

Electronic Supplementary Information for
Concomitant Shape and Palladium Engineering of Hollow Conjugated Microporous Photocatalysts to Boost Visible Light-Induced Hydrogen Evolution

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Experimental

General: TEM and EDS elemental mapping images were obtained using a JEOL-2100F. SEM images were obtained using a JSM6700F. N₂ adsorption-desorption isotherm curves were obtained at 77K using a Micromeritics ASAP2020. Surface areas were obtained based on the Brunauer-Emmett-Teller (BET) theory. The pore size distribution diagrams were obtained from the adsorption branches of the N₂ isotherm curves based on the nonlocal density functional theory (NLDF) method. The pore volumes were obtained by the t-plot. IR absorption spectra were obtained using a Bruker VERTEX70. Solid state ¹³C NMR spectra were obtained in the CP/TOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer. A 4 mm magic angle spinning probe was used. The spinning rate, pulse length, and power were 5 kHz, 2 ms, and 138W, respectively. PXRD patterns were obtained using a Rigaku MAX-2200 with a Cu K-alpha 1 light source. TGA curves were obtained using a Seiko Exstar 7300. Combustion elemental analysis was conducted using a CE EA1110 analyzer. The reflectance spectra of power samples were obtained using a Shimadzu UV-3600. The UV/vis absorption spectra were obtained through the conversion of the reflectance spectra. The emission spectra of aqueous suspensions (0.125 mg/mL) of materials were obtained using a JASCO FP-6200. ICP analysis was conducted using an OPTIMA8300. XPS spectra were obtained using a Thermo VG spectrometer. Water contact angles were obtained using a Theta Optical Tensiometer model (KSV instruments, Ltd.). Hydrodynamic diameters were measured using a Zetasizer ZS90 (Malvern). Time-resolved emission decay curves were obtained at the KBSI (Daegu center) using a confocal microscope (MicroTime-200, Picoquant, Germany). A single-mode pulsed diode laser (375 nm with 30 ps pulse width, average power of 10 nW) was used as an excitation light source. A dichroic mirror (Z375RDC, AHF), a long pass filter (HQ405lp, AHF), a 75 μm pinhole, and an avalanche photodiode detector (PDM series, MPD) were used to collect emission photons. A time-correlated single-photon counting system (PicoHarp300, PicoQuant GmbH, Germany) was used to count the emission photons. Exponential fitting was conducted using the Symphotime-64 software (ver. 2.2). Steady-state PL spectrum was obtained by dividing and guiding emission photons through an optical fiber to the external spectrometer (F-7000, Hitachi). GC analysis was conducted using an Agilent 6890. A 300 W Xe lamp with an optical filter (cut off < 400 nm) was used as a light source (Luxtel Ceralus CL300BF). Light intensities were measured by a THORLABS PM100D.

Synthesis H-MOP templates

To be used as templates, silica spheres with a diameter of 200 ~240 nm were prepared by following the Stöber method in the literature.¹ In this work, the following synthetic procedures were applied. Ethanol (200 mL), distilled water (8 mL), and ammonia aqueous solution (28~30%, 5 mL) were added to a 250 mL flask. The reaction mixture was stirred at room temperature for 30 min. After tetraethyl orthosilicate (TEOS, 14 mL) was added, the reaction mixture was stirred at room temperature for 18 h. The silica spheres (2 g) were separated by centrifugation and washed with ethanol (40 mL) five times. After being dried at room temperature, the silica spheres were heated at 500°C under air and cooled to room temperature. Tetra(4-ethynylphenyl)methane was prepared by following the synthetic method reported in the literature.² For the preparation of H-MOP, silica spheres (0.50 g), (PPh₃)₂PdCl₂ (14 mg, 20 μmol), CuI (4.0 mg, 40 μmol), distilled toluene (20 mL), and distilled triethylamine (40 mL) were added to a flame-dried 100 mL two-necked Schlenk flask under argon. The reaction mixture was sonicated at room temperature for 30 min. After tetra(4-ethynylphenyl)methane (83 mg, 0.20 mmol) and 1,4-diiodobenzene (132 mg, 0.40 mmol) were added, the reaction mixture was stirred at 90°C for 24 h. After being cooled to room temperature, the SiO₂@MOP was separated by centrifugation, washed with a mixture of methylene chloride (10 mL) and methanol (30 mL) five times, and dried under vacuum. After the SiO₂@MOP was added to a 50 mL Falcon tube, a mixture of aqueous HF solution (45%, 5 mL), distilled water (15 mL), and methanol (10 mL) was added. The reaction mixture was stirred at room temperature for 4 h. *Caution: The HF solution is very toxic and should be handled with special gloves under a hood. The excess HF solution was quenched with NaOH solution.* The H-MOP (0.10~0.12 g) was separated by centrifugation, washed with a mixture of water (10 mL) and methanol (30 mL) three times and methanol (40 mL) three times, and dried under vacuum.

Synthesis of H-MOP@SCMP-Pds and SCMP-Pd

For the preparation of H-MOP@SCMP-Pd2, H-MOP (20 mg), tris(4-trimethylstannylphenyl)amine and 3,7-dibromodibenzothiophene sulfone were prepared by following the synthetic methods in the literature.³ (PPh₃)₄Pd (37 mg, 32 μmol), and distilled DMF (20 mL) were added to a flame-dried 50 mL two-necked Schlenk flask under argon. After the reaction mixture was sonicated at room temperature for 30 min, tris(4-trimethylstannylphenyl)amine (59 mg, 80 μmol) and 3,7-dibromodibenzothiophene sulfone (45 mg, 0.12 mmol) were added. The reaction mixture was stirred at 110°C for 24 h. After being cooled to room temperature, the H-MOP@SCMP-Pd2 (37 mg) was separated by centrifugation, washed with a mixture of methylene chloride (10 mL) and methanol (30 mL) eight times and methanol (40 mL) once, and dried under vacuum. For the preparation of H-MOP@SCMP-Pd1 (33 mg), the same synthetic procedures of H-MOP@SCMP-Pd2 were applied except using (PPh₃)₄Pd (9.2 mg, 8.0 μmol). For the preparation of H-MOP@SCMP-Pd3 (42 mg), the same synthetic procedures of H-MOP@SCMP-Pd2 were applied except using (PPh₃)₄Pd (74 mg, 64 μmol). For the preparation of SCMP-Pd (27 mg), the same synthetic procedures of H-MOP@SCMP-Pd2 were applied without using H-MOP templates.

Photocatalytic reactions for hydrogen evolution

For the photocatalytic reaction for hydrogen evolution, H-MOP@SCMP-Pds, SCMP-Pd, or H-MOP (1.0 mg), triethanolamine (TEOA, 0.80 mL), distilled water (7.2 mL), and a spin bar were added to a tube-type glassware under nitrogen. The tube was closed with a septum and sealed completely with an insulating tape. After the reaction mixture was sonicated for 30 min at room temperature, it was bubbled by N₂ gas for 15 min. To be used as an internal standard, the 1 mL N₂ gas of the reaction mixture was replaced with 1 mL methane gas (an internal standard) by using a GC syringe. Then, the reaction mixture was stirred under irradiation of a 300 W Xe lamp (530 mW/cm² light intensity at the position of the tube, Luxtel Ceralus CL300BF). The light < 400 nm was cut off by an optical filter. During the photocatalytic reactions, the reaction temperature was maintained at room temperature (21±1°C) with a circulating water bath. The generated amounts of hydrogen at every 1 h were measured for 5 h using a GC (Agilent 6890) equipment with a thermal conductivity detector (TCD). The TCD detector has different detection sensitivities towards methane and hydrogen. Thus, the detection sensitivity of the GC equipment was calibrated by the average value from ten data points obtained by using the same amount of methane and hydrogen. For the recycling tests of H-MOP@SCMP-Pd₂, after the photocatalytic reaction for 5 h, the reaction mixture was bubbled with N₂ gas for 15 min to evacuate the generated hydrogen. Then, the next photocatalytic reaction was conducted. The results of the five independent reactions were obtained and treated statistically.

