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1. Experimental Section

General methods: All reagents were obtained from Sigma-Aldrich or from Fluorochem and used as received. CP-CMP1 was synthesised according to a previously published procedure.^[1] Water for the hydrogen evolution experiments was purified using an ELGA LabWater system with a Purelab Option S filtration and ion exchange column without pH level adjustment. Reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. CHN Analysis was performed on a Thermo EA1112 Flash CHNS-O Analyzer using standard microanalytical procedures. Palladium content was determined via ICP-OES by Butterworth Laboratories Ltd (Teddington, United Kingdom). Isotherms were measured using Micromeritics 2420 volumetric adsorption analyser. Surface areas were calculated in the relative pressure (P/P_0) range from 0.01 to 0.10 of the adsorption branch. Transmission FT-IR spectra were recorded on a Bruker Tensor 27 at room temperature; samples were prepared as pressed KBr pellets. Thermogravimetric analysis was performed on a Q500 TGA by heating samples at 10 °C min⁻¹ under air in open aluminium pans to 750 °C. The UV-visible absorption spectra of the polymer networks were recorded on a Shimadzu UV-2550 UV-vis spectrometer as powders in the solid state. The fluorescence spectra of the polymer powders were measured with a Shimadzu RF-5301PC fluorescence spectrometer at room temperature. Imaging of the polymer morphology was performed on a Hitachi S4800 Cold Field Emission SEM, with secondary electron, backscatter and transmission detectors. EDX Measurements were performed on an Oxford Instruments INCA ENERGY 250 M/X. 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. Time-correlated single photon counting (TCSPC) was performed on a Horiba DeltaFlex TCSPC system, equipped with NanoLED pulsed excitation sources and a PPD-650 photon counting detector. Either 404 nm diode (instrument response 200 ps fwhm), with a 435 nm high pass filter for emission detection, or a 282 nm diode (instrument response 1 ns fwhm), with a 315 nm high pass filter for emission detection were used. CMP suspensions were prepared by ultrasonicating 2 mg of the polymer in 5 mL of THF for 10 min and diluting them until the stop count rate was below 2% (typically around 1% was used). The prompt was measured for THF at the excitation wavelength without filter. Decay times were fitted in the DAS 6 software using suggested lifetime estimates.

Hydrogen evolution experiments: A flask was charged with the polymer powder (25 mg), water (7.5 mL), triethylamine (7.5 mL), methanol (7.5 mL), and sealed with a septum. The resulting suspension was ultrasonicated until the photocatalyst was dispersed before degassing by N₂ bubbling for 30 minutes. The reaction mixture was illuminated with a 300 W Newport Xe light-source (Model: 6258, Ozone free) for the time specified using appropriate filters. NIR light was absorbed by circulating water through a fused silica window. Gas samples were taken with a gas-tight syringe, and run on a Bruker 450-GC gas chromatograph equipped with a Molecular Sieve 13X 60-80 mesh 1.5 m $\times \frac{1}{3}$ " \times 2 mm ss column at 50 °C with an argon flow of 40.0 mL min⁻¹. Hydrogen was detected with a thermal conductivity 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. The rates were determined from a linear regression fit (from 1 hour to 5 hours) and the error is given as the standard deviation of the amount of hydrogen evolved. No hydrogen evolution was observed for a mixture of water/methanol/trimethylamine under >295 nm illumination in absence of a photocatalyst.

General procedure for the synthesis of the conjugated microporous polymers via Suzuki-Miyaura-type polycondensation: A flask was charged with the monomers, *N*,*N*dimethylformamide, an aqueous solution of K_2CO_3 (2.0 M) and degassed by bubbling with N_2 for 20 minutes. [Pd(PPh_3)_4] was added and the reaction mixture was degassed by bubbling with N_2 for further 10 minutes before heating 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 to remove any low-molecular weight by-products and the product was dried under reduced pressure. Note: The yields were calculated ignoring the presence of end functional groups whose nature is unclear.

