

Supporting Information

Nanoporous Thin Films Formed from Photocleavable Diblock Copolymers on Gold Substrates Modified with Thiolate Self-Assembled Monolayers

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Synthetic procedure for PS-*h* ν -PEO (**Figures S1**) and their ^1H -NMR and GPC data (**Figures S2-S7**), UV-Vis spectra of PS-*h* ν -PEO solutions at different periods of UV irradiation (**Figure S8**), AFM phase images (**Figure S9**), AFM height images of PS-*h* ν -PEO (8k–2k) films with different thicknesses on different substrates (**Figure S10**), FTIR-ERS spectra of PS-*h* ν -PEO (8k–2k) films with different thicknesses on different substrates and PS-*h* ν -PEO (18k–5k) films with *ca.* 30 nm thick on bare gold and NH_2 -SAM (**Figure S11**), cyclic voltammograms of $\text{Fc}(\text{CH}_2\text{OH})_2$ for PS-*h* ν -PEO (8k–2k)-derived nanoporous films on NH_2 -SAMs with different thicknesses (**Figure S12**), cyclic voltammograms of $\text{Fc}(\text{CH}_2\text{OH})_2$ for different samples at pH 7 and 3 (**Figure S13**), cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}$ for different samples at different pH (**Figure S14**), cyclic voltammograms of L-AA and $\text{Fc}(\text{CH}_2\text{OH})_2$ upon SAM displacement for PS-*h* ν -PEO (8k–2k)-derived nanoporous films (**Figure S15**), and surface free energies of the substrates (**Table S1**).

Synthesis of PS-*h*-PEO

Chemicals and Materials. 5-Hydroxy-2-nitrobenzaldehyde (98%, Oakwood Chemical), propargyl bromide (>97%, TCI), sodium borohydride (NaBH₄, fine granular for synthesis, Sigma-Aldrich), poly(ethylene glycol) methyl ether (PEO2k, M_n = 2 kg/mol, Sigma-Aldrich; PEO5k, M_n = 5 kg/mol, JenKem), copper (I) bromide (CuBr, 99.999%, Sigma-Aldrich), *N,N,N',N'',N''*-pentamethyldiethylene triamine (PMDETA, 99%, Sigma-Aldrich), 2-bromoisobutyric acid (98%, Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Sigma-Aldrich), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 99%, Oakwood Chemical) were used as received. Styrene (\geq 99%, Sigma-Aldrich) was washed with 10% NaOH solution, water and brine, and then purified by vacuum distillation.

Instrumentation and Analysis. ¹H- and ¹³C-NMR spectra were acquired with a VXR400 spectrometer in DMSO-d₆ or CDCl₃. GPC analysis for determining polymer molecular weight and polydispersity was performed on a Waters Breeze HPLC system at 35 °C with THF as the eluent at a flow rate of 1 mL/min. The system is equipped with a refractive index detector and a dual UV/Vis detector together with Styragel HR2, HR4 and HR5 columns. Polystyrene standards were used to generate the calibrate curve. The photodegradation of PS-*h*-PEO in dichloromethane solution was monitored on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. UV light at 300 and 365 nm was irradiated in a Rayonet RPR photochemical mini reactor equipped with four 300 nm lamps (6 W; S.N.E. Ultraviolet Co. RMR 3000A) and using a UVP UVGL-25 compact UV-lamp (4 W), respectively.

Synthesis of 5-Propargyloxy-2-nitrobenzyl Alcohol (Figure S1). 5-Propargyloxy-2-nitrobenzaldehyde was prepared quantitatively from 5-hydroxy-2-nitrobenzaldehyde and propargyl bromide by Williamson etherification.^{R1} Then, 5-propargyloxy-2-nitrobenzaldehyde (4.4 g, 21.4 mmol) was dissolved in anhydrous CH₃OH (160 mL) in a 500 mL Schlenk flask. After the clear solution was kept stirring in an ice/water bath for 15 minutes, NaBH₄ (2.1 g, 55.5 mmol) was slowly added into the flask. The clear solution gradually turned milky as precipitates formed. The yellow mixture was kept stirring under Ar overnight, poured into ice/water, and its pH was adjusted to 2 using 1.0 M HCl. After extraction with ethyl acetate 3 times, the organic phase was dried under anhydrous MgSO₄. The solvent was evaporated to give yellow solid (4.2 g; Yield: 95%). The ¹H- and ¹³C-NMR spectra of the product in DMSO-d₆, which are consistent to those reported previously,^{R2} are given in **Figure S2**. ¹H-NMR (400 MHz, DMSO-d₆) δ 8.12 (d, 1H, *J* = 12 Hz), 7.40 (s, 1H), 7.06 (d, 2H, *J* = 12 Hz), 5.60 (s, 1H), 4.95 (s, 2H), 4.84 (s, 2H), 3.64 (s, 1H). ¹³C-NMR (150.9 MHz, DMSO-d₆) δ 161.48, 142.27, 139.89, 127.32, 113.77, 113.10, 79.01, 78.32, 60.17, 56.15.

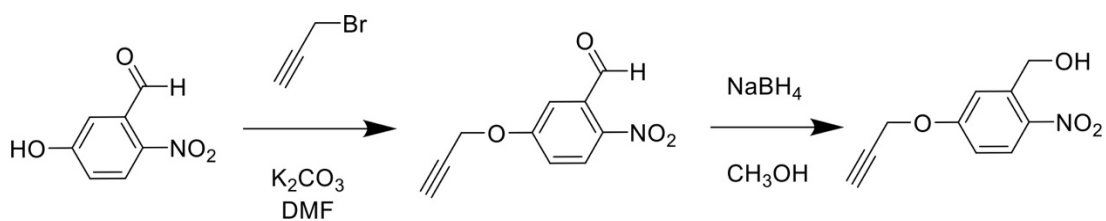


Figure S1. Synthesis of 5-propargyloxy-2-nitrobenzyl alcohol.

