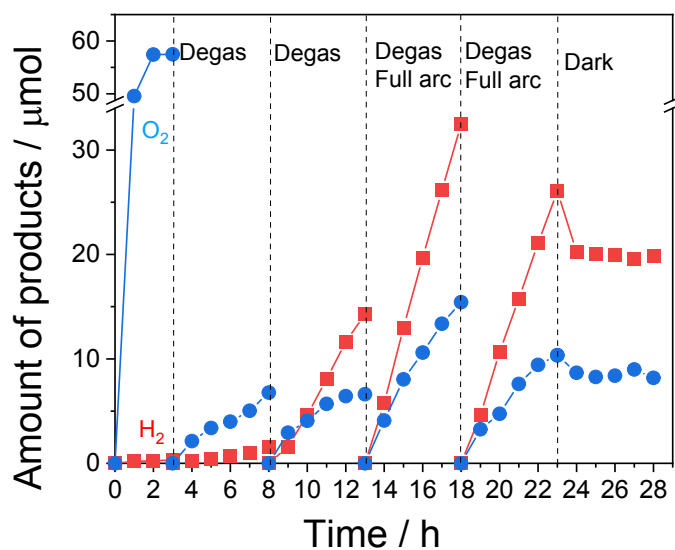


Figure S-23. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (7 mg) in an aqueous FeCl₃ solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

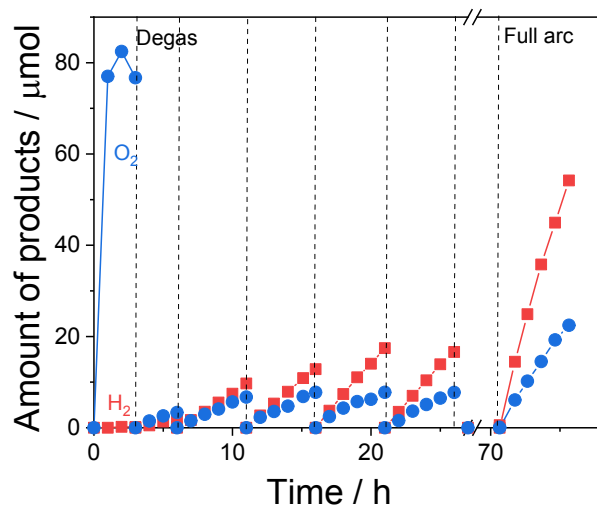


Figure S-24. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (4 mg) in an aqueous FeCl₃ solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) followed by full arc irradiation in a top-irradiation cell with a Pyrex window.

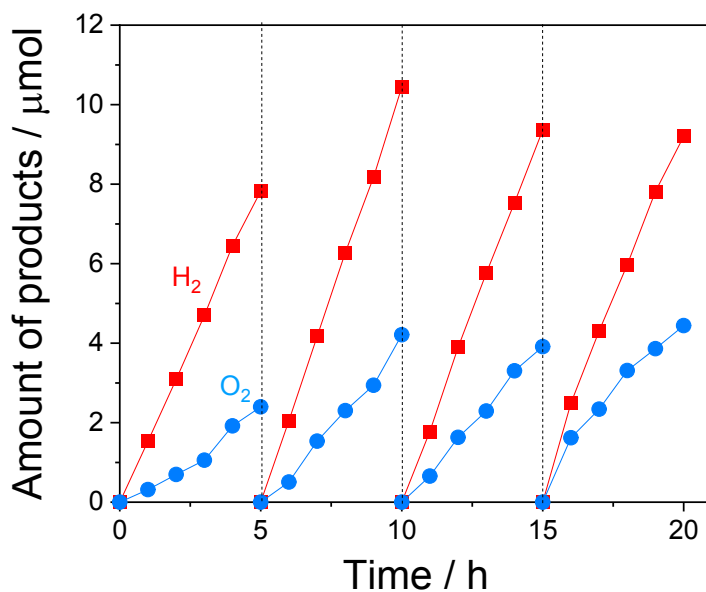


Figure S-25. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (4 mg) in an aqueous **FeCl₂** solution (0.5 mmol L⁻¹, 120 mL, pH 2.4). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window. The increase in activity after the first run can be ascribed to the system reaching an equilibrium of **Fe²⁺/Fe³⁺** after conversion of a proportion of the **Fe²⁺** to **Fe³⁺**.