For the measurement of apparent quantum yields (AQYs) of H-MOP@SCMP-Pd₂, monochromatic light sources were obtained by using optical filters (400FS10-25, 420FS10-25, and 500FS10-25 for 400, 420, and 500 nm, respectively). AQYs were calculated by using the following equations.⁴

$$\text{AQY(\%)} = (\text{number of reacted electrons} \times 100) / \text{number of incident photons} = (2 \times \text{number of H}_2 \text{ molecules} \times N_A \times h \times c \times 100) / (S \times P \times t \times \lambda);$$

 N_A : Avogadro constant, h : Planck constant, c : speed of light, S : area value, P : light intensity, t : time, λ : wavelength. In our study, the light intensities at 400, 420, and 500 nm were 5.86, 5.86, and 10.7 mW/cm₂, respectively. The light intensities were measured by using a THORLABS PM100D. The irradiated area value was measured to be 7.73 cm².

Computation simulation

To estimate the HOMO and LUMO energy levels of the SCMP, the density functional theory (DFT) calculations were carried out. From the molecular aspect, SCMP consists of the electron-donating (triphenylamine, TA) and electron-withdrawing moieties (dibenzothiophene sulfone, DS). These moieties are alternately connected with π -conjugation. As shown in Fig. S7 in the ESI, we designed the model systems (M-1~5) representing the parts of SCMP. M-1~4 correspond to the gradually extended molecular structures of the conjugated triphenylamine and dibenzothiophene sulfone moieties, whereas M-5 is a branched networking case. These model systems were optimized at the B3LYP/6-31G* level using the Gaussian 16 program package.⁵

The calculated HOMO and LUMO energy levels for the model systems are depicted in Fig. S9 in the ESI. Interestingly, the HOMO energy levels of M-1~5 (-5.01~-5.05 eV) are located near to that of TA-donor (-

4.95 eV). On the contrary, the LUMO energy levels of M-1~5 (-1.84 ~ -2.02 eV) are close to that of DS-acceptor (-1.81 eV). In addition, the frontier molecular orbitals show that the electron densities of HOMO and LUMO for all M-1~5 are mainly distributed over TA-donor and DS-acceptor building blocks, respectively (Fig. S8 in the ESI). This implies that TA-donor and DS-acceptor contribute largely to the HOMO and LUMO of SCMP, respectively. For this reason, the extended/branched networking via Stille coupling might not lead to significant changes in the positions of HOMO and LUMO for SCMP. As a result, the calculated HOMO and LUMO energy levels of SCMP were expected to be around -2.0 and -5.1 eV based on our DFT calculations, respectively. Based on the frozen orbital approximation that is highly related to Koopmans' theorem, we can simply verify the possibility of hydrogen evolution reaction from the light harvesting process of SCMP bearing Pd nanoparticles. Because the standard hydrogen electrode (SHE) potential from vacuum level is located at round -4.44 eV below the LUMO energy level of SCMP (-2.0 eV), the photo-generated electrons on SCMP can promote the hydrogen generation through the reduction of H⁺. The triethanolamine (TEOA) having higher HOMO energy level (-4.99 eV), compared with that of SCMP (-5.1 eV), can act as an electron donor to compensate the charge of oxidized SCMP. Additionally, it is possible to understand the reason why SCMP cannot induce oxygen evolution reaction by taking into account the higher HOMO energy level of SCMP (-5.1 eV) compared with oxygen evolution reaction potential (-5.57 eV).

Reference

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Fig. S1. BET surface area plots of H-MOP, H-MOP@SCMP-Pds, and SCMP-Pd.

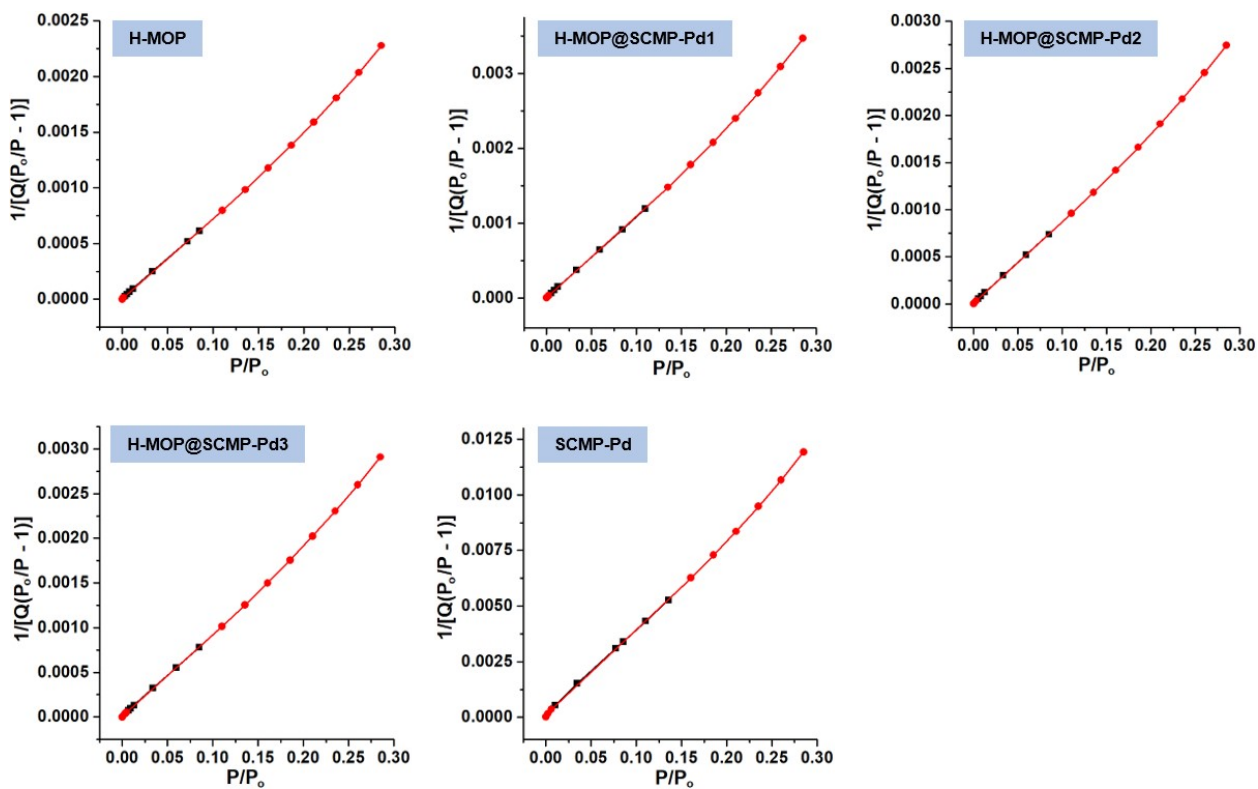


Fig. S2. XPS spectra of H-MOP, H-MOP@SCMP-Pds, and SCMP-Pd.