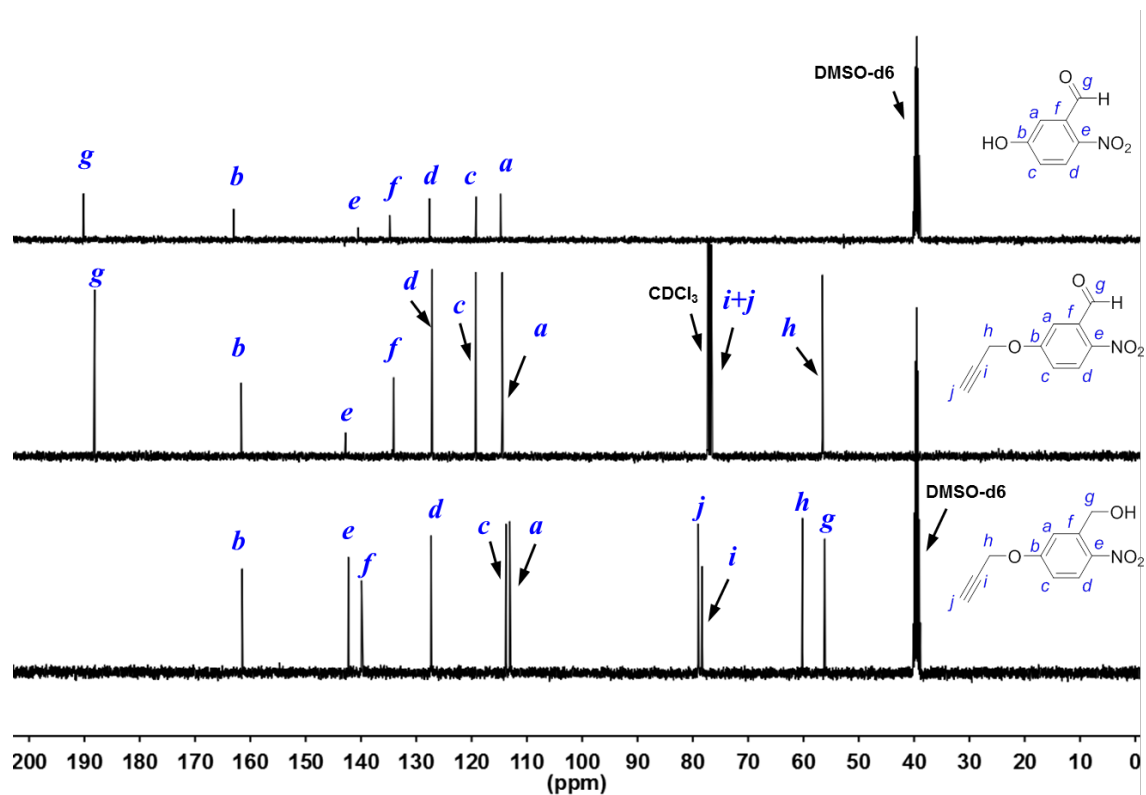
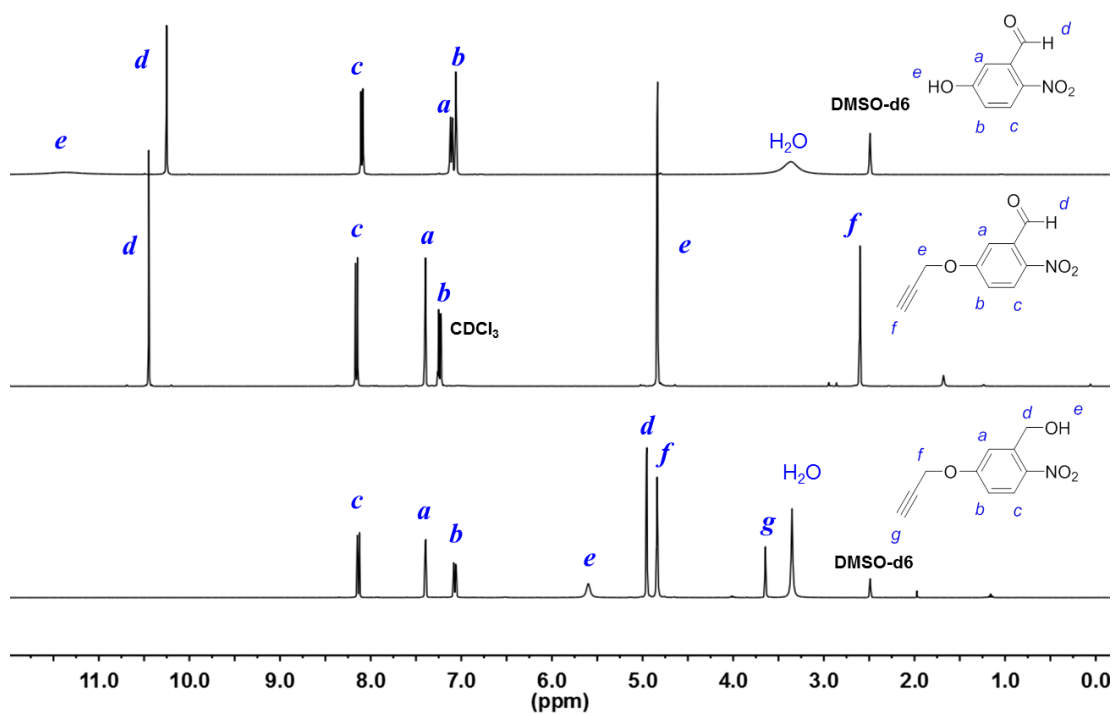


Figure S2. The ^1H - and ^{13}C -NMR spectra of 5-propargyloxy-2-nitrobenzyl alcohol and its precursors.

Synthesis of PEO-ONB-OH. PEO2k-N₃ and PEO5k-N₃ were synthesized from PEO2k and PEO5k, respectively, according a procedure reported previously.^{R3} PEO2k-N₃ (4.0 g, 2.0 mmol) and 5-propargyloxy-2-nitrobenzyl alcohol (0.54 g, 2.6 mmol) were dissolved in anhydrous THF (40 mL) in a 100 mL Schlenk flask. After three cycles of freeze-pump-thaw, CuBr (144 mg, 1.0 mmol) and PMDETA (0.2 mL, 1.0 mmol) were added successively. The flask was covered with aluminum foil to avoid exposure to light. The mixture was kept stirring at room temperature under Ar overnight. Subsequently, neutral alumina was added into the flask to remove the copper complex. After filtration, the polymer solution was concentrated. Diethyl ether was then added to obtain a white solid precipitate, which was dried under vacuum at 35 °C overnight to obtain PEO2k-ONB-OH (4.1 g; Yield: 90%). PEO5k-ONB-OH was synthesized in the same procedure and obtained as white solid (Yield: 93%). The ¹H-NMR spectra of PEO2k-ONB-OH and PEO5k-ONB-OH are very similar, and thus only the latter is shown in **Figure S3**. ¹H-NMR (400 MHz, CDCl₃) δ 8.21 (d, 1H, J = 8 Hz), 7.95 (s, 1H), 7.46 (s, 1H), 6.97 (d, 1H, J = 8 Hz), 5.32 (s, 2H), 5.00 (d, 2H, J = 4 Hz), 4.56 (t, 2H, J = 4 Hz), 3.85 (t, 2H, J = 4 Hz), 3.8-3.4 (m, 450H), 3.36 (s, 3H).