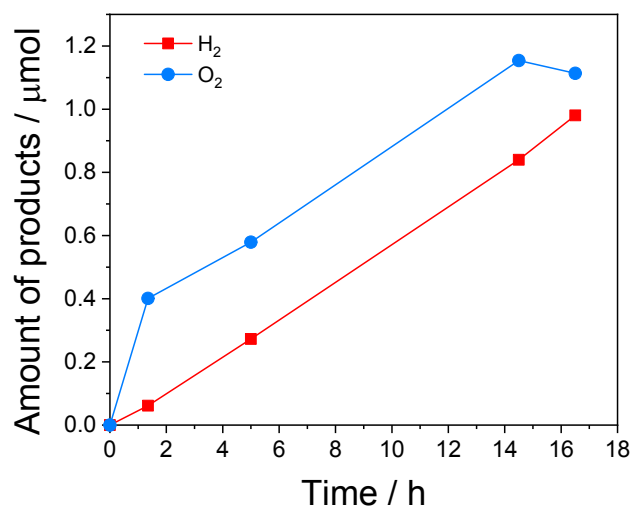


Figure S-26. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (4 mg) in an aqueous **FeCl₃** solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 480$ nm) in a top-irradiation cell with a Pyrex window.

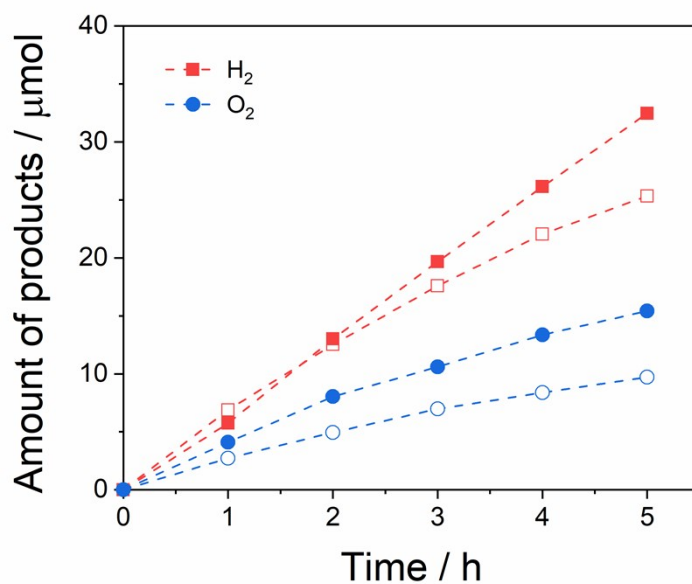


Figure S-27. Time course of overall water splitting for a Z-scheme consisting of **P10** (7 mg), **BiVO₄** (50 mg) in an aqueous **FeCl₃** solution (2 mmol L⁻¹, 120 mL) under pH 2.7(close) and pH 2.4 (open). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

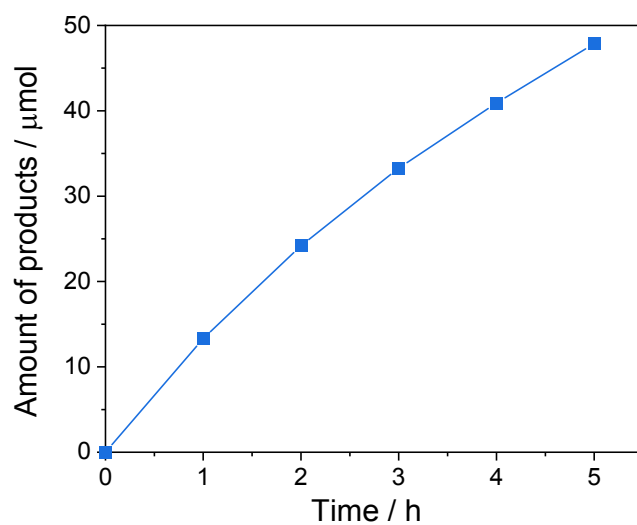


Figure S-28. Time course of the hydrogen evolution of **P10** (7 mg) from an aqueous **FeCl₂** solution (2 mmol L⁻¹, 120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

