

Supporting Information

Embedding Molecular Photosensitizers and Catalysts in Nanoporous Block Copolymer Membranes for Visible-light Driven Hydrogen Evolution

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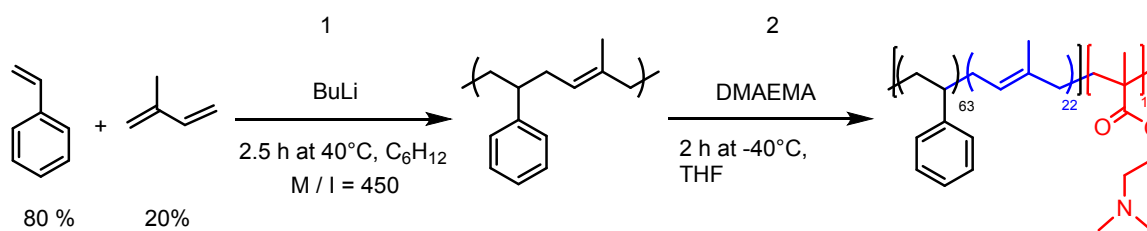
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1. Synthesis of poly(styrene-*co*-isoprene)-*block*-poly(*N,N*-dimethylaminoethyl methacrylate) (P(S-*co*-I)-*b*-PDMAEMA)



Scheme 1. Synthesis of the amphiphilic **P(S-*co*-I)-*b*-PDMAEMA** block copolymer *via* sequential anionic polymerization.