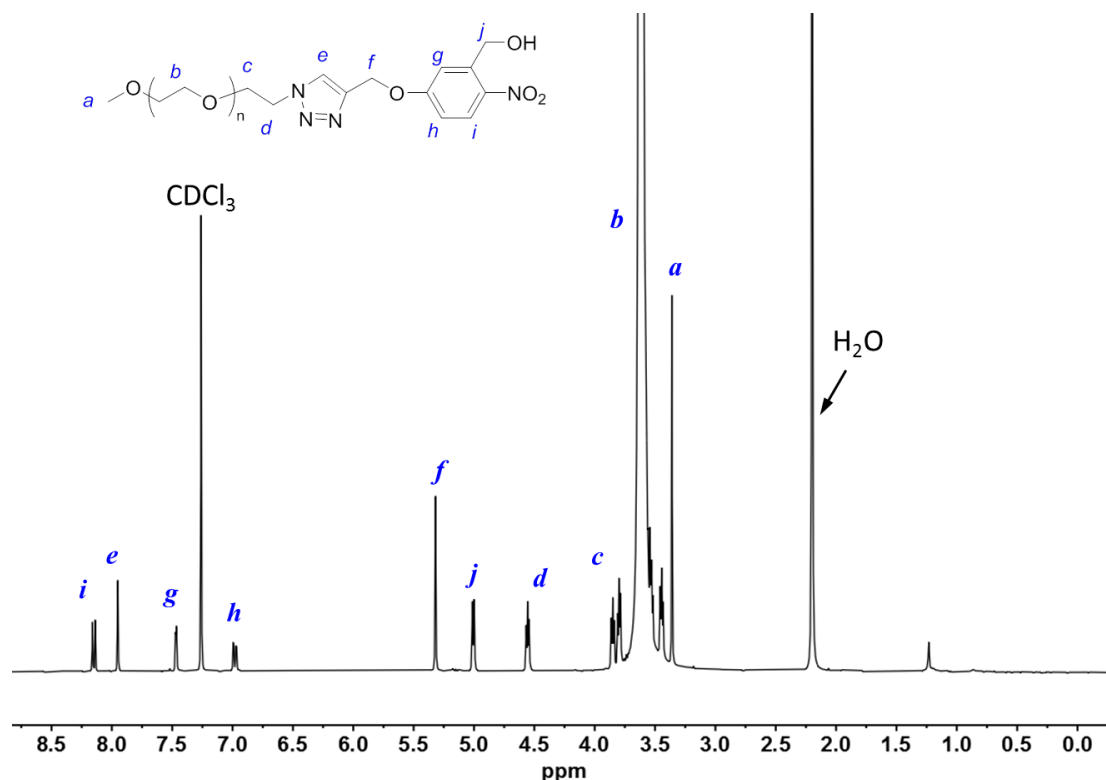


Figure S3. ^1H -NMR spectrum of PEO5k-ONB-OH in CDCl_3

Synthesis of PEO-ONB-Br. PEO2k-ONB-OH (4.0 g, 1.8 mmol), 2-bromoisobutyric acid (1.3 g, 7.8 mmol) and DMAP (188 mg, 1.6 mmol) were dissolved in anhydrous CH_2Cl_2 (50 mL) in a 250 mL Schlenk flask. The flask was covered with aluminum foil to avoid exposure to light. An anhydrous CH_2Cl_2 solution (30 mL) of EDC·HCl (3.1 g, 16.2 mmol) was slowly added into the flask at 0 °C. The mixture was kept stirring at room temperature under Ar overnight. Subsequently, the CH_2Cl_2 solution was washed with saturated NaHCO_3 solution, water and brine successively before dried with anhydrous MgSO_4 . The polymer solution was concentrated and poured into cold ethyl ether to gain a white solid precipitate. The solid was isolated and dried under vacuum at 35 °C overnight to obtain PEO2k-ONB-Br (3.9 g; Yield 90%). PEO5k-ONB-Br was synthesized in the same procedure and obtained as white solid (Yield: 95%). The ^1H -NMR

spectra of PEO2k-ONB-Br and PEO5k-ONB-Br are very similar, and thus only the latter is shown in **Figure S4**. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.20 (d, 1H, $J = 8$ Hz), 7.89 (s, 1H), 7.29 (s, 1H), 7.07 (d, 1H, $J = 8$ Hz), 5.65 (s, 2H), 5.29 (s, 2H), 4.54 (t, 2H, $J = 4$ Hz), 3.85 (t, 2H, $J = 4$ Hz), 3.8-3.4 (m, 450H), 3.35 (s, 3H), 1.99 (s, 6H).

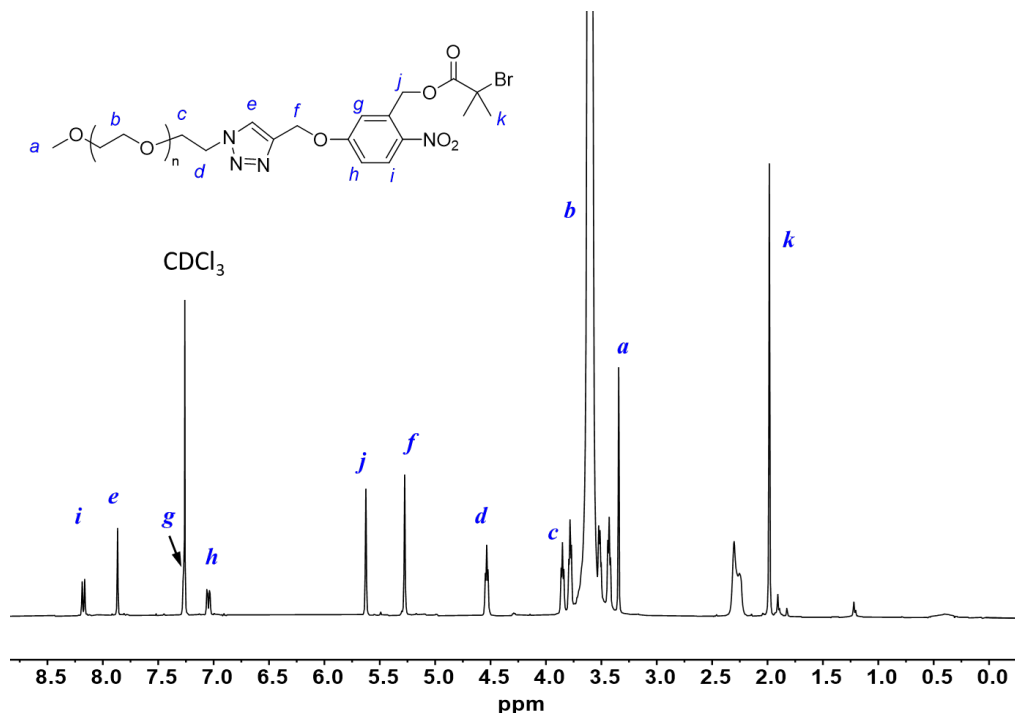


Figure S4. $^1\text{H-NMR}$ spectrum of PEO5k-ONB-Br in CDCl_3 .