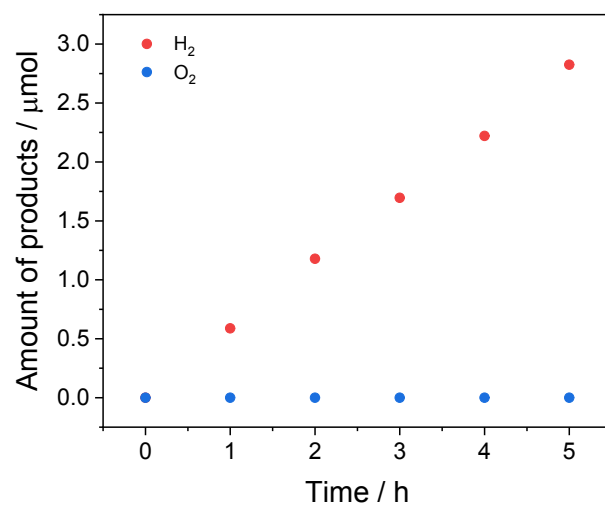


Figure S-29. Time course of overall water splitting for a Z-scheme consisting of **BiVO₄** (50 mg) and **P10** (4 mg) in water (120 mL, pH 2.7) without added redox mediator. The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window. No overall water splitting occurs in the absence of redox mediator.

5. Post-Illumination Characterization

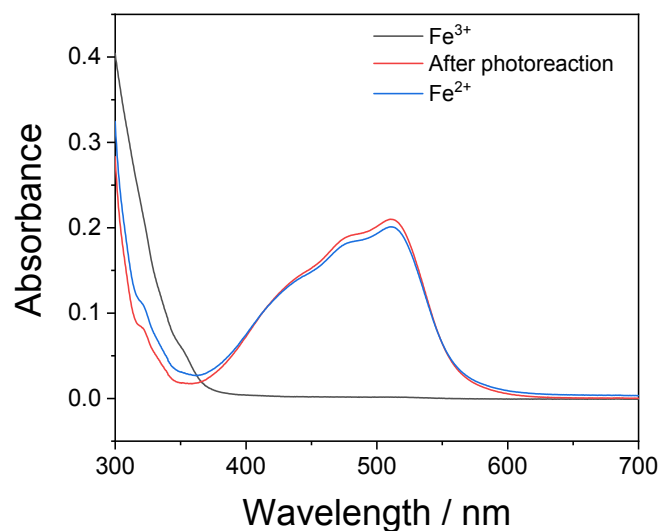


Figure S-30. UV-Vis absorption spectra of FeCl₃ solution (2 mmol L⁻¹, pH 2.7), FeCl₂ solution (2 mmol L⁻¹, pH 2.7), and a filtered solution of **P10/BiVO₄**/FeCl₃ after photocatalysis experiment. In all cases 0.1 mL of the solutions were added to a buffer solution 10 mL (pH 4.5; prepared with 20 g ammonium acetate, 25 mL acetic acid and 75 mL water) containing 0.6 μmol 1,10-phenanthroline and measured in a 1 cm cuvette.

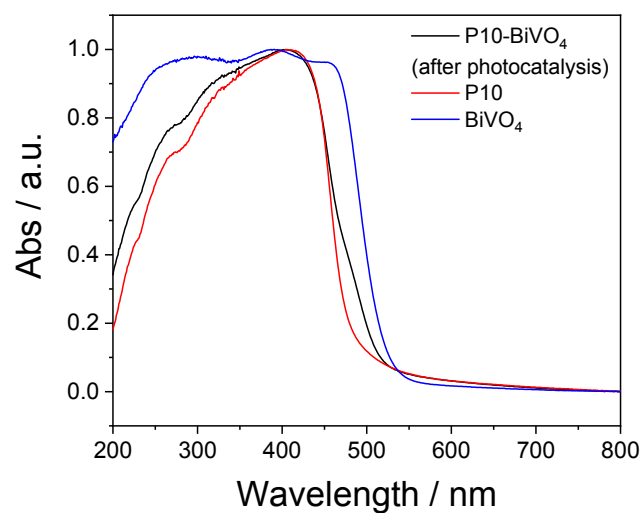


Figure S-31. UV-Vis absorption spectra of **P10-BiVO₄ mixture** (after photocatalysis), **P10**, and **BiVO₄** measured as powders in the solid-state.