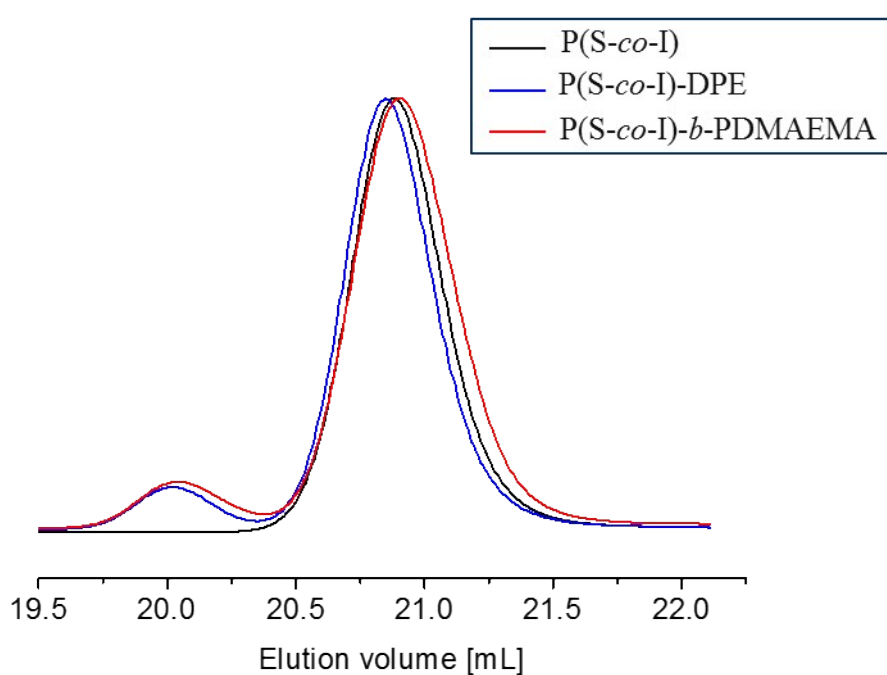


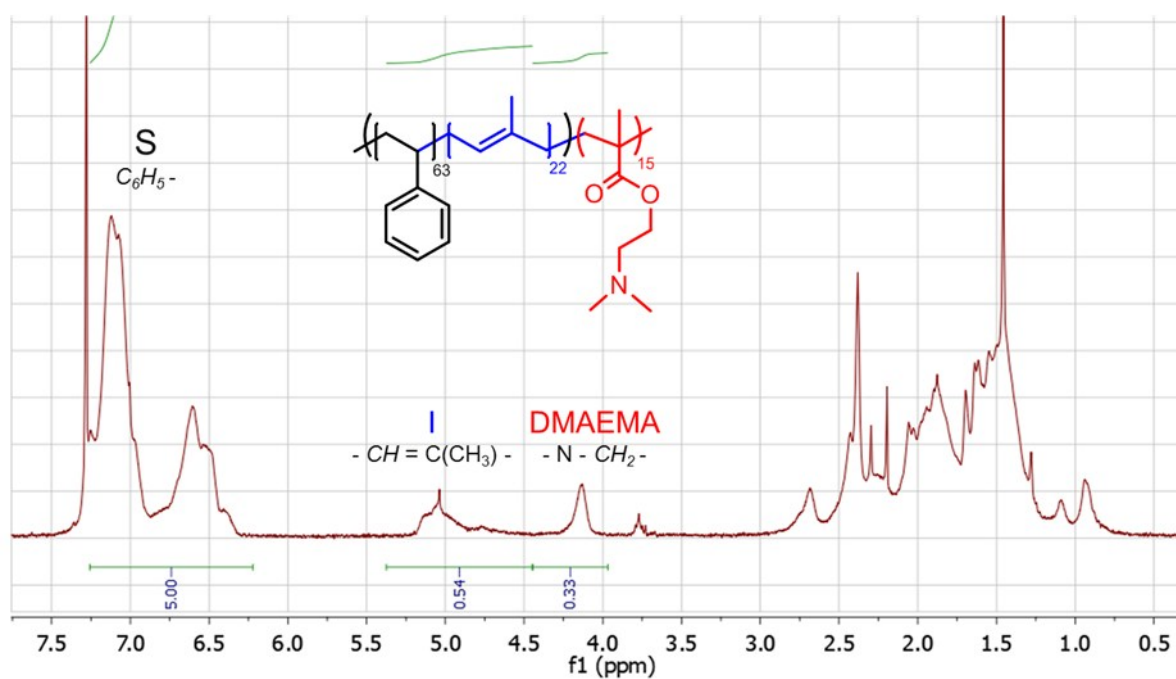
Figure S1. SEC elution traces (solvent: THF) of poly(styrene-*co*-isoprene) (P(S-*co*-I)), poly(styrene-*co*-isoprene) capped with diphenylethylene (P(S-*co*-I)-DPE) and poly(styrene-*co*-isoprene)-*block*-poly(*N,N*-dimethylaminoethyl methacrylate) (P(S-*co*-I)-*b*-PDMAEMA); upon the addition of DPE a certain amount of chain-chain coupling occurred as visible from the SEC traces.

Table S1. Characteristics of obtained amphiphilic **P(S-co-I)-b-DMAEMA** diblock terpolymer

Sample	Weight fraction, %			M_n , g mol ⁻¹	\bar{D}
	(S)	(I)	(DMAEM A)		
P(S-co-I)	73	27	-	54 660 ^b	1.03 ^b
P(S-co-I)-b-PDMAEMA	63	22	15	64 700 ^a	1.13 ^b

[a] Determined by ¹H NMR. [b] Determined by SEC using PS calibration.

¹H NMR

**Figure S2.** ¹H NMR of poly(styrene-co-isoprene)-*block*-poly(*N,N*-dimethylaminoethyl methacrylate).

2. SEM characterization

Porous block copolymer membranes were fabricated using the NIPS process. To this end, we used a 50:50 weight % mixture of THF and DMF as casting solvent, a block copolymer concentration of 10 wt. % and open times of 15 – 90 seconds. Note that 15 second open times resulted in the formation of a finger-like morphology, while longer open times led to sponge-like membranes.