Synthesis of PE-CMP: 1,2,4,5-Tetrabromobenzene (0.984 g, 2.5 mmol), 4,4'biphenyldiboronic acid (1.21 g, 5.0 mmol), $[Pd(PPh_3)_4]$ (75 mg), *N*,*N*-dimethylformamide (75 mL) and aqueous K₂CO₃ (2.0 M, 15 mL) were used in this reaction. After work-up and Soxhlet extraction with chloroform, the product was obtained as a grey powder (1.52 g, 80%). Anal. Calcd for (C₃₀H₁₈)_n: C, 95.21; H, 4.79%; Found C, 81.64; H, 4.46%. **Synthesis of M-CMP:** 1,3,5-Tribromobenzene (1.05 g, 3.33 mmol), 1,4-benzene diboronic acid (829 mg, 5.0 mmol), $[Pd(PPh_3)_4]$ (75 mg), *N*,*N*-dimethylformamide (75 mL) and aqueous K₂CO₃ (2.0 M, 15 mL) were used in this reaction. After work-up and Soxhlet extraction with chloroform, the product was obtained as a light brown solid (654 mg, 69%). Anal. Calcd for $(C_{15}H_9)_n$: C, 95.21; H, 4.79%; Found C, 81.48; H, 4.55%.

Synthesis of ME-CMP: 1,3,5-Tris(4-bromophenyl)benzene (543 mg, 1.0 mmol), 1,4-benzene diboronic acid (249 mg, 1.5 mmol), $[Pd(PPh_3)_4]$ (15 mg), *N*,*N*-dimethylformamide (15 mL) and aqueous K₂CO₃ (2.0 M, 3 mL) were used in this reaction. After work-up and Soxhlet extraction with THF, the product was obtained as a white powder (320 mg, 77%). Anal. Calcd for $(C_{20.2}H_{12.8})_n$: C, 94.75; H, 5.42%; Found C, 86.86; H, 4.83%.

Synthesis of SP-CMP: 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (1.26 g, 2.0 mmol), 1,4benzene diboronic acid (663 mg, 4.0 mmol), $[Pd(PPh_3)_4]$ (40 mg), *N*,*N*-dimethylformamide (40 mL) and aqueous K₂CO₃ (2.0 M, 8 mL) were used in this reaction. After work-up and Soxhlet extraction with THF, the product was obtained as a dark grey powder (1.02 g, quant.). Anal. Calcd for $(C_{37}H_{20})_n$: C, 95.66; H, 4.34%; Found C, 86.19; H, 4.18%.

Synthesis of ESP-CMP: 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (1.14 g, 1.8 mmol), 4,4'biphenyldiboronic acid (873 mg, 3.6 mmol), $[Pd(PPh_3)_4]$ (55 mg), *N*,*N*-dimethylformamide (55 mL) and aqueous K₂CO₃ (2.0 M, 11 mL) were used in this reaction. After work-up and Soxhlet extraction with chloroform, the product was obtained as a grey-green powder (1.27 g, quant.). Anal. Calcd for $(C_{49}H_{28})_n$: C, 95.42; H, 4.58%; Found C, 77.96; H, 4.01%.

	Pd content / %ª		
M-CMP	0.91 (±0.01)		
ME-CMP	0.39 (±0.01)		
PE-CMP	0.42 (±0.02)		
SP-CMP	0.38 (±0.08)		
ESP-CMP	0.40 (±0.01)		

Table S-1. Pd content of the CMPs determined via ICP-OES.

[a] Average of two measurements, the standard deviation is given in the brackets.

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2. Gas Sorption Isotherms



Figure S-1. Nitrogen sorption isotherm (left) for polymer network **CP-CMP1**, measured at 77.3 K and up to 1 bar, and hydrogen sorption isotherm (right) for polymer network **CP-CMP1**, measured at 77.3 K.



Figure S-2. Nitrogen sorption isotherm (left) for polymer network **M-CMP**, measured at 77.3 K and up to 1 bar, and hydrogen sorption isotherm (right) for polymer network **M-CMP**, measured at 77.3 K.