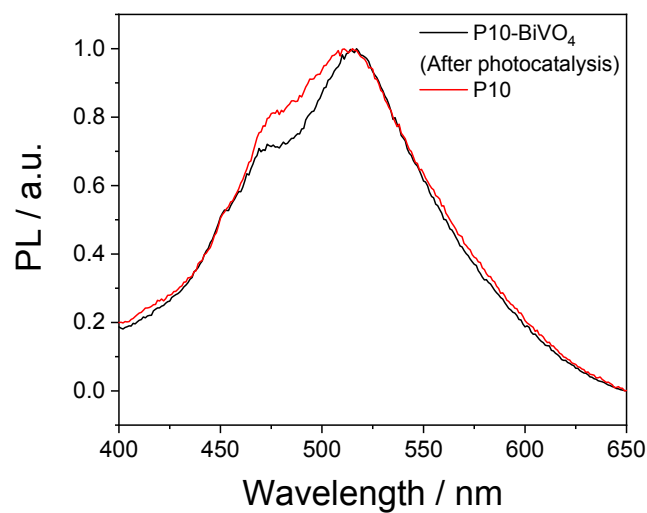


Figure S-32. Photoluminescence spectra ($\lambda_{\text{exc}} = 350 \text{ nm}$) of **P10**, **BiVO₄** before photocatalysis and the **P10-BiVO₄** mixture after 20 hours under visible light irradiation (300 W Xe light source, $\lambda > 420 \text{ nm}$).

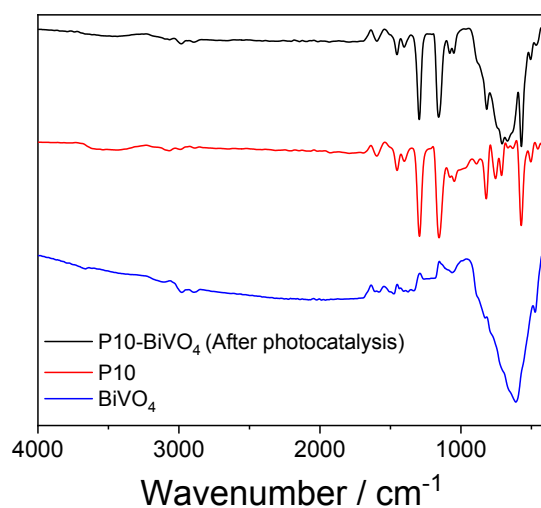


Figure S-33. Transmission FT-IR spectra of **P10** and **BiVO₄** before photocatalysis and **P10-BiVO₄** mixture after photocatalysis.

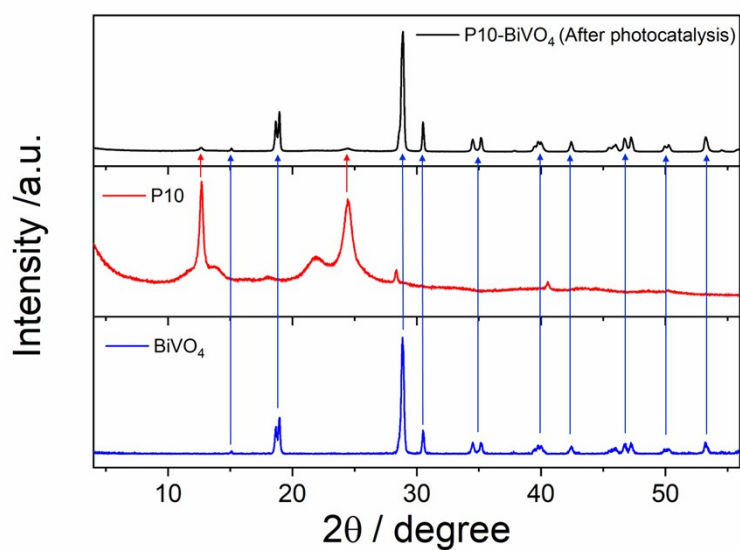


Figure S-34. pXRD patterns of **P10-BiVO₄** (after photocatalysis), **P10**, and **BiVO₄**.

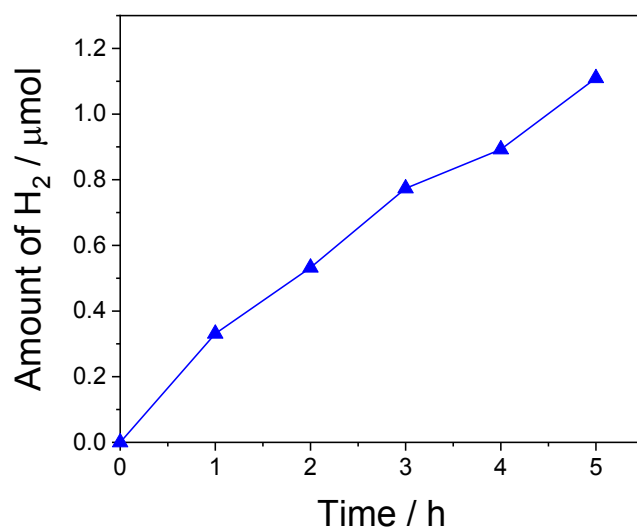


Figure S-35. Time course of hydrogen evolution of 4 mg **P10** in water (120 mL, pH 2.7). The reactions were carried out under visible light illumination (PerkinElmer CERMAX PE300BF 300 W Xe light source, $\lambda > 420$ nm) in a top-irradiation cell with a Pyrex window.