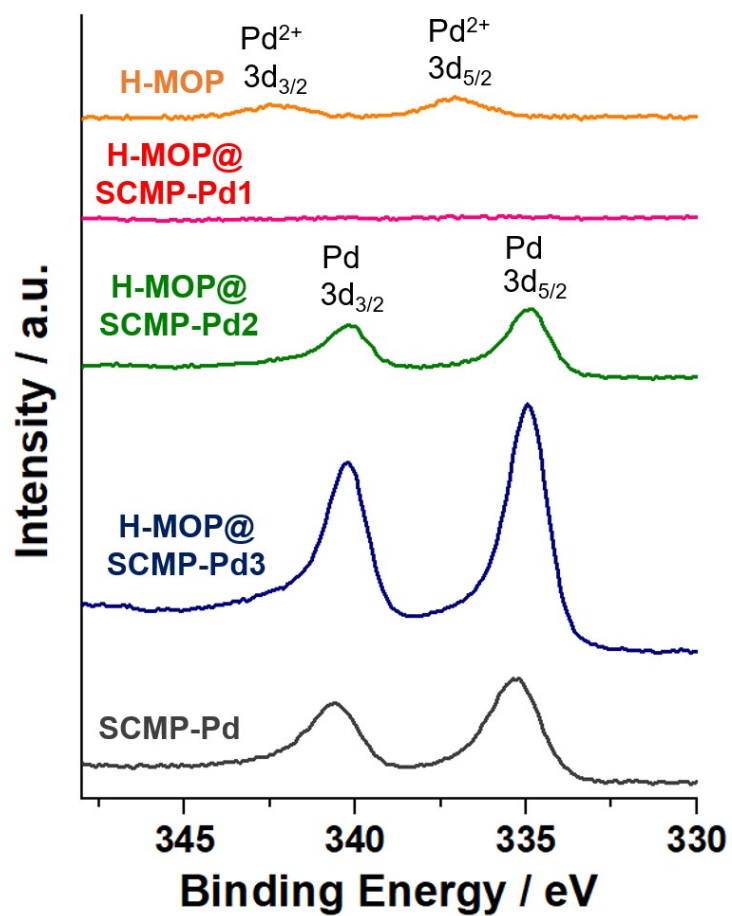
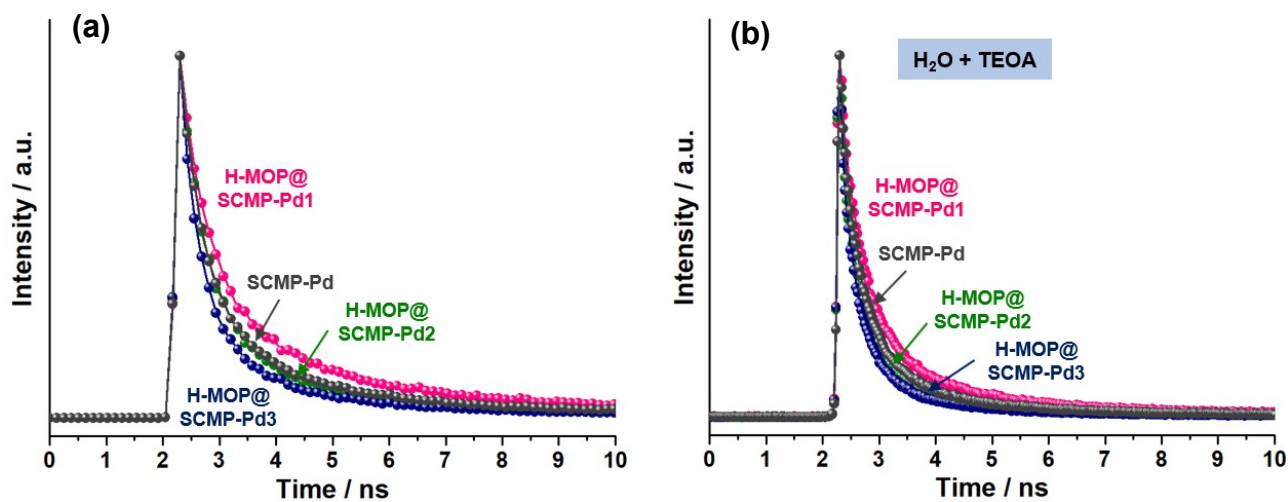


Fig. S3. Time-resolved emission decay curves of (a) powders and (b) suspensions in a mixture of water and TEOA of H-MOP@SCMP-Pds and SCMP-Pd. (c) The fitting parameters



(c)

Materials	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_{avg} (ns)
H-MOP@SCMP-Pd1	0.87 (0.13)	47.0 (2.3)	5.4 (0.4)	9.4 (0.2)
H-MOP@SCMP-Pd2	0.67 (0.04)	40.0 (5.0)	4.2 (0.3)	7.3 (0.4)
H-MOP@SCMP-Pd3	0.58 (0.10)	40.0 (4.4)	3.9 (0.5)	7.0 (0.5)
SCMP-Pd	0.70 (0.03)	46.0 (4.5)	4.6 (0.4)	8.6 (0.4)
H-MOP@SCMP-Pd1 (H ₂ O + 10% v/v TEOA)	0.44 (0.02)	10.0 (0.3)	2.0 (0.1)	2.9 (0.1)
H-MOP@SCMP-Pd2 (H ₂ O + 10% v/v TEOA)	0.35 (0.02)	9.0 (0.4)	1.6 (0.1)	2.3 (0.1)
H-MOP@SCMP-Pd3 (H ₂ O + 10% v/v TEOA)	0.31 (0.02)	8.9 (0.4)	1.4 (0.1)	2.0 (0.1)
SCMP-Pd (H ₂ O + 10% v/v TEOA)	0.37 (0.02)	9.7 (0.4)	1.6 (0.1)	2.5 (0.1)

Fig. S4. (a) Hydrodynamic diameters (obtained from DLS studies) of H-MOP@SCMP-Pds and nonhollow SCMP-Pd in aqueous suspensions and (b) water contact angles.

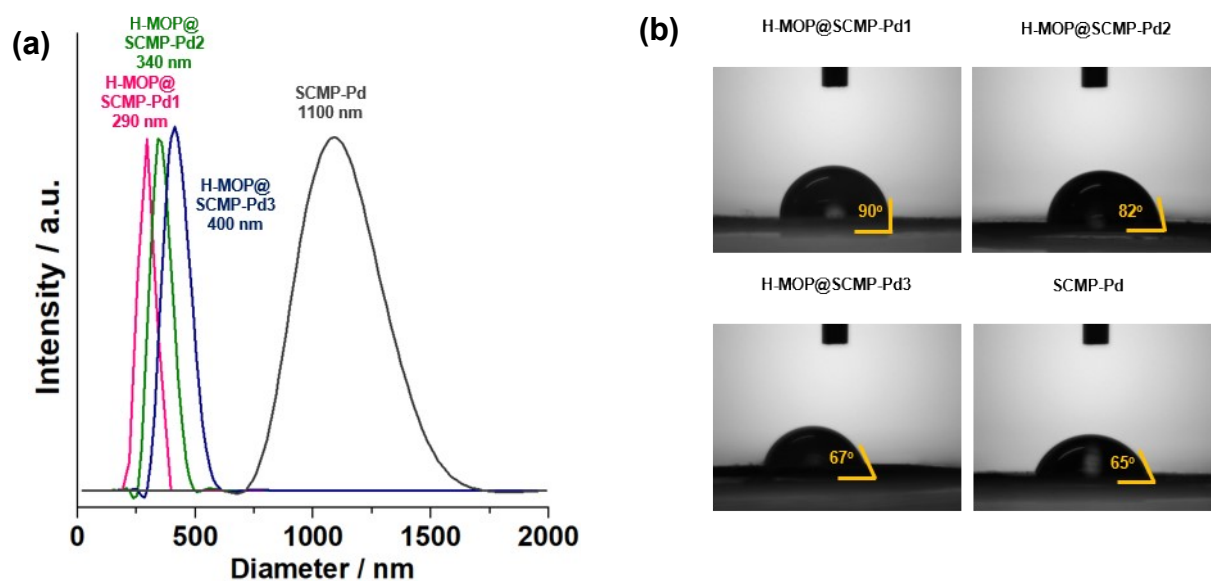


Fig. S5. Control studies: (a) Light intensity, (b) electron sacrificers, (c) Pd nanoparticles-dependent hydrogen evolution of H-MOP@SCMP-Pd2 (Standard reaction conditions: a 300 W Xe lamp with a < 400 nm optical filter and light intensity of 530 mW/cm^2 , 0.13 mg/mL photocatalyst, $10 \text{ v/v\%}$ electron sacrificial, $21 \pm 1^\circ\text{C}$, a reaction time of 5 h). The DEA corresponds to diethylamine. The H-MOP@SCMP was prepared through the Pd etching from H-MOP@SCMP-Pd2 by the treatment of aqua regia solution.

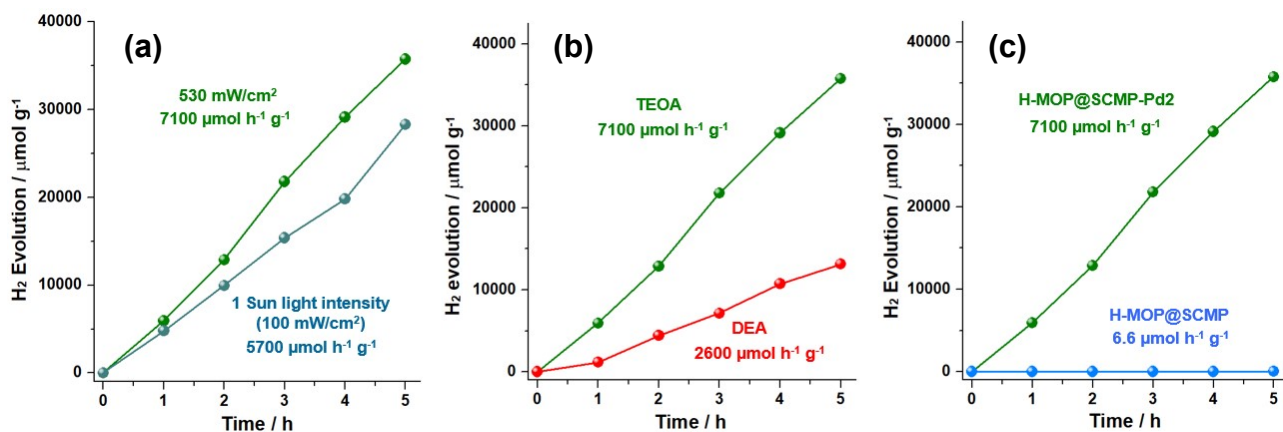


Fig. S6. Concentration-dependent hydrogen evolution of H-MOP@SCMP-Pd2 (a 300 W Xe lamp with an <400 nm optical filter and light intensity of 530 mW/cm², 10 v/v% TEOA as an electron sacrifier, 21±1°C, a reaction time of 5 h).