Synthesis of PS-*h*-PEO. Freshly distilled styrene (14 mL, 120 mmol), PEO2k-ONB-Br (0.5 g, 0.21 mmol), and CuBr (36 mg, 0.25 mmol) were mixed in a 50 mL Schlenk flask with a magnetic stirrer bar. The mixture was subjected to three cycles of freeze-pump-thaw. Under Ar, PMDETA (100 μL , 0.5 mmol) was added into the flask via a microsyringe. The mixture was kept stirring at room temperature for 10 minutes before placing the flask into an oil bath at 90 $^\circ\text{C}$. The polymerization was monitored with $^1\text{H-NMR}$. After 19 hours, the polymerization was quenched by taking the flask out of the oil bath and putting it into an ice/water bath. The viscous liquid was cooled down and directly precipitated into hexanes. The crude product was isolated and dissolved

in 20 mL THF. Neutral alumina was added into the THF solution to remove the copper complex. The mixture was kept stirring at room temperature until the THF solution became colorless. After filtration, the THF solution was concentrated and dropped into hexanes to obtain a pale yellow solid precipitate. The product was further purified by dissolving in a small amount of THF and precipitated into hexanes twice. The solid was isolated and dried under vacuum at 40 °C overnight to obtain PS-*h* ν -PEO (8k–2k) (1.2 g, Yield: 60%). PS-*h* ν -PEO (18k–5k) was synthesized similarly and was obtained as white solid (Yield: 65%). The ¹H-NMR spectra of PS-*h* ν -PEO (8k–2k) (**Figures S5**) and PS-*h* ν -PEO (18k–5k) (**Figures S6**) are very similar, and thus the assignments are given only in **Figure S5**. In addition, GPC data of the two polymers are given in **Figures S7**. ¹H-NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.24-6.44 (m, 398H), 5.20 (s, 2H), 4.53 (s, 2H), 3.85 (m, 2H), 3.63-3.57 (s, 183H), 3.36 (s, 3H), 2.18-1.24 (m, 288H) for PS-*h* ν -PEO (8k–2k); δ 7.88 (s, 1H), 7.24-6.44 (m, 1023H), 5.20 (s, 2H), 4.53 (s, 2H), 3.85 (m, 2H), 3.63-3.57 (s, 474H), 3.36 (s, 3H), 2.18-1.24 (m, 653H) for PS-*h* ν -PEO (18k–5k).

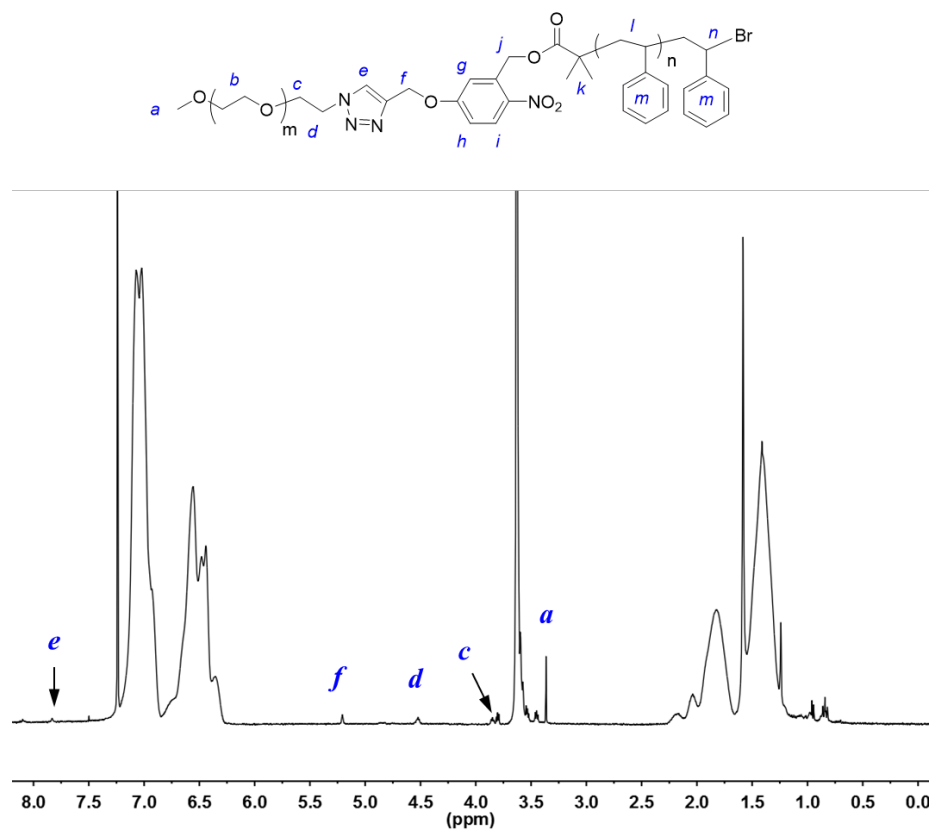


Figure S5. ¹H-NMR spectrum of PS-*h ν*-PEO (8k-2k) in CDCl₃.