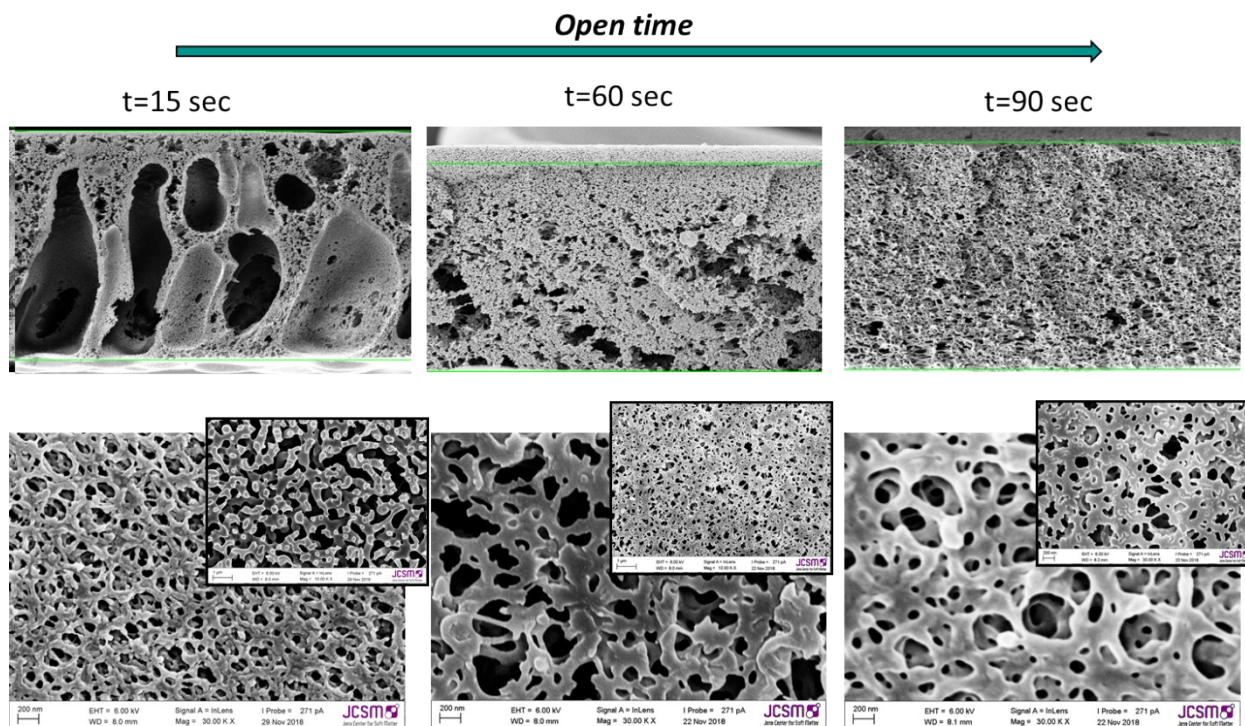


Figure S3. SEM micrographs of membranes prepared from P(S-co-I)-b-PDMAEMA block copolymer *via* the NIPS process by applying different open times (15, 60, 90 sec). The first row represents membrane cross-sections and the second row shows membrane top and bottom views.