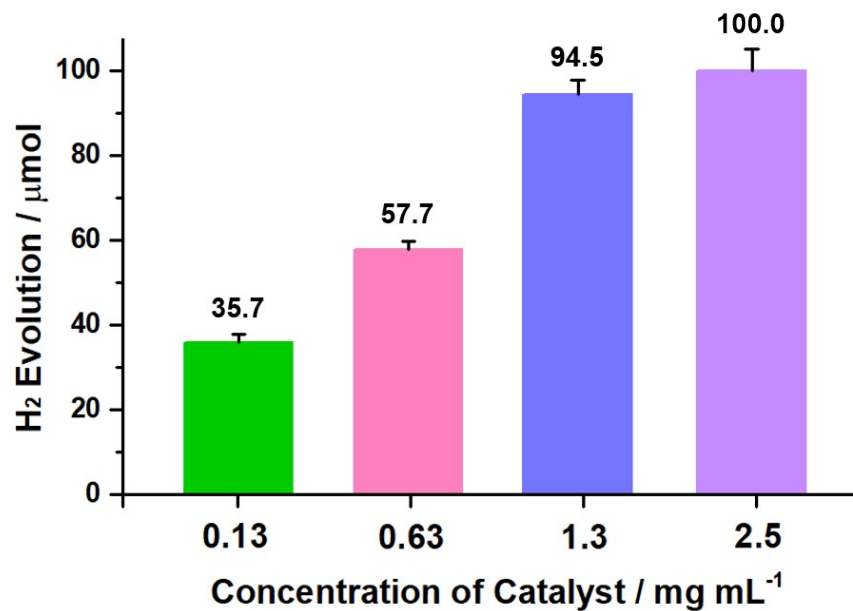


Fig. S7. The model systems for SCMP (TA-donor, DS-acceptor, and M-1~5).

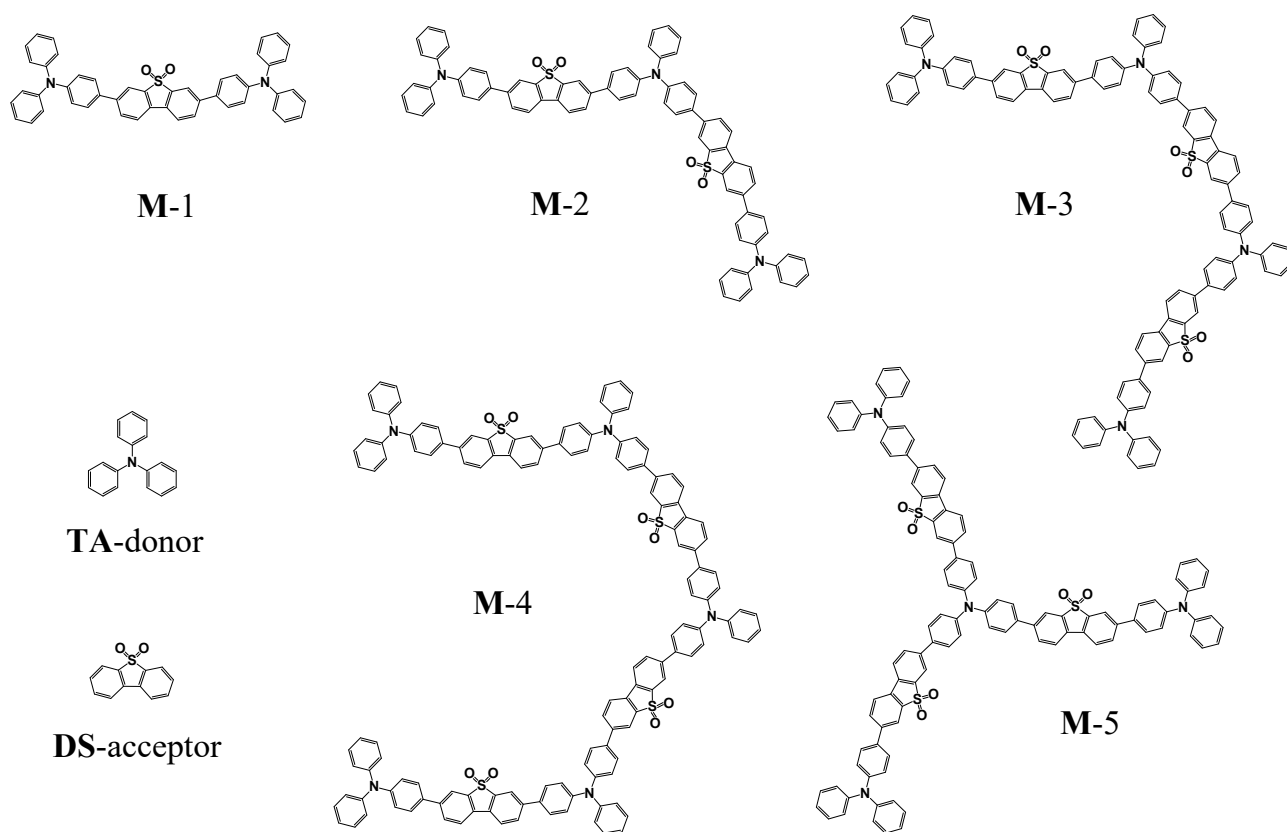


Fig. S8. The frontier molecular orbitals of model systems (TA-donor, DS-acceptor and M-1~5) for SCMP calculated at B3LYP/6-31G* level of theory.