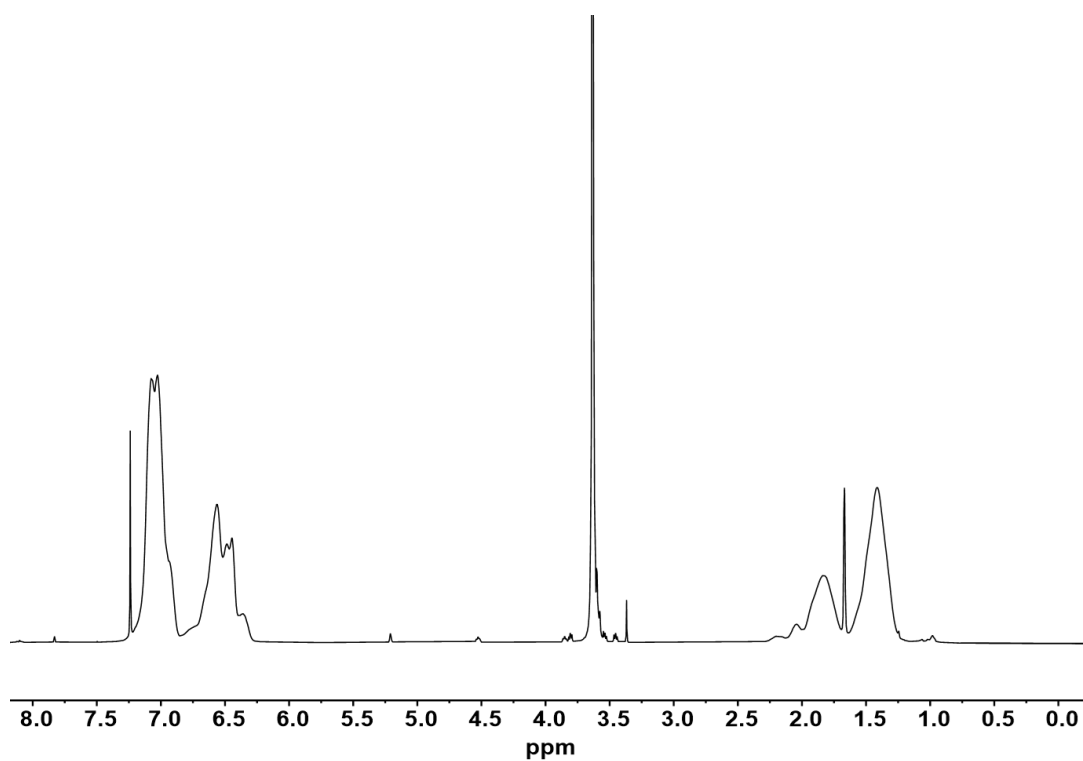


Figure S6. ¹H-NMR spectrum of PS-*h ν*-PEO (18k-5k) in CDCl₃.

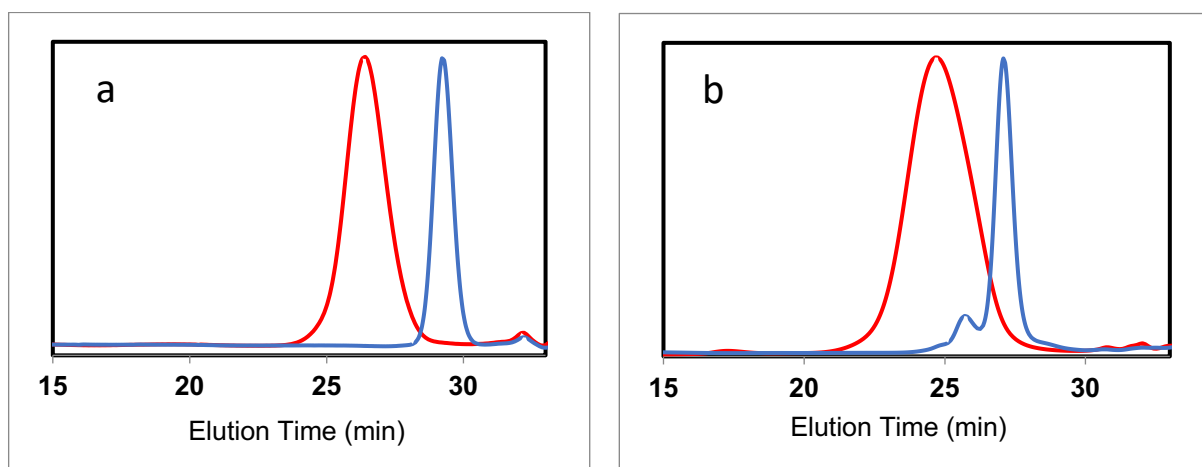


Figure S7. The GPC curves of (a) PS-*hν*-PEO (8k–2k) (red) and PEO2k-ONB-Br (blue) and (b) PS-*hν*-PEO (18k–5k) (red) and PEO5k-ONB-Br (blue).

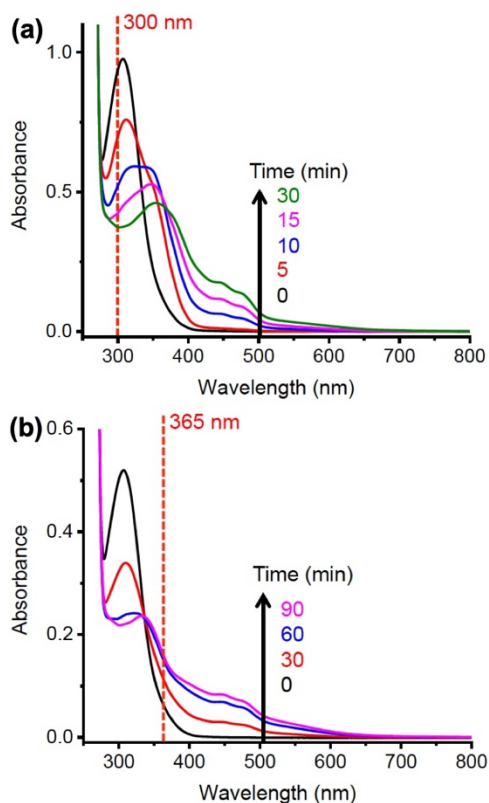


Figure S8. UV-Vis spectra of PS-*hν*-PEO solutions at different periods of UV irradiation: (a) A PS-*hν*-PEO (8k–2k) solution (1 mg/mL in dichloromethane) upon irradiation of 300 nm light. (b) A PS-*hν*-PEO (18k–5k) solution (1 mg/mL in dichloromethane) upon irradiation of 300 nm light. The observation of an isosbestic point in **Figure S8b** suggests the involvement of one reactant and one product in the photocleavage reaction.