3. EDX characterization

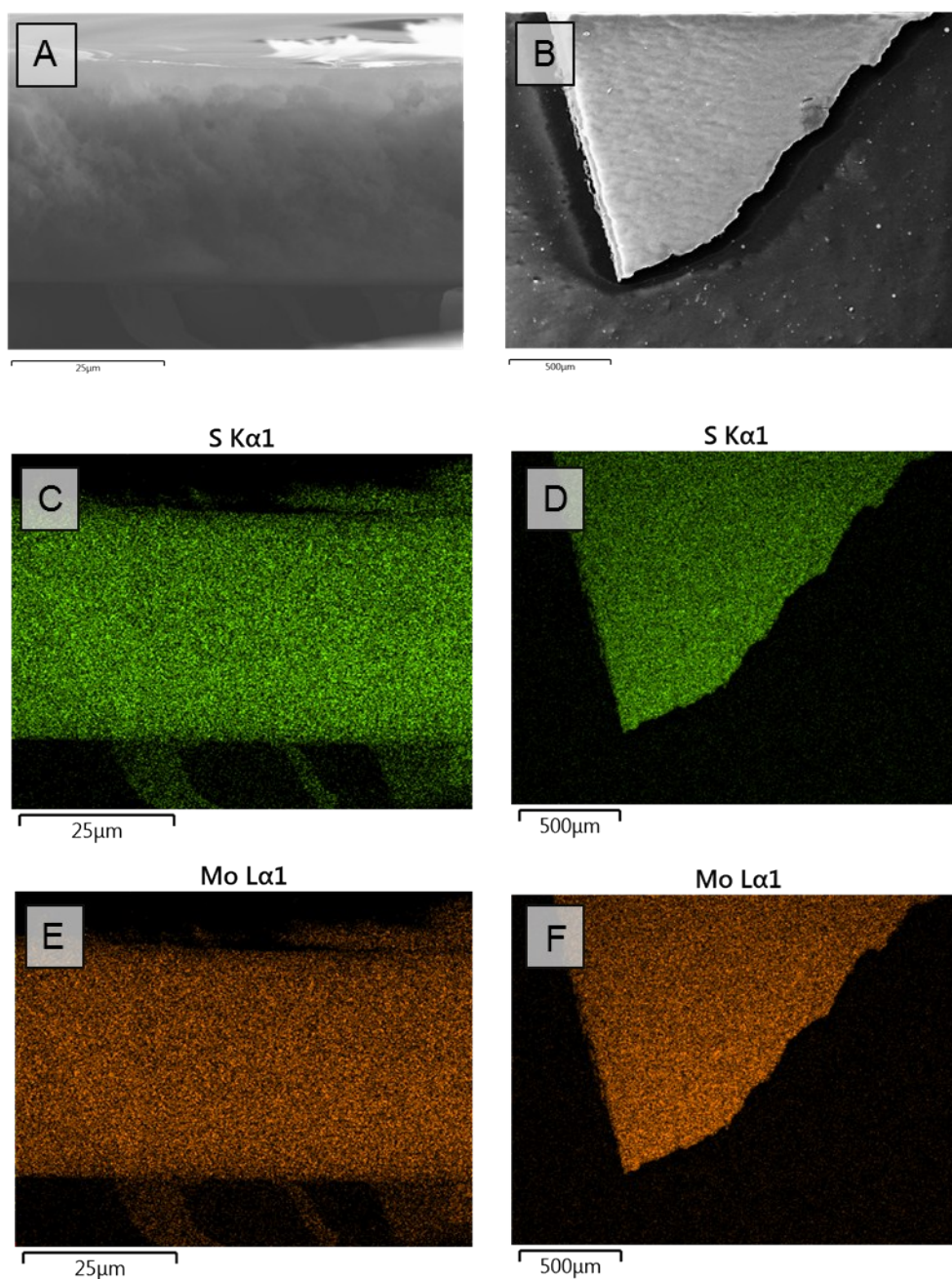


Figure S4. SEM micrographs of $[\text{Mo}_3\text{S}_{13}]^{2-}$ containing membrane **2** cross-section (A) and top view (B). EDX mapping of sulphur (C, D) and molybdenum (E, F) on membrane **2** cross-section (left) and top view (right).