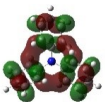
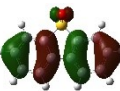
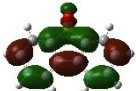
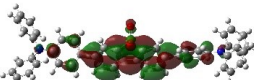
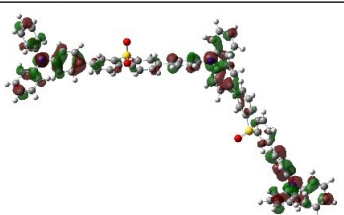
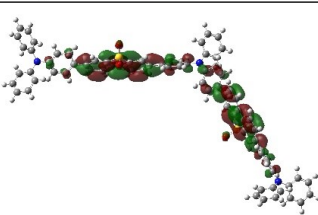
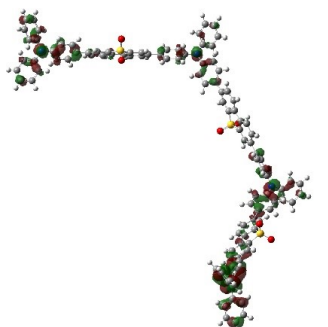
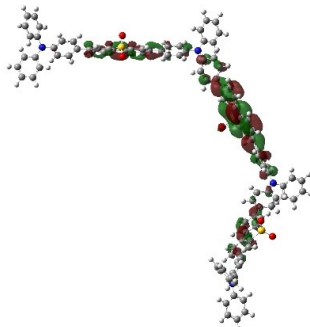
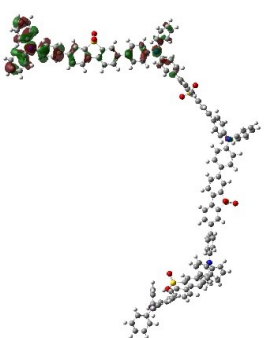
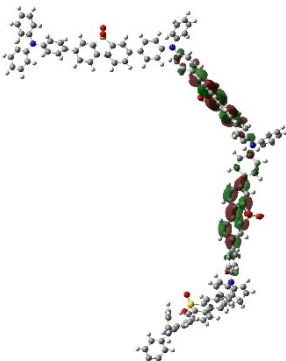
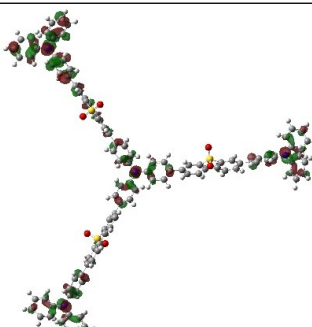
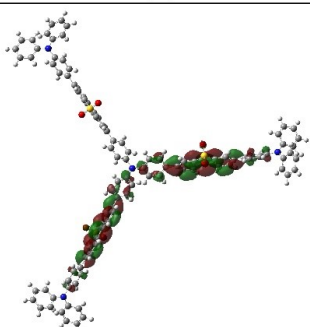
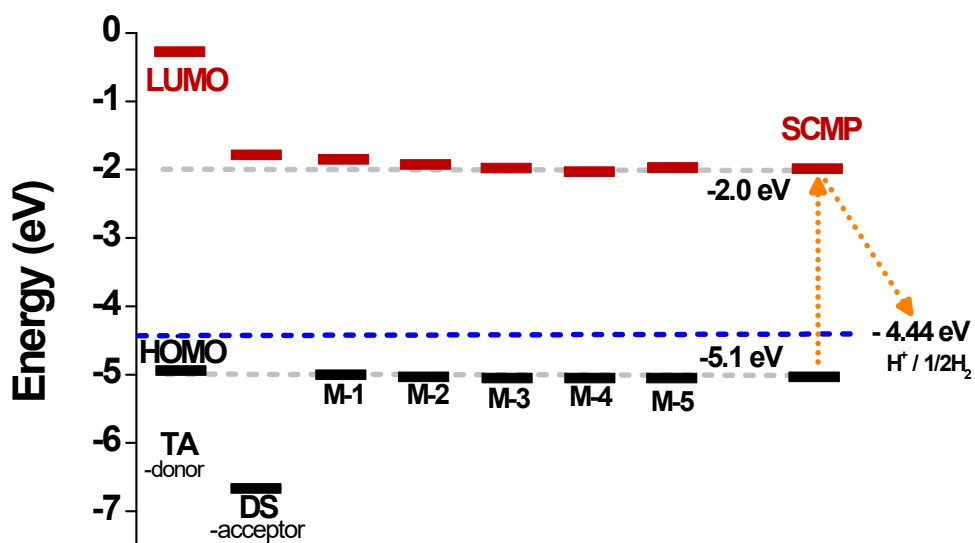
	HOMO	LUMO
TA-donor		
DS-acceptor		
M-1		
M-2		
M-3		
M-4		
M-5		

Fig. S9. The calculated HOMO-LUMO energy diagrams (in eV) of model systems (TA-donor, DS-acceptor and M-1~5) for SCMP and TEOA.



Compounds	HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)
TA-donor	-4.95	-0.30	4.65
DS-acceptor	-6.66	-1.81	4.85
M-1	-5.01	-1.84	3.17
M-2	-5.03	-1.92	3.11
M-3	-5.04	-1.98	3.07
M-4	-5.05	-2.02	3.03
M-5	-5.05	-1.97	3.08
TEOA	1.88	-4.99	6.87

Fig. S10. Cartesian coordinates (in Å) of model systems (TA-donor, DS-acceptor and M-1–5) and TEOA.

TA-donor

N	0.00011000	0.00005900	0.00008500
C	1.42160000	-0.01925500	0.00007400
C	2.12290200	-0.93267600	-0.80397900
C	2.14756100	0.87480100	0.80400500
C	3.51624200	-0.95388000	-0.79357800
H	1.56972800	-1.62237200	-1.43349500
C	3.54096400	0.85822400	0.79338900
H	1.61335400	1.57931200	1.43349600
C	4.23532400	-0.05740900	-0.00016500
H	4.04161500	-1.66788100	-1.42263300
H	4.08560900	1.55773700	1.42232600
H	5.32148200	-0.07214900	-0.00028400
C	-0.72730700	-1.22140900	-0.00009300
C	-0.31630600	-2.29679400	0.80440000
C	-1.86862500	-1.37230300	-0.80459700
C	-1.02743400	-3.49521000	0.79399300
H	0.56068700	-2.18624400	1.43417300
C	-2.58376200	-2.56833200	-0.79396100
H	-2.18915200	-0.54861900	-1.43448800
C	-2.16730500	-3.63895800	0.00011200
H	-0.69425400	-4.31643200	1.42336100
H	-3.46458900	-2.66654300	-1.42326100
H	-2.72321100	-4.57219400	0.00022500
C	-0.69404100	1.24070600	0.00016700
C	-1.83189300	1.42187800	0.80339100
C	-0.25327600	2.30520100	-0.80310500
C	-2.51450700	2.63673000	0.79270100
H	-2.17532900	0.60668700	1.42226800
C	-0.93180600	3.52234400	-0.79269200
H	0.62115700	2.17145900	-1.43195400
C	-2.06834700	3.69629900	-0.00007300
H	-3.39312900	2.75821100	1.42102000
H	-0.57579600	4.33466600	-1.42111100
H	-2.59884900	4.64420500	-0.00016700

DS-acceptor

C	2.98527400	-1.83337200	-0.00015000
C	3.51142200	-0.53775900	-0.00015100
C	2.65721200	0.56984900	-0.00010100
C	1.29120100	0.33438500	-0.00005500
C	0.73939200	-0.95432300	-0.00004800
C	1.60502500	-2.05053800	-0.00009800
H	3.65873800	-2.68572400	-0.00019100
H	4.58710500	-0.38909300	-0.00018900
H	3.04948600	1.58217100	-0.00010000
H	1.21400400	-3.06388500	-0.00009200
C	-1.29120100	0.33438500	0.00006700
C	-2.65721200	0.56984900	0.00012600
C	-3.51142200	-0.53775800	0.00014100
C	-2.98527500	-1.83337100	0.00009200
C	-1.60502500	-2.05053700	0.00002900
C	-0.73939300	-0.95432300	0.00001600
H	-3.04948600	1.58217200	0.00016000
H	-4.58710500	-0.38909200	0.00019200
H	-3.65873900	-2.68572300	0.00010000
H	-1.21400500	-3.06388400	-0.00001000
S	0.00000000	1.58905600	0.00002400
O	0.00006800	2.33431100	1.26802500
O	-0.00006600	2.33434500	-1.26795700

M-1

C	2.99019600	0.00366700	2.04074800
C	3.54095100	0.00628100	0.74365900
C	2.65331200	0.00614300	-0.35144200
C	1.29206100	0.00714300	-0.11134600
C	0.73670500	0.00135400	1.17635200
C	1.61419200	-0.00165200	2.26357800
H	3.65947700	0.03128300	2.89537100
H	3.03222200	-0.02026800	-1.36826500
H	1.23361000	0.00326600	3.28114800
C	-1.29206100	-0.00715900	-0.11134500
C	-2.65331200	-0.00616200	-0.35144000
C	-3.54095100	-0.00628600	0.74366200
C	-2.99019400	-0.00365500	2.04075000
C	-1.61419000	0.00166800	2.26357900
C	-0.73670500	-0.00135300	1.17635300
H	-3.03222300	0.02023600	-1.36826200
H	-3.65947400	-0.03126000	2.89537500
H	-1.23360700	-0.00323800	3.28114900
S	-0.00000100	-0.00001600	-1.36663900
O	-0.00538700	1.26750800	-2.11343400
O	0.00538600	-1.26755000	-2.11341700
C	-5.00641300	-0.01022200	0.53262700
C	-5.58777300	-0.70747200	-0.54088800