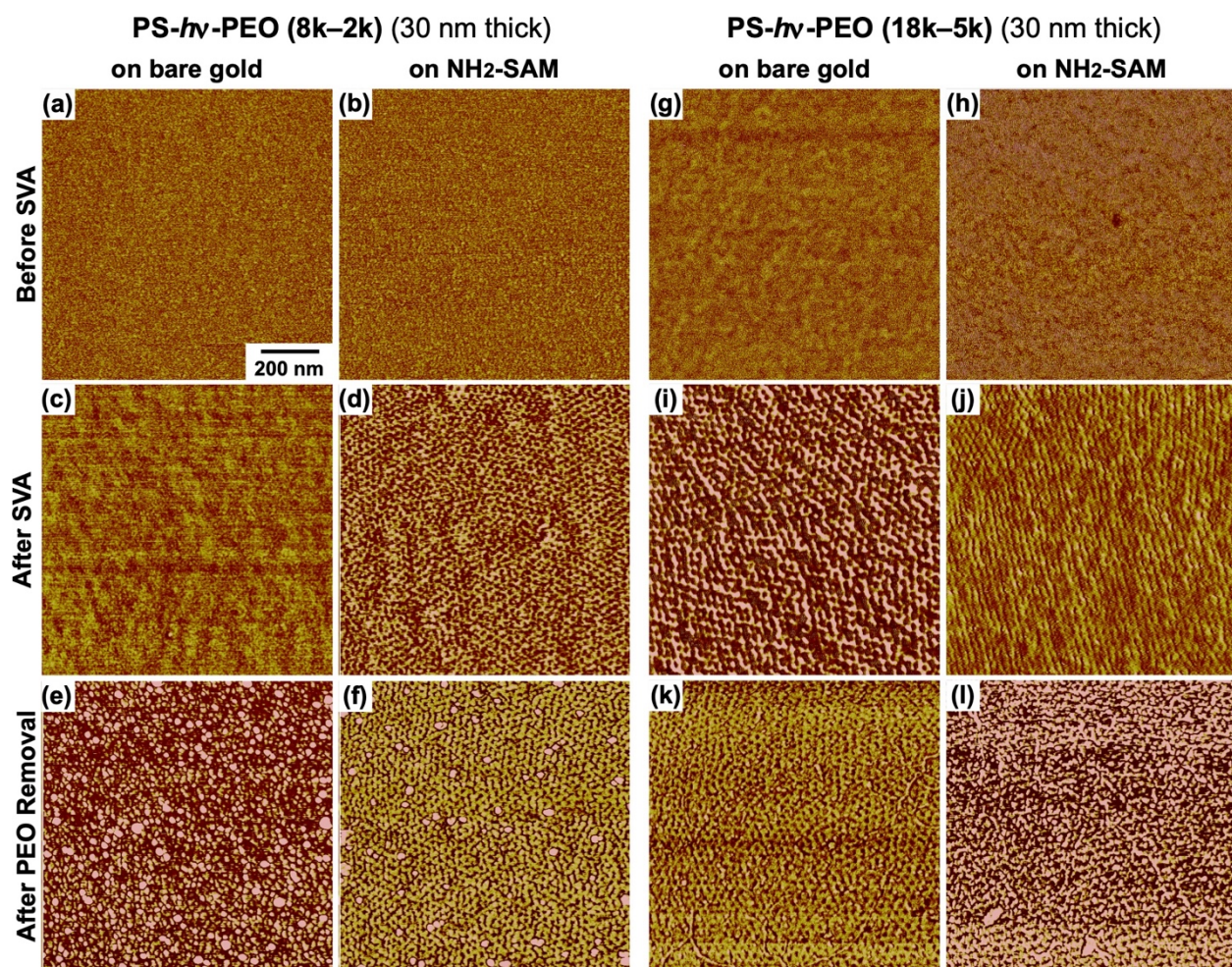


Figure S9. AFM phase images ($1 \times 1 \mu\text{m}^2$; $\Delta z = 60^\circ$) that were obtained simultaneously with the AFM height images of PS- $h\nu$ -PEO films in **Figure 2**.

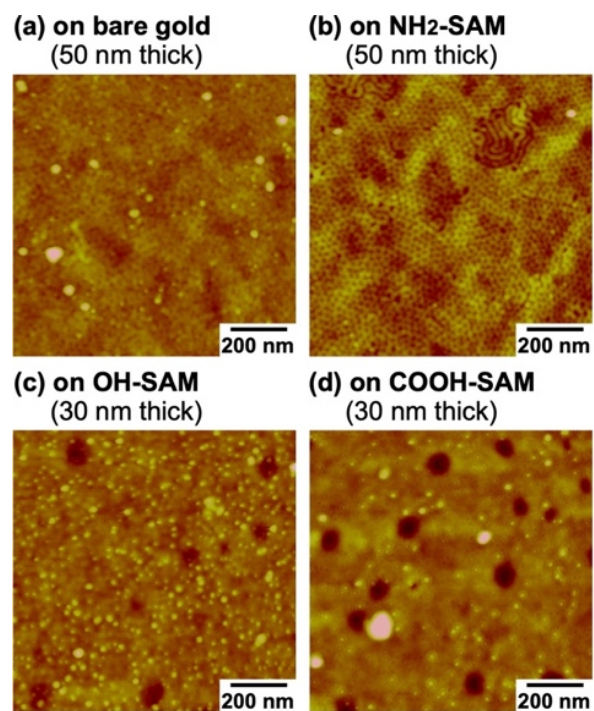


Figure S10. AFM height images ($1 \times 1 \mu\text{m}^2$; $\Delta z = 20 \text{ nm}$) of PS-*h*ν-PEO (8k–2k) films on (a) bare gold (50 nm thick), on (b) NH₂-SAM (50 nm thick), (c) OH-SAM (30 nm thick) and (d) COOH-SAM (30 nm thick) after PEO removal. The upper regions of **Figure S10b** show horizontally-oriented trenches, possibly reflecting the imperfect vertical orientation of the nanopores.