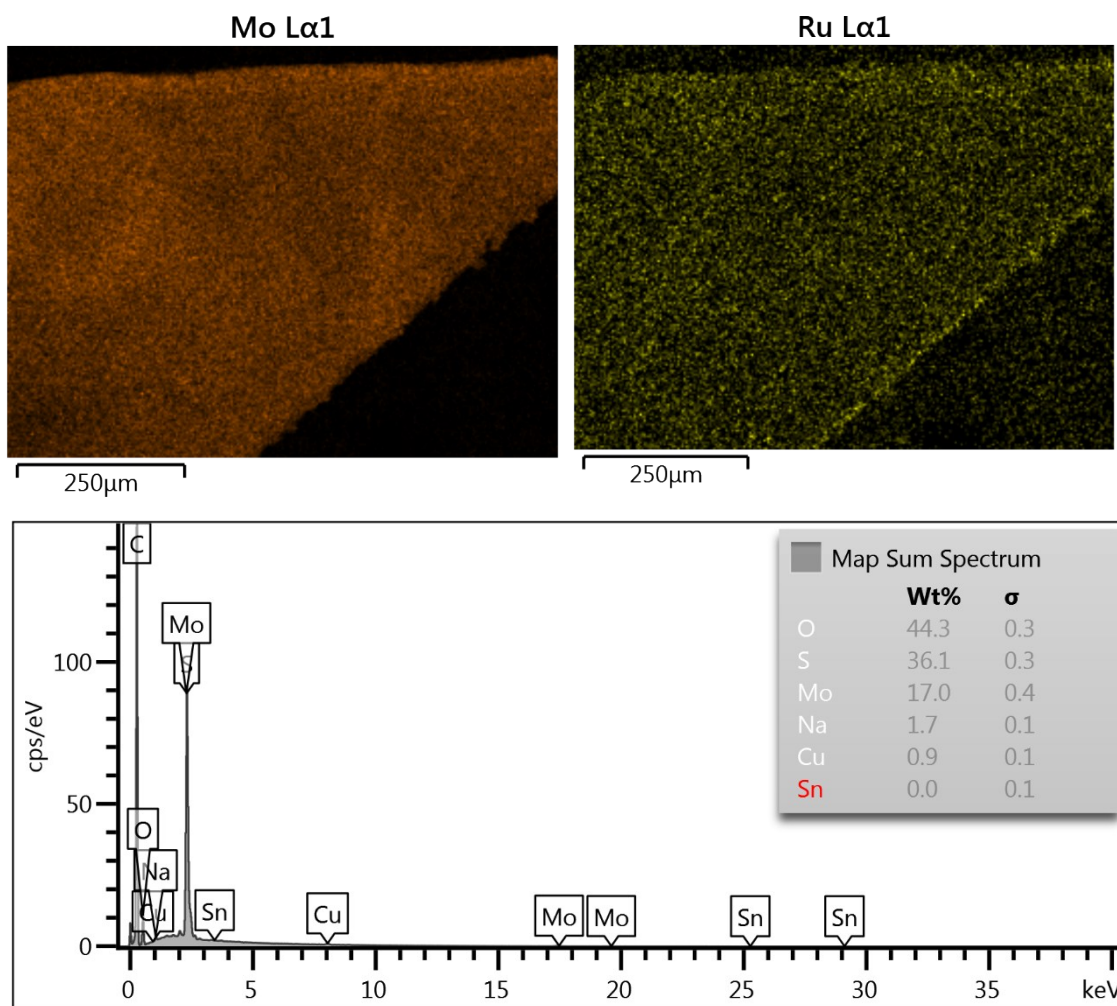


Figure S5. EDX spectra and elemental mapping of membrane **3** containing $[\text{Mo}_3\text{S}_{13}]^{2-}$ catalyst and $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer top view.

4. XPS characterization of membrane after immobilization of $[\text{Mo}_3\text{S}_{13}]^{2-}$

For the non-modified membrane **1** the high resolution C 1s XPS spectrum showed the expected signature according to the chemical structure of the block copolymer. The signals can be attributed to C-C (red, 284.6 eV), C-N (green, 285.6 eV) and COO groups (blue, 288.9 eV). The N 1s and O 1s signals are confirming the presence of C-N and COO bonds, respectively. The presence of an additional signal in the C-N bond region (turquoise, 402.5 eV) is characteristic for ammonium groups and indicates the protonation of part of the DMAEMA units ($-\text{NMe}_2\text{H}^+$).