C	-5.87259200	0.68327600	1.39576900
C	-6.96175000	-0.70927000	-0.74867300
H	-4.95564600	-1.27147700	-1.22106700
C	-7.24903900	0.67733200	1.20502800
H	-5.46232500	1.25256900	2.22522800
C	-7.81997300	-0.01793000	0.12446400
H	-7.37871500	-1.25416500	-1.58899600
H	-7.89080700	1.22086000	1.89040000
N	-9.21985800	-0.02088400	-0.07863200
C	-9.87332100	-1.18791700	-0.56829300
C	-9.98917400	1.14497600	0.19993000
C	-9.55519600	-2.45386600	-0.05173500
C	-10.85149600	-1.08547100	-1.56960500
C	-11.21261100	1.04111600	0.87997000
C	-9.54032200	2.41091700	-0.20834200
C	-10.19605000	-3.59187900	-0.53816200
H	-8.80592400	-2.53857700	0.72910600
C	-11.50026700	-2.22712500	-2.03663300
H	-11.09788100	-0.10964800	-1.97600500
C	-11.97132000	2.18135800	1.13816700
H	-11.56232700	0.06504800	1.20115900
C	-10.29702700	3.54755700	0.07065700
H	-8.59987800	2.49659900	-0.74358400
C	-11.17451800	-3.48661500	-1.52902300
H	-9.93757900	-4.56462700	-0.12805300
H	-12.25506300	-2.13050000	-2.81261900
C	-11.51767200	3.44089600	0.74077800
H	-12.91665700	2.08361500	1.66547500
H	-9.93540400	4.52014600	-0.25263300
H	-11.67692700	-4.37502700	-1.90076500
H	-12.10843800	4.32819700	0.94962300
C	5.00641300	0.01021300	0.53262300
C	5.87259200	-0.68327200	1.39577600
C	5.58777500	0.70745300	-0.54089800
C	7.24903900	-0.67733100	1.20503700
H	5.46232500	-1.25255300	2.22524300
C	6.96175100	0.70924800	-0.74868200
H	4.95564800	1.27145200	-1.22108200
C	7.81997400	0.01791300	0.12446100
H	7.89080600	-1.22084600	1.89041900
H	7.37871900	1.25413700	-1.58900600
N	9.21985900	0.02087900	-0.07863100
C	9.98919000	-1.14497200	0.19993600
C	9.87330700	1.18791700	-0.56829400
C	9.54036800	-2.41091700	-0.20835600
C	11.21261700	-1.04109500	0.87999100
C	10.85150100	1.08548100	-1.56958900
C	9.55513900	2.45386600	-0.05176300
C	10.29709100	-3.54754600	0.07064300
H	8.59993500	-2.49661300	-0.74361200
C	11.97134400	-2.18132600	1.13818900
H	11.56231100	-0.06502400	1.20119200
C	11.50025200	2.22714400	-2.03662200
H	11.09791600	0.10965800	-1.97597100
C	10.19597400	3.59188800	-0.53819600
H	8.80585000	2.53857100	0.72906200
C	11.51772400	-3.44086900	0.74078200
H	9.93549200	-4.52013900	-0.25266300
H	12.91667200	-2.08357100	1.66551000
C	11.17446200	3.48663400	-1.52903700
H	12.25506400	2.13052500	-2.81259400
H	9.93747000	4.56463600	-0.12810800
H	12.10850400	-4.32816000	0.94962700
H	11.67685600	4.37505300	-1.90078300

M-2

C	-5.52605200	2.88562000	-2.07280000
C	-4.93127900	2.97255600	-0.79857500
C	-5.58443100	2.34565800	0.28147500
C	-6.76997700	1.67390000	0.04903700
C	-7.36937300	1.58470800	-1.21555400
C	-6.72514000	2.20777200	-2.28738000
H	-5.02169900	3.34023900	-2.92021000
H	-5.17687100	2.41048600	1.28545600
H	-7.14441500	2.15930300	-3.28840300
C	-8.98382500	0.34162900	0.05836900
C	-10.12243500	-0.40469900	0.29768100
C	-10.98418300	-0.70167000	-0.77769400
C	-10.63578800	-0.22105800	-2.05583900
C	-9.47957700	0.52467700	-2.27942800
C	-8.62907400	0.82011900	-1.21115100
H	-10.33560600	-0.77797400	1.29436500
H	-11.30221700	-0.41738800	-2.89030800
H	-9.25364600	0.88031400	-3.28080400
S	-7.75871400	0.81986000	1.28931500
O	-7.04389900	-0.35968200	1.80085600
O	-8.33193600	1.77761500	2.24764800
C	-12.21692500	-1.49368300	-0.56591100
C	-12.96658000	-1.37572600	0.61761100
C	-12.68487900	-2.39453200	-1.53841600
C	-14.12053100	-2.12139400	0.82553000
H	-12.65017200	-0.67742900	1.38741400

C	-13.84462800	-3.13548000	-1.34652500
H	-12.12340300	-2.53196200	-2.45833800
C	-14.58381000	-3.01480800	-0.15645200
H	-14.67414100	-2.00987400	1.75177600
H	-14.18027500	-3.82080000	-2.11765900
N	-15.76058200	-3.77239600	0.04704700
C	-16.86730800	-3.20996700	0.74547200
C	-15.84956600	-5.10762800	-0.44123600
C	-17.29464100	-1.90138700	0.47044400
C	-17.55136500	-3.96228100	1.71291200
C	-17.01273000	-5.54835200	-1.09137600
C	-14.78121800	-6.00235400	-0.27177500
C	-18.37645900	-1.35669800	1.15990500
H	-16.77537600	-1.31787200	-0.28332900
C	-18.64372600	-3.41565100	2.38400000
H	-17.22223800	-4.97295400	1.93271000
C	-17.10382500	-6.85957600	-1.55492500
H	-17.84014200	-4.85926800	-1.22819900
C	-14.87436000	-7.30625900	-0.75509800
H	-13.88300300	-5.67024700	0.23929700
C	-19.06032800	-2.10988500	2.11663900
H	-18.69426500	-0.34185500	0.93558300
H	-19.16234400	-4.01142800	3.13051400
C	-16.03562900	-7.74475500	-1.39508700
H	-18.01164200	-7.18529300	-2.05595000
H	-14.03836200	-7.98657900	-0.61557600
H	-19.90750200	-1.68453200	2.64697200
H	-16.10754400	-8.76403200	-1.76362300
C	-3.65708600	3.69960000	-0.59516300
C	-2.69728600	3.24471400	0.32581500
C	-3.36122400	4.87166400	-1.31249600
C	-1.50364600	3.92757600	0.52780700
H	-2.88047100	2.33291600	0.88727100
C	-2.16448400	5.55414100	-1.12809200
H	-4.08665800	5.26756800	-2.01764900
C	-1.21496800	5.09389500	-0.20055900
H	-0.78457500	3.55486900	1.24986800
H	-1.96293500	6.45577900	-1.69704900
N	-0.00003100	5.79647400	0.00010300
C	1.21491900	5.09387700	0.20071900
C	-0.00001600	7.22263800	0.00006000
C	1.50363500	3.92765000	-0.52777400
C	2.16437200	5.55400900	1.12837300
C	0.97569400	7.93230700	-0.71637100
C	-0.97574100	7.93235000	0.7164280

C 17.01301400 -5.54793200 1.09153600
C 17.55085700 -3.56623500 -1.71345100
C 17.29477600 -1.90146800 -0.47083700
C 14.87491500 -7.30621600 0.75548300
H 13.88326800 -5.67044800 -0.23903600
C 17.10433400 -6.85909800 1.55521000
H 17.84031600 -4.85869600 1.22826200
C 18.64310700 -3.41585900 -2.38483100
H 17.22152300 -4.97298000 -1.93317700
C 18.37647700 -1.35690500 -1.16058200
H 16.77579100 -1.31791700 0.28310300
C 16.03627400 -7.74446000 1.39548200
H 14.03902500 -7.98668600 0.61605000
H 18.01221600 -7.18462500 2.05624000
C 19.05996500 -2.11016200 -2.11753600
H 19.16143500 -4.01167900 -3.13151100
H 18.69449600 -0.34211600 -0.93631700
H 16.10836100 -8.76369100 1.76411400
H 19.90705000 -1.68491000 -2.64809100