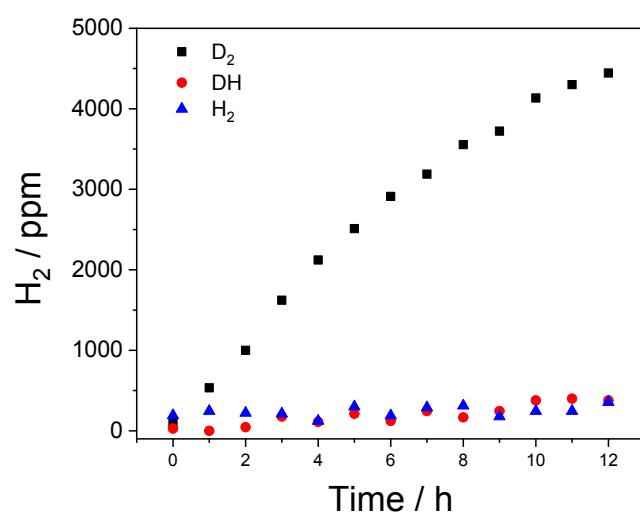


Figure S-36. Time course of hydrogen and deuterium evolution of **P10** (20 mg) in a $\text{FeCl}_2\text{D}_2\text{O}$ solution (2 mmol L^{-1} , 20 mL, pH 2.7, pH adjusted with D_2SO_4). The reactions were carried out under broadband illumination (Newport 300 W Xe light source, $\lambda > 295 \text{ nm}$) with side-illumination through a quartz window.

6. TA Measurements

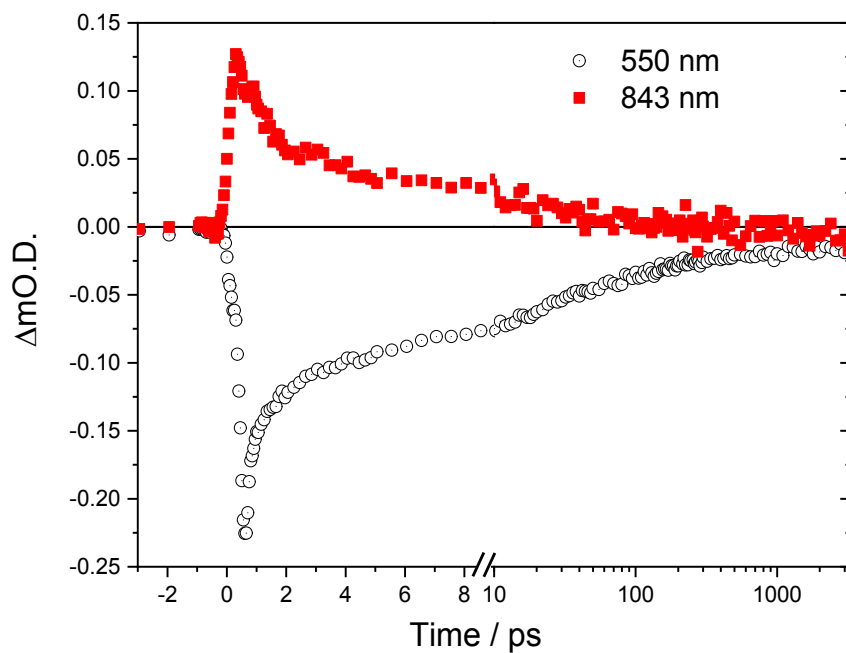


Figure S-37. TA decay traces following 400 nm excitation (150 nJ, 5 kHz) of **P10** suspension in water at pH 2.7 (0.24 g L⁻¹).