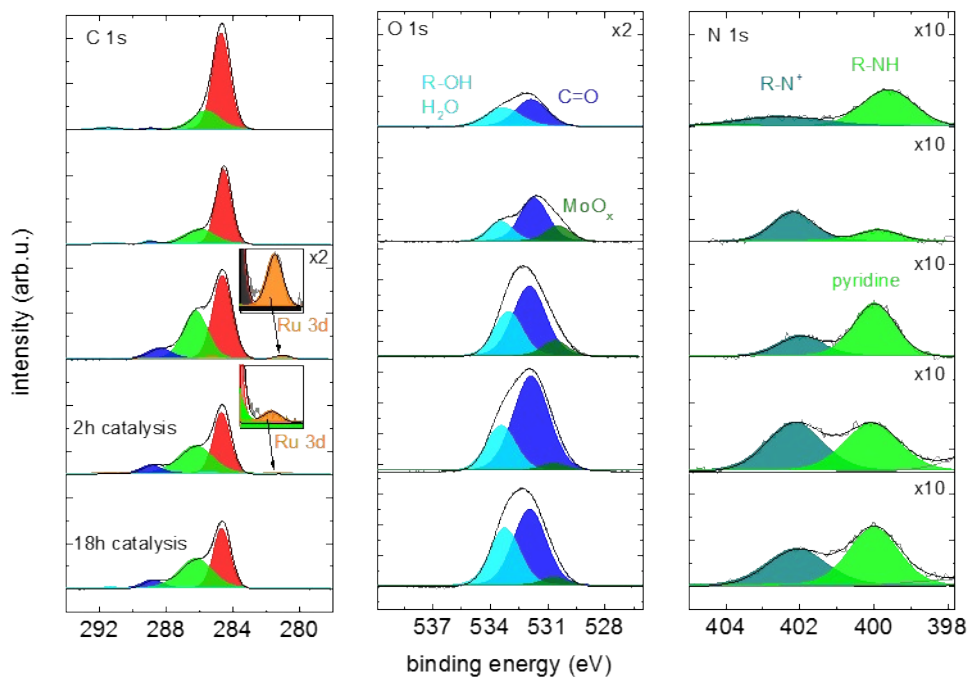


Figure S6. High-resolution C 1s, O 1s and N 1s XPS spectra of membrane **1**, membrane **2** (containing $[\text{Mo}_3\text{S}_{13}]^{2-}$), membrane **3** (containing $[\text{Mo}_3\text{S}_{13}]^{2-}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$), as well as post-catalytic samples of membrane **3** after 2h and 18h of HER catalysis.

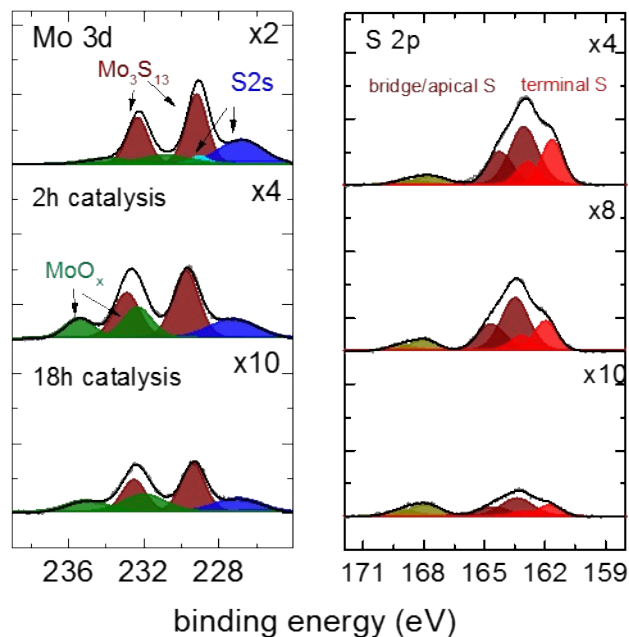


Figure S7. High-resolution Mo 3d and S 2p XPS spectra of membrane **3** (containing $[\text{Mo}_3\text{S}_{13}]^{2-}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$), as well as post-catalytic samples of membrane **3** after 2h and 18h of HER catalysis.

Table S2. Chemical composition of membranes determined by XPS. For calculation the relative sensitivity factors (RSF) of 1.68 (S 2p), 1 (C 1s), 2.93 (O 1s), 1.8 (N 1s), 5.65 (Mo 3d_{5/2}) and 7.39 (Ru 3d_{5/2}) are used, respectively.

Sample	S (at%)	C (at%)	O (at%)	N(at%)	Mo(at%)	Ru (at %)
1	0.5	87.9	8.9	2.8	-	-
2	18.0	63.7	11.8	1.7	4.8	-
3	14.0	56.8	22.2	3.0	3.7	0.2
3 after 2h catalysis	4.8	66.6	22.4	4.0	2.1	0.1
3 after 10h catalysis	3.7	73.9	17.8	3.0	1.6	-
3 after 18h catalysis	2.1	71.4	21.7	4.2	0.7	-
3 after 48h catalysis	1.9	75.1	19.1	3.0	0.8	-