Figure S-3. Nitrogen sorption isotherm (left) for polymer network **ME-CMP**, measured at 77.3 K and up to 1 bar, and hydrogen sorption isotherm (right) for polymer network **ME-CMP**, measured at 77.3 K.



Figure S-4. Nitrogen sorption isotherm (left) for polymer network **PE-CMP**, measured at 77.3 K and up to 1 bar, and hydrogen sorption isotherm (right) for polymer network **PE-CMP**, measured at 77.3 K.



Figure S-5. Nitrogen sorption isotherm (left) for polymer network **SP-CMP**, measured at 77.3 K and up to 1 bar, and hydrogen sorption isotherm (right) for polymer network **SP-CMP**, measured at 77.3 K.



Figure S-6. Nitrogen sorption isotherm (left) for polymer network **ESP-CMP**, measured at 77.3 K and up to 1 bar, and hydrogen sorption isotherm (right) for polymer network **ESP-CMP**, measured at 77.3 K.

3. UV and Photoluminescence Spectra



Figure S-7. Solid-state UV-Vis and photoluminescence spectra (λ_{exc} = 360 nm) of **CP-CMP1**.



Figure S-8. Solid-state UV-Vis and photoluminescence spectra (λ_{exc} = 360 nm) of **PE-CMP**.



Figure S-9. Solid-state UV-Vis and photoluminescence spectra (λ_{exc} = 360 nm) of **M-CMP**.



Figure S-10. Solid-state photoluminescence spectra of **M-CMP** with different λ_{exc} .



Figure S-11. Solid-state UV-Vis and photoluminescence spectra (λ_{exc} = 360 nm) of **ME-CMP**.



Figure S-12. Solid-state UV-Vis and photoluminescence spectra (λ_{exc} = 360 nm) of SP-CMP.



Figure S-13. Solid-state UV-Vis and photoluminescence spectra of (λ_{exc} = 360 nm) **ESP-CMP**.

	SA _{BET} ^a / m ² g ⁻¹	Quantity H ₂ adsorbed ^b / cm ³ g ⁻¹	<i>SA</i> _{Langmuir} ^c / m ² g ⁻¹	Eg ^d / eV	λ _{em} e / nm
CP-CMP1	683	102.8	391	2.95	443
PE-CMP	489	84.0	329	2.90	438
M-CMP	570	62.3	241	3.46	379
ME-CMP	41	60.9	331	3.07	410
SP-CMP	895	151.4	581	2.84	453
ESP-CMP	522	106.3	406	2.86	456

Table S-2. Sorption and photo-physical properties of the CMPs.

[a] Calculated in the relative pressure (P/P₀) range from 0.01 to 0.10 of the adsorption branch,[b] Maximum amount of hydrogen adsorbed at 113 kPa, [c] Calculated of the adsorption branch, [d]Calculated from the UV-visible absorption on-set; [e] Measured upon λ = 360 nm excitation.



Figure S-14. Transmittance characteristics of the quartz flask, >295 nm, >400 nm, and >420 nm filter used in this work.





Figure S-15. Transmission FT-IR spectra of the conjugated microporous polymer networks as KBr pellets.

5. Powder X-Ray Diffraction



Figure S-16. PXRD patterns of the conjugated microporous polymer networks.

6. Thermogravimetric Analysis



Figure S-17. Thermogravimetric analysis of the conjugated microporous polymer networks (heating rate 10 °C min⁻¹).



7. Scanning Electron Microscope/Energy-dispersive X-ray spectroscopy

Figure S-18. Scanning electron microscope (SEM) pictures of all CMPs.

Polymer		Element /	wt. %ª	
l'orymer	С	Br	К	Pd
CP-CMP1	86.55	0.23	0.86	_b
M-CMP	93.21	0.24	0.11	0.25
ME-CMP	90.14	0.71	_b	_b
PE-CMP	92.60	0.45	2.19	0.44
SP-CMP	92.21	0.96	0.76	0.31
ESP-CMP	91.20	0.66	0.42	_b

Table S-3. Energy-dispersive X-ray spectroscopy of the CMPs in this study.