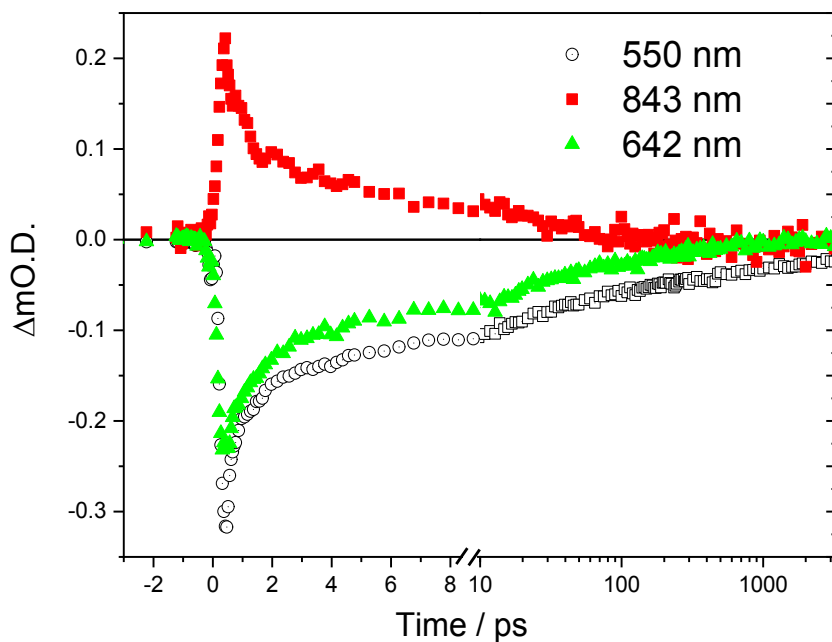


Figure S-38. TA decay traces following 400 nm excitation (150 nJ, 5 kHz) of **P10** suspension in water at pH 2.7 (0.24 g L⁻¹) in the presence of 4 mM Fe²⁺.

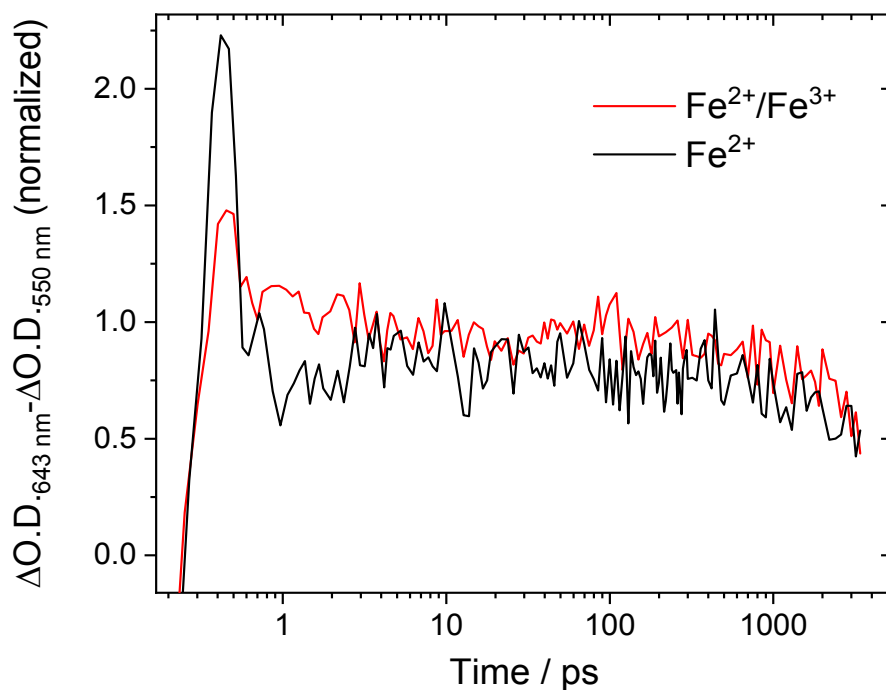


Figure S-39. Estimation of **P10** electron polaron lifetime for suspensions of **P10** with Fe^{2+} in the absence and presence of Fe^{3+} . To visualise the lifetime of the smaller PIA at 643 nm of the polaron the effect of the large bleach due to stimulated emission has been subtracted (550 nm). The TA decay traces are recorded following 400 nm excitation (150 nJ, 5 kHz) of **P10** suspension in water at pH 2.7 (0.24 g L^{-1}).

7. References

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2. M. Sachs, R. S. Sprick, D. Pearce, S. A. J. Hillman, A. Monti, A. A. Y. Guilbert, N. J. Brownbill, S. Dimitrov, X. Shi, F. Blanc, et al. Understanding Structure-activity Relationships in Linear Polymer Photocatalysts for Hydrogen Evolution. *Nat. Commun.* **2018**, *9*, 1–11.