5. RDS spectroscopy

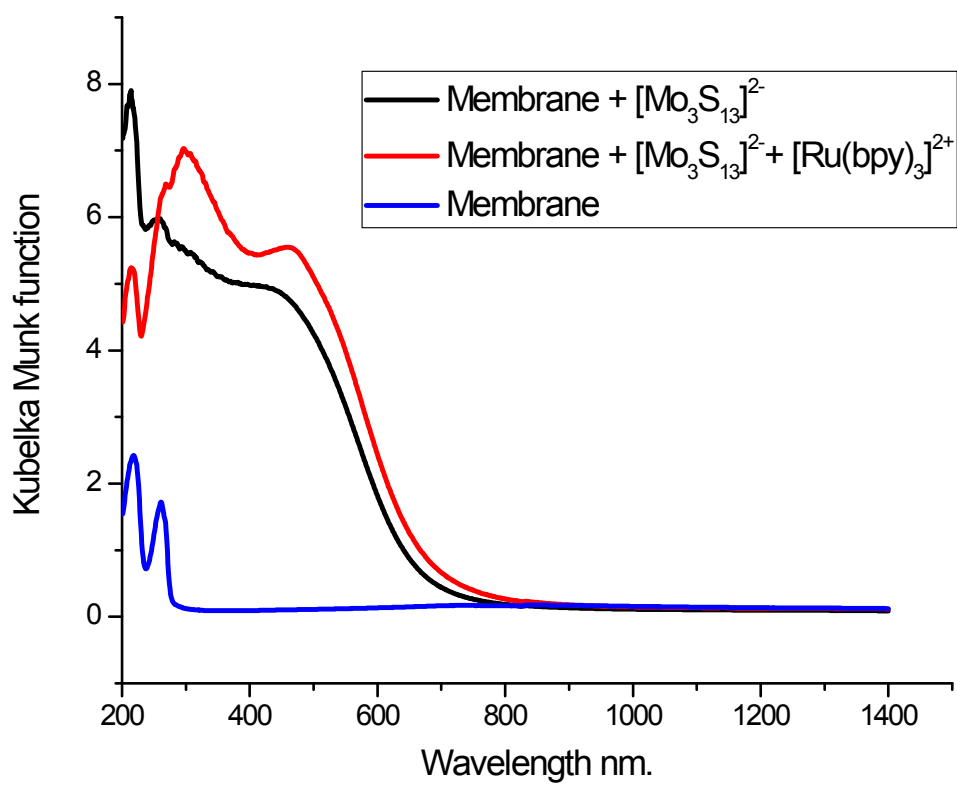


Figure S8. RDS spectra of net membrane, membrane containing [Mo₃S₁₃]²⁻ catalyst (24 wt. % of Mo) and membrane containing both [Mo₃S₁₃]²⁻ and photosensitizer [Ru(bpy)₃]²⁺. Here, the membrane with 24 wt. % of Mo was used for PS attachment.