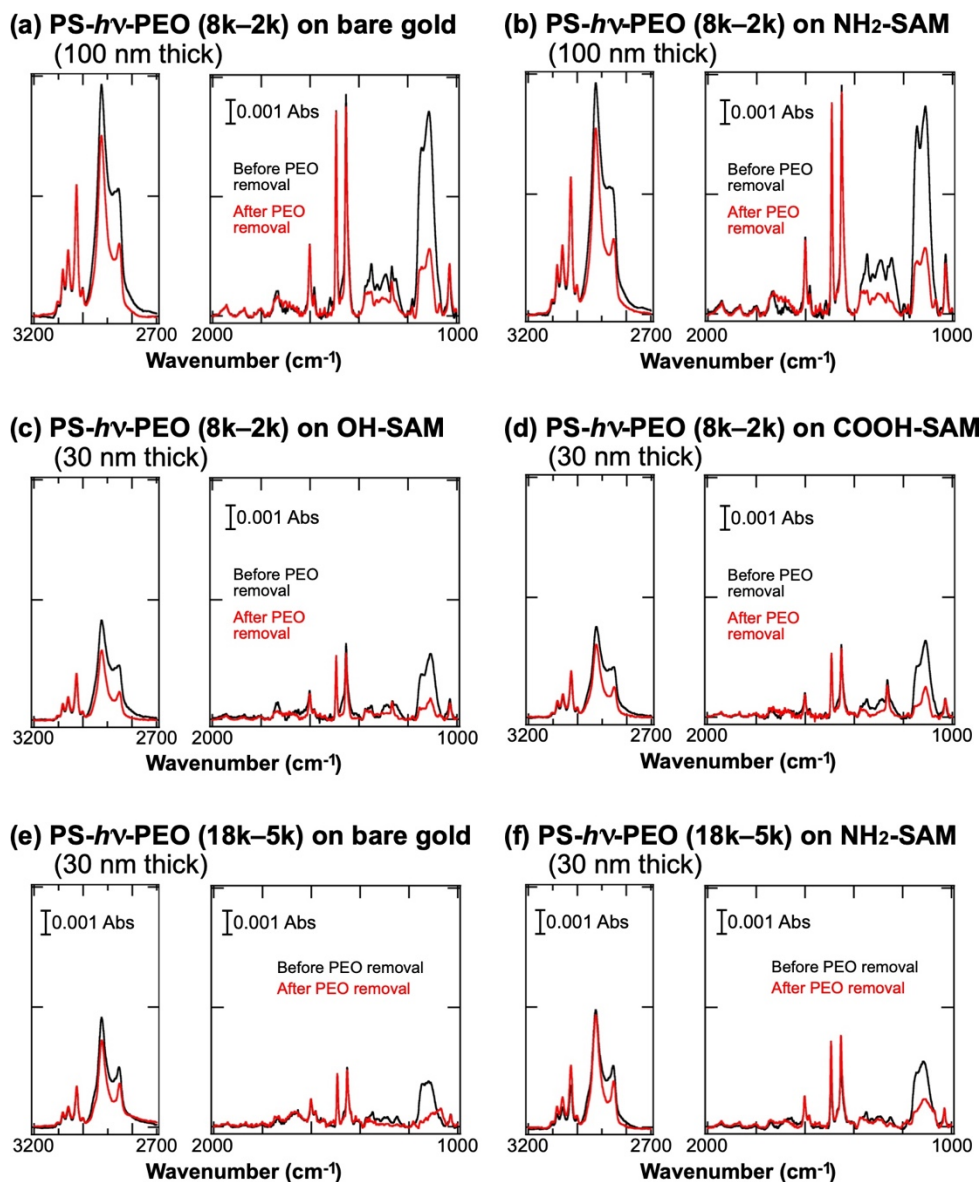


Figure S11. FTIR-ERS spectra of PS- $h\nu$ -PEO films before and after PEO removal: PS- $h\nu$ -PEO (8k-2k) films on (a) bare gold (100 nm thick), (b) NH₂-SAM (100 nm thick), (c) OH-SAM (30 nm thick), and (d) COOH-SAM (30 nm thick); PS- $h\nu$ -PEO (18k-5k) films on (e) bare gold (30 nm thick), (f) NH₂-SAM (30 nm thick).

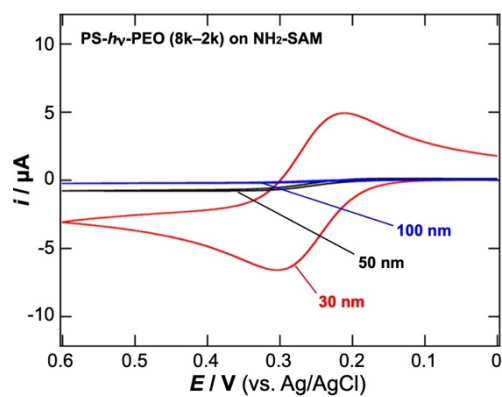


Figure S12. Cyclic voltammograms of 0.3 mM $\text{Fc}(\text{CH}_2\text{OH})$ ($\nu = 0.02$ V/s) in 0.1 M KCl + 10 mM phosphate (pH 7.0) at room temperature for nanoporous films formed from PS- $h\nu$ -PEO (8k-2k) on NH_2 -SAMs with different thicknesses: 30 nm (red), 50 nm (black) and 100 nm (blue).

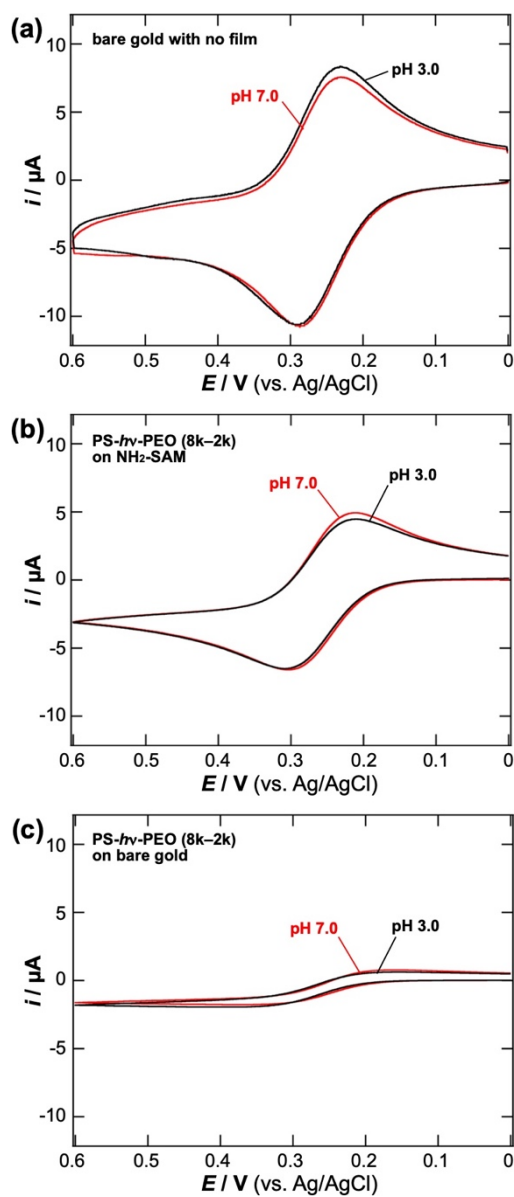


Figure S13. Cyclic voltammograms of 0.3 mM $\text{Fc}(\text{CH}_2\text{OH})$ ($\nu = 0.02$ V/s) at pH 7 and 3 (a) at a bare gold substrate with no nanoporous film, (b) for a nanoporous film formed from PS- $h\nu$ -PEO (8k-2k) on NH_2 -SAM (30 nm thick), and (c) for a nanoporous film formed from PS- $h\nu$ -PEO (8k-2k) on bare gold (30 nm thick). Measured in 0.1 M KCl + 10 mM phosphate at room temperature.