[a] Average apparent composition of the sample determined *via* energy-dispersive X-ray spectroscopy in at least three points of the sample [b] Element not detected or not determined as characteristic peaks overlap with other element.

8. Hydrogen Evolution Experiments for Polymers



Figure S-19. Hydrogen evolution of **CP-CMP1** (25 mg) from a triethylamine/water/methanol mixture under $\lambda > 295$ nm, $\lambda > 400$ nm, and $\lambda > 420$ nm irradiation.



Figure S-20. Hydrogen evolution of **PE-CMP** (25 mg) from a triethylamine/water/methanol mixture under λ > 295 nm, λ > 400 nm, and λ > 420 nm irradiation.



Figure S-21. Hydrogen evolution of **M-CMP** (25 mg) from a triethylamine/water/methanol mixture under $\lambda > 295$ nm, $\lambda > 400$ nm, and $\lambda > 420$ nm irradiation.



Figure S-22. Hydrogen evolution of **ME-CMP** (25 mg) from a triethylamine/water/methanol mixture under λ > 295 nm, λ > 400 nm, and λ > 420 nm irradiation.



Figure S-23. Hydrogen evolution of **SP-CMP** (25 mg) from a triethylamine/water/methanol mixture under λ > 295 nm, λ > 400 nm, and λ > 420 nm irradiation.



Figure S-24. Hydrogen evolution of **ESP-CMP** (25 mg) from a triethylamine/water/methanol mixture under λ > 295 nm, λ > 400 nm, and λ > 420 nm irradiation.



Figure S-25. Hydrogen evolution of **SP-CMP** (25 mg) from a triethylamine/water/ethanol mixture under $\lambda > 420$ nm irradiation.



Figure S-26. Hydrogen evolution of **SP-CMP** (25 mg) from a triethylamine/water/acetonitrile mixture under $\lambda > 420$ nm irradiation.



Figure S-27. Hydrogen evolution of **SP-CMP** (25 mg) from a triethanolamine/water mixture under λ > 420 nm irradiation.



Figure S-28. Hydrogen evolution of **SP-CMP** (25 mg) from a triethylamine/water/methanol mixture under $\lambda > 420$ nm irradiation for a total of 74 hours.



Figure S-29. Wavelength dependency of the photocatalytic hydrogen evolution of **SP-CMP** (40 mg) from a triethylamine/water/methanol mixture with 400, 420 and 470 nm (± 10 nm, fwhm) filters.

	HERª > 420 nm / μmol h ⁻¹	Amount H ₂ evolved ^b > 420 nm / μmol	HERª > 400 nm / μmol h ⁻¹	Amount H ₂ evolved ^b > 400 nm / μmol	HERª >295 nm / μmol h ⁻¹	Amount H₂ evolved ^b > 295 nm / μmol
CP-CMP1	0.2	1.0	1.4	6.9	4.1	17.4
PE-CMP	0.5	2.1	2.5	10.5	17.9	85.1
M-CMP	0	0	0	0	<0.1	0.1
ME-CMP	0	0	0.2	0.7	9.8	44.6
SP-CMP	3.0	10.6	8.0	33.6	28.8	131.1
ESP-CMP	2.2	9.0	9.8	45.3	28.2	117.1

Table S-4. Hydrogen evolution rates and amounts of hydrogen evolved.

[a] Reaction conditions: 25 mg of the polymer was suspended in 22.5 mL of a triethylamine/methanol/water solution (1:1:1 ratio), irradiated by 300 W Xe lamp. [b] After 5 hours.

9. Stability Test for SP-CMP



Figure S-30. Hydrogen evolution of **SP-CMP** (25 mg) from a triethylamine/water/methanol mixture under $\lambda > 420$ nm and $\lambda > 295$ nm irradiation after degas with N₂.



Figure S-31. Solid-state UV-Vis and photoluminescence spectra of **SP-CMP**. After 74 hours under λ > 420 nm followed by 44 hours under λ > 295 nm irradiation showing no significant change in neither UV/Vis and PL spectra.