6. Catalysis

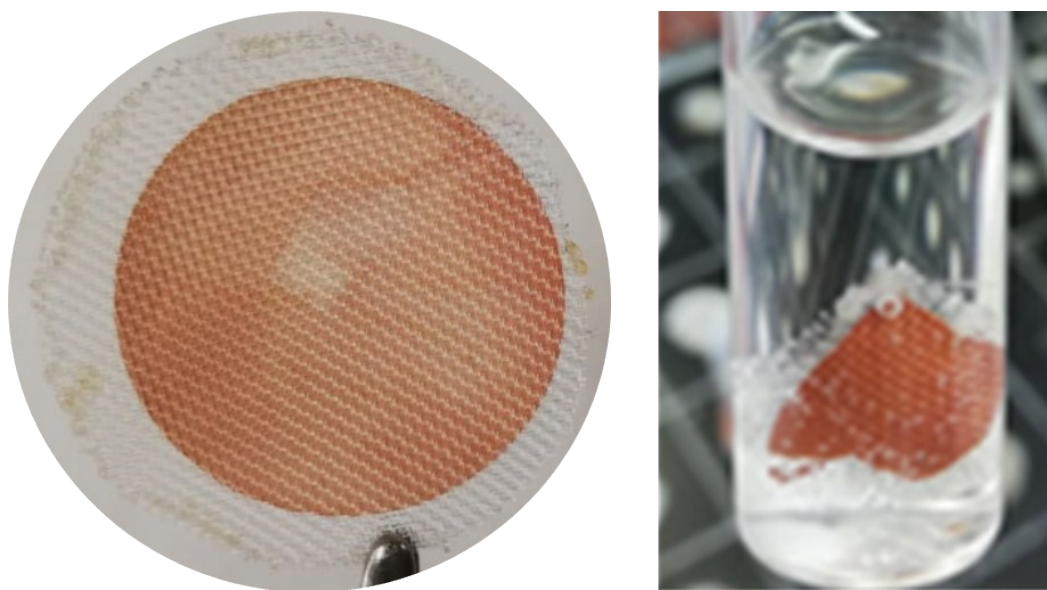


Figure S9. Photo of sandwiched membrane between two polyamide meshes (left) and photo of GC vials containing caged membrane (right).

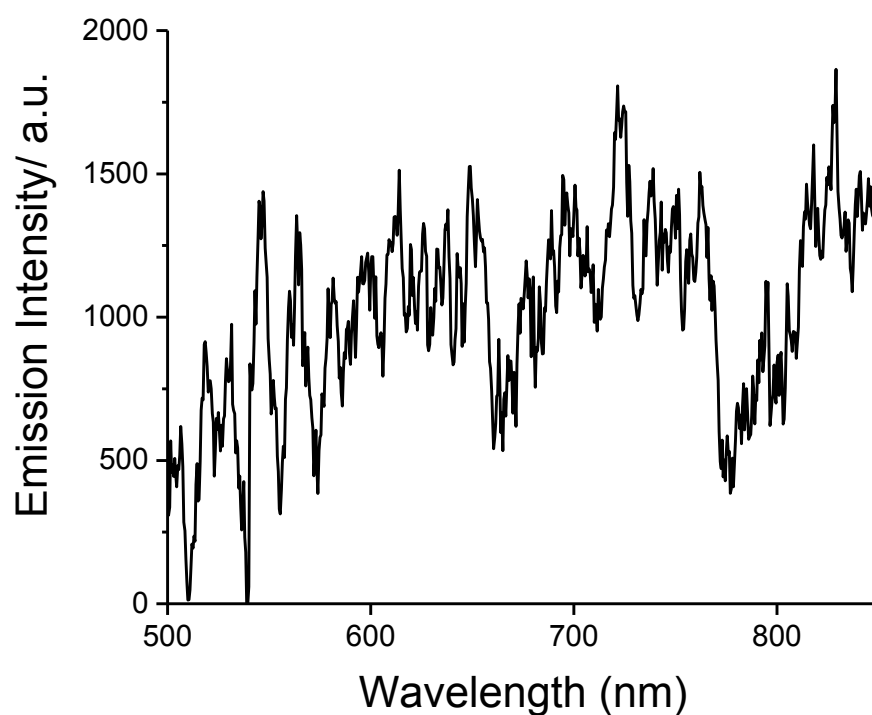


Figure S10. Emission spectrum of supernatant solution withdrawn from HER reaction with photocatalytic membrane after 48 h of irradiation. No emission related to $[Ru(bpy)_3]^{2+}$ could be found, showing that no intact Ru-PS is leached.

Catalytic performance of membrane 3 over time.

A standard catalytic run was performed as described above in a Schlenk flask equipped with a H₂-impermeable septum to enable sampling over time. The GC analyses show that the membrane produced hydrogen for up to 18 h and then reaches a plateau after which hydrogen evolution stops.

Table S3. HER activity over time shows the formation of a plateau after ~ 20 h irradiation.

<i>Time, h</i>	<i>Amount of H₂ (μmol/g)</i>
<i>0</i>	<i>0</i>
<i>18</i>	<i>32.3</i>
<i>24</i>	<i>40.3</i>
<i>40</i>	<i>41.0</i>
<i>46</i>	<i>40.2</i>

Experimental details: the experiment was performed in Schlenk flask with total volume of 21.85 mL. 15 mL of the catalytic reaction mixture were used, the headspace gas volume was 6.85 mL. 8.35 mg of caged membrane was used in this case. Conditions: MeOH:H₂O (9:1, v:v), ascorbic acid (0.1 M), pH ~ 5.8