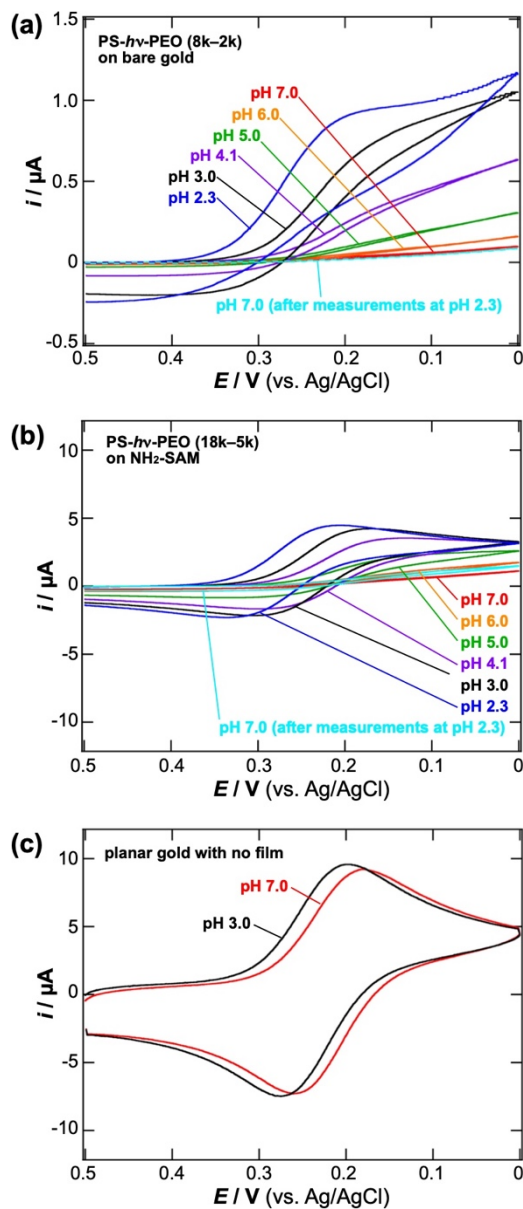


Figure S14. (a, b) Cyclic voltammograms of 0.3 mM $\text{Fe}(\text{CN})_6^{3-}$ ($\nu = 0.02 \text{ V/s}$) in 0.1 M KCl + 10 mM phosphate (pH 2.3–7) at room temperature (a) for a nanoporous film (30 nm thick) formed from PS- $h\nu$ -PEO (8k–2k) on bare gold and (b) for a nanoporous film (30 nm thick) formed from PS- $h\nu$ -PEO (18k–5k) on NH_2 -SAM. (c) Cyclic voltammograms ($\nu = 0.02 \text{ V/s}$) of 0.3 mM $\text{Fe}(\text{CN})_6^{3-}$ in 0.1 M KCl + 10 mM phosphate (pH 3 and 7) at a bare gold substrate with no nanoporous film.

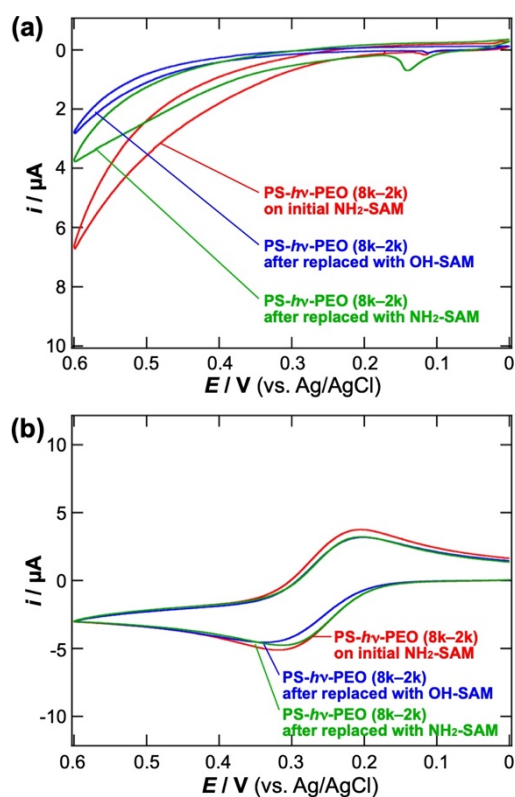


Figure S15. Cyclic voltammograms (0.02 V/s) of (a) 1.3 mM L-AA and (b) 0.3 mM $\text{Fc}(\text{CH}_2\text{OH})_2$ for a nanoporous film (30 nm thick) formed from PS- $h\nu$ -PEO (8k-2k) on NH_2 -SAM (red), after treatment with 1 mM 6-hydroxy-1-hexanethiol in water for 3 h (blue) and subsequent treatment with 5 mM cysteamine in ethanol for 3 h (green). Measured in 0.1 M KCl + 10 mM phosphate (pH 7.0) at room temperature.

Table S1. Contact Angles of Water and Diiodomethane ($\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$),^{a)} the Dispersion and Polar Components of the Surface Energies (γ_s^d and γ_s^p)^{b)} and Surface Free Energies of the Solid-Air Interface (γ_{SV})^{b)} for Gold Substrates with and without Thiolate SAMs

	$\theta_{\text{H}_2\text{O}}$ (°)	$\theta_{\text{CH}_2\text{I}_2}$ (°)	γ_s^d (mJ/m ²)	γ_s^p (mJ/m ²)	γ_{SV} (mJ/m ²)
Bare gold (no SAM)	57.4 ± 3.6	14.5 ± 2.5	42.6	12.8	55.4
NH ₂ -SAM	48.3 ± 3.0	29.2 ± 5.0	36.3	20.7	57.0
OH-SAM	37.3 ± 2.1	24.9 ± 2.0	36.5	27.1	63.6
COOH-SAM	58.7 ± 2.1	22.8 ± 1.4	40.4	12.9	53.3

^{a)} 95% confidence interval obtained from 4-8 measurements on two different samples. ^{b)} Calculated from the dispersion and polar components of the surface energy values of water ($\gamma^d = 21.8 \text{ mJ/m}^2$ and $\gamma^p = 51.0 \text{ mJ/m}^2$) and diiodomethane ($\gamma^d = 49.5 \text{ mJ/m}^2$ and $\gamma^p = 1.3 \text{ mJ/m}^2$) according to the geometric mean method.^{R4, R5}

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