Figure S-32. Nitrogen sorption isotherm for polymer network **SP-CMP**, measured at 77.3 K and up to 1 bar, before and after photocatalysis. After 74 hours under $\lambda > 420$ nm followed by 44 hours under $\lambda > 295$ nm irradiation no significant change in the sorption properties is observed.



Figure S-33. Transmission FT-IR spectra of SP-CMP as KBr pellets before and after photocatalysis. Note that a small amount of triethylamine is still present in the polymer despite extensive washing with water and methanol and drying under vacuum at 100 °C.

10. Suspension Photoluminescence Spectra



Figure S-34. Excitation and photoluminescence spectra of CP-CMP1 in THF suspension.



Figure S-35. Excitation and photoluminescence spectra of M-CMP in THF suspension.



Figure S-36. Excitation and photoluminescence spectra of ME-CMP in THF suspension.



Figure S-37. Excitation and photoluminescence spectra of PE-CMP in THF suspension.



Figure S-38. Excitation and photoluminescence spectra of SP-CMP in THF suspension.



Figure S-39. Excitation and photoluminescence spectra of **ESP-CMP** in THF suspension.

11.Time-Correlated Single Photon Counting Measurements

	λ _{exc} / nm	λ _{em} / nm	T1ª / ns	T2ª / ns	Х ^{2 b}
CP-CMP1	282	400	0.76	3.05	0.46
M-CMP	282	400	1.91	7.63	0.65
ME-CMP	282	400	0.05	0.21	1.30
CP-CMP1	404	450	0.79	3.16	0.40
M-CMP	404	450	0.82	3.29	0.81
ME-CMP	404	450	0.28	1.12	0.65
PE-CMP	404	450	0.42	1.68	0.73
SP-CMP	404	450	0.54	2.15	0.52
ESP-CMP	404	450	0.49	1.94	0.55

Table S-5. Time-correlated single-photon counting results.

[a] Calculated by fitting the following equation: $A + B1 \times exp(-i/T1) + B2 \times exp(-i/T2)$. Initial amplitudes (A, B1, B2) are estimated and iterated along with the lifetimes (T1, T2) until a fit is found. The prompt is measured separately and used for deconvolution of the instrument response. [b] Chi-square test.

We note that the physical significance of the two exponential components is not determined, and most probably results from sample inhomogenieties. Similar trends were observed for both T1 and T2 between polymers, such that plots correlating either T1 or T2 versus photocatalytic behaviour gave similar results. For simplicity only T2 versus activity is shown in the main manuscript.



Figure S-40. Time-correlated single-photon counting measurement of **CP-CMP1**, **M-CMP**, **ME-CMP**, and **PE-CMP** in THF suspension with $\lambda_{exc} = 282$ nm and $\lambda_{em} = 400$ nm (left: 0-100 ns window, right: 5-40 ns window of the same experiments).



Figure S-41. Time-correlated single-photon counting measurement of CP-CMP1 (left), and PE-CMP (right) in THF suspension with λ_{exc} = 282 nm and λ_{em} = 400 nm.



Figure S-42. Time-correlated single-photon counting measurement of M-CMP (left), and ME-CMP (right) in THF suspension with λ_{exc} = 282 nm and λ_{em} = 400 nm.



Figure S-43. Time-correlated single-photon counting measurement of **PE-CMP**, **SP-CMP**, and **ESP-CMP** in THF suspension with λ_{exc} = 404 nm and λ_{em} = 450 nm (left: 0-100 ns window, right: 5-40 ns window of the same experiments).



Figure S-44. Time-correlated single-photon counting measurement of PE-CMP in THF suspension with λ_{exc} = 404 nm and λ_{em} = 450 nm.



Figure S-45. Time-correlated single-photon counting measurement of **SP-CMP** (left), and **ESP-CMP** (right) in THF suspension with λ_{exc} = 404 nm and λ_{em} = 450 nm.



Figure S-46. Correlation of the TCSPC experimental fits for T2 with the hydrogen evolution rates of the polymers under >420 nm illumination.

References

[1] R. S. Sprick, J. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* **2015**, *137*, 3265–3270.