M-3

C 13.28517700 -2.10758900 -1.19168900
C 12.60213700 -2.16255600 0.03935300
C 12.71048600 -1.05714600 0.90681200
C 13.47307300 0.02805000 0.51747000
C 14.15830500 0.08905600 -0.70447600
C 14.05440200 -1.00663200 -1.56513200
H 13.18988400 -2.93939700 -1.88316800
H 12.22386000 -1.06733200 1.87704900
H 14.55858600 -1.00373100 -2.52740800
C 14.79081300 2.22672500 0.19268400
C 15.40333700 3.46521100 0.23274700
C 16.19342200 3.87340300 -0.86110400
C 16.31670500 2.99071600 -1.95279600
C 15.68558200 1.74816400 -1.97862600
C 14.90588000 1.34504600 -0.89169600
H 15.25670100 4.12352700 1.08318800
H 16.94363600 3.27731300 -2.79172800
H 15.81368800 1.09718500 -2.83890900
S 13.74291700 1.52682800 1.47986400
O 12.49320300 2.29183600 1.60990700
O 14.52962100 1.23489500 2.68821200
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C 17.38505700 5.74376500 0.32756200
H 17.02810100 5.93577400 -2.03903600
C 18.01626900 6.98158500 0.33863600
H 17.30209200 5.19173500 1.25959300
C 17.66947100 7.16842300 -2.04186900
H 16.62673100 5.55386600 -2.97361000
C 18.17351700 7.71724800 -0.84935300
H 18.39757800 7.38308300 1.27149300
H 17.77583100 7.71850700 -2.97086700
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C 20.01319800 10.41500000 0.74192800
C 19.29290100 10.79296100 -2.42303000
C 16.99863900 10.29111100 -1.83818100
C 22.02170400 8.49921900 1.00901700
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C 18.85118000 11.82306800 -3.25143800
H 20.35347000 10.58328500 -2.32598800
C 16.56534100 11.31123500 -2.68320400
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H 22.80243000 7.74916200 1.10443000
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H 19.57942800 12.41417500 -3.80052100
H 15.50081800 11.51006600 -2.77515000
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C 12.18709800 -4.64513800 0.05563800
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C 10.24124800 -5.61005900 1.13938700
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C 5.21886400 -6.62817500 1.40052200
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H 11.93739500 -11.21046300 3.01995500
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H -6.65931200 -7.72609900 -2.74222500
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C -11.79885000 -1.57225200 -1.41732800
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S -14.85524500 0.17688600 0.72464200
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O -14.32373800 0.32993000 2.08781600
O -16.02229100 -0.69202800 0.50753800
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H -13.62209400 3.36338400 -2.65911100
C -16.11089300 3.94671000 -0.37240600
H -16.72033600 2.52794300 1.15597600
H -15.24652500 5.07943500 -1.98961400
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H -17.47946000 5.65364000 -2.01188100
H -18.37130400 6.17506900 1.71271200
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C -18.97730700 6.98758300 0.73810600
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H -18.62533300 6.31312500 2.75828200
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C -19.75478400 8.71515000 2.31176900
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C -20.85505200 8.94582700 3.15192000
C -18.49856200 9.22461500 2.67620200
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C -22.51236400 9.84999000 -0.81298300
H -20.83190400 10.39586800 0.42320200
C -20.69901700 9.67724900 4.32798700
H -21.82756100 8.54994400 2.87692400
C -18.34841700 9.93899600 3.86344000
H -17.64574300 9.05713900 2.02584300
C -23.24752200 8.80634400 -1.37908000
H -23.44004100 6.66386200 -1.54605200
H -22.78965100 10.88213900 -1.01052900
C -19.44624100 10.17385700 4.69407100
H -21.56103800 9.84679100 4.96779700
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H -24.10322900 9.01877700 -2.01355000
H -19.32684700 10.73715300 5.61511600

M-4

C -18.86925900 1.24905600 -0.00322600
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C -17.49271700 2.60445700 -1.45432300
C -17.86984400 3.70372300 -0.50586200
C -18.74032000 3.62667900 0.39084000
H -19.24268700 2.36975400 0.73697500
H -19.24452500 0.27471500 0.29507100
H -16.83914000 2.72189500 -2.31301100
H -19.91294000 2.25632900 -1.58436500
C -18.32512100 5.99356100 0.40119200
C -18.41453000 7.30480300 0.82938900
C -19.22266800 7.60668500 1.94430400
C -19.90214300 6.54510300 2.57471900
C -19.79462100 5.22751600 2.13274500
C -18.99563900 4.93187400 1.02546800
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H	-9.59029200	5.10771100	-3.09371700
C	-11.99039800	4.93762500	-0.64955500
H	-11.71758000	3.93999400	1.26108200
H	-11.89300600	5.81571500	-2.61546300
C	-13.38410600	5.36162200	-0.38635200
C	-14.34565400	5.39470400	-1.41137700
C	-13.80004200	5.74656300	0.90032200
C	-15.65343700	5.79753900	-1.17033700
H	-14.07157400	5.08432300	-2.41583900
C	-15.10841400	6.13874000	1.15537000
H	-13.08431000	5.75319600	1.71763600
C	-16.06101800	6.17468000	0.12162900
H	-16.37097800	5.81396800	-1.98383900
H	-15.39803500	6.42607100	2.16053200
N	-17.39248700	6.57815000	0.37383100
C	-18.47519700	5.95626300	-0.31203600
C	-17.66646800	7.60691300	1.32048900
C	-18.51886400	4.56113600	-0.46130000
C	-19.51866200	6.73251400	-0.83966800
C	-18.71286700	7.45947700	2.24403900
C	-16.90170900	8.78392600	1.33696300
C	-19.58031000	3.96042800	-1.13580600
H	-17.71991700	3.95474700	-0.04624100
C	-20.58526000	6.12143000	-1.49651200
H	-19.48759200	7.81194900	-0.72994700
C	-18.98950000	8.47367100	3.15909900
H	-19.30416400	6.54928500	2.23835700
C	-17.17388800	9.78477500	2.26789900
H	-16.09698700	8.90749200	0.61898800
C	-20.62123600	4.73428400	-1.65353500
H	-19.59938800	2.87901400	-1.24245100
H	-21.38566800	6.73672900	-1.89899100
C	-18.22049000	9.63909400	3.18097900
H	-19.80308300	8.34381300	3.86789400
H	-16.57202700	10.68974600	2.26801400
H	-21.45078100	4.26190700	-2.17183200
H	-18.43423000	10.42428500	3.90047000

TEOA

N	-0.00682900	-0.20940400	-0.31679200
C	-1.31405900	-0.26643400	-0.95950700
H	-1.65844300	0.76261500	-1.09491000
H	-1.19395600	-0.69579800	-1.96591500
C	0.66224600	-1.48430600	-0.11898000
H	0.52227100	-1.89290900	0.89879100
H	0.22678200	-2.21468500	-0.81284000
C	0.13226100	0.77464500	0.76450900
H	-0.84036800	0.99088700	1.22103400
H	0.77641000	0.35850200	1.54472000
C	-2.41452500	-1.07424800	-0.26113800
H	-3.28975700	-1.11478300	-0.93275400
H	-2.07841100	-2.11214300	-0.10204700
O	-2.74796700	-0.45490600	0.97798100
H	-3.38831200	-1.02124200	1.43388100
C	2.15979900	-1.44664000	-0.41721100

Fig. S11. TEM and SEM images of H-MOP@SCMP-Pd2 before and after five recycle reactions.

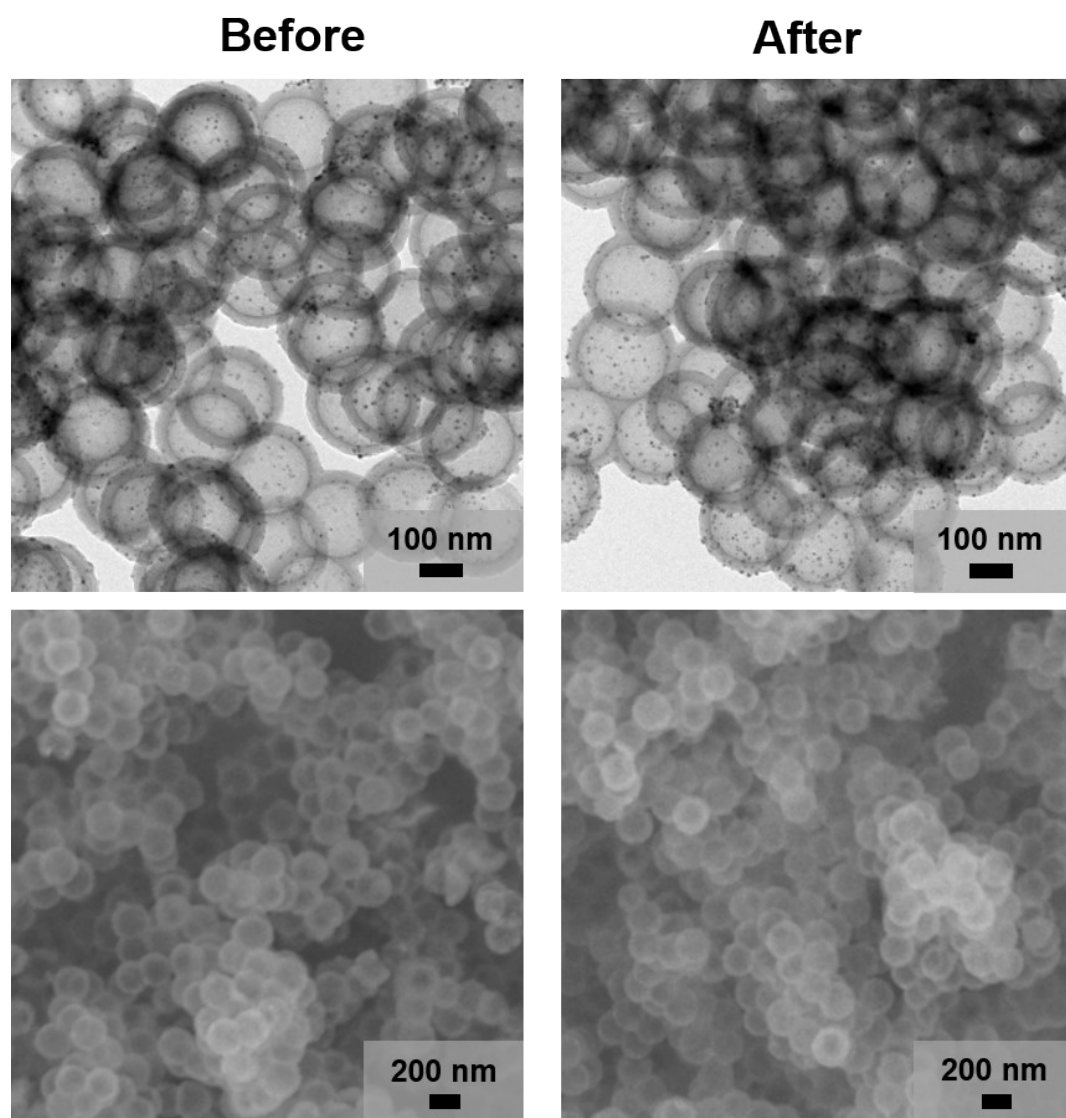


Fig. S12. The HERs of H-MOP@SCMP-Pd2 at the monochromatic light sources with wavelengths of 400, 420, and 500 nm.

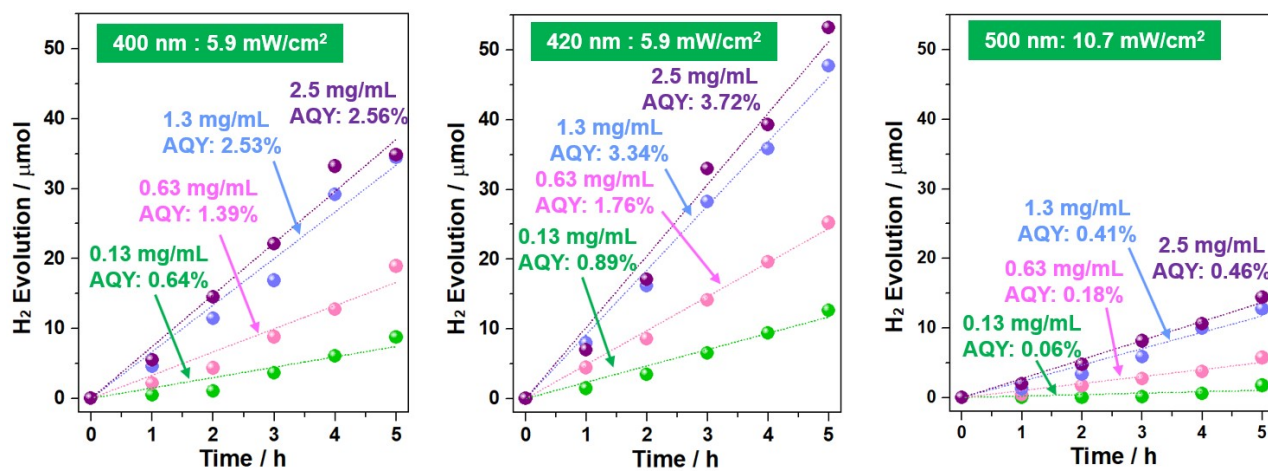


Table S1. Physical parameters and HERs of H-MOP, H-MOP@SCMP-Pds, and SCMP-Pd.

Materials	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	HER ^a ($\mu\text{mol} / \text{g} \cdot \text{h}$)
H-MOP	610	0.14	0
H-MOP@SCMP-Pd1	405	0.10	1400
H-MOP@SCMP-Pd2	507	0.11	7100
H-MOP@SCMP-Pd3	482	0.11	4800
SCMP-Pd	115	0.02	3200

^aReaction conditions: a 300 W Xe lamp with an <400 nm optical filter and light intensity of 530 mW/cm², 10 v/v% TEOA as an electron sacrifier, 0.13 mg/mL photocatalyst, 21±1°C.

Table S2. HERs of the recent CMP-based photocatalysts in the literature (Referring to the recent review paper¹ of CMP-based photocatalysts for hydrogen evolution).

CMP Materials	Edge Absorption (nm)	Light Source	Optical Filter (nm)	Metal Catalyst	HER ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	AQY(@420 nm) (%)	Year	Ref
ANW2	504	300 W Xe	300	Pt	70		2010	2
VH-MON	550	200 W Xe	420	Pt	1250		2014	3
CP-CMP10	532	300 W Xe	420	Pd	174	0.42	2015	4
B-BT-1,3,5	508	300 W Xe	420	Pd/Pt	400		2016	5
PCP4e	600	150 W Xe	400	Pd	1900	0.34 (@350 nm)	2016	6
PCP2-100%PDI	605	150 W Xe	Full	Pd/Cu	2171		2016	7
PCP2-100%PDI	605	150 W Xe	Full	Pd/Cu	3142		2016	7
SP-CMP	437	300 W Xe	420	Pd	120	0.23	2016	8
PTEB	422	300 W Xe	420	Cu	102		2017	9
PTEPB	435	300 W Xe	420	Cu	218		2017	9
PrCMP-3	810	300 W Xe	300	Pt	121		2017	10
PrPy	879	300 W Xe	420	Pt	3020		2017	11
aza-CMP/C2N	-	300 W Xe	420	N/A	100	4.3 (@600 nm)	2018	12
PyDOBT-1	-	300 W Xe	420	Pd	5697 ^a		2018	13
PyDOBT-1	-	300 W Xe	420	Pt	8523 ^b		2018	13
DBTD-CMP1	-	300 W Xe	420	Pd	2460 ^c		2018	14
DBTD-CMP1	-	300 W Xe	420	Pt	4600		2018	14
S-CMP3	484	300 W Xe	420	Pd	3106 ^d	13.2	2019	15
BDP-bdy-TPA	534	300 W Xe	440	Pd	2780		2020	16
H-MOP@SCMP-Pd2	500	300 W Xe	400	Pd	7100 ^e	3.72	2021	This work

^a The surface area (SA) of PyDOBT-1 was reported to be 723 m² g⁻¹ and the HER per SA corresponds to 7.88 $\mu\text{mol h}^{-1} \text{m}^{-2}$. ^b The SA of PyDOBT-1/Pt was not reported. ^c The SA of DBTD-CMP1 was measured to be 811 m² g⁻¹ and the HER per SA corresponds to 3.03 $\mu\text{mol h}^{-1} \text{m}^{-2}$. ^d The SA of S-CMP3 was measured to be 431 m² g⁻¹ and the HER per SA corresponds to 7.20 $\mu\text{mol h}^{-1} \text{m}^{-2}$. ^e The SA of H-MOP@SCMP-Pd2 was measured to be 507 m² g⁻¹ and the HER per SA corresponds to 14 $\mu\text{mol h}^{-1} \text{m}^{-2}$.

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