**Supporting Information**

**Catalyst-Free Spontaneous Polymerization with 100% Atom Economy: Facile Synthesis of Photoresponsive Polysulfonates with Multifunctionalities**

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**Figure S44.** Change of molecular weight of P1c/2a/3a (1 mg/mL) in H2O/THF mixture (v/v, 1/99) at different UV irradiation time.

**References**
Materials and Instruments

Disulfonic acid 2a–c, hexafluoroisopropanol (HFIP), hexane and all other chemicals and reagents were purchased from Meryer, J&K Scientific, Aldrich, or Merck and used as commercially received unless stated otherwise. All the sulfonic acid used in this work were anhydrous. Dichromethane (DCM) was superdry with molecular sieves and was purchased from J&K Scientific. Dihaloalkynes 1a–e were prepared according to the previous reported procedures1–4.

Weight- ($M_w$) and number-average molecular weights ($M_n$) and polydispersity indices ($M_w/M_n$) of the obtained polymers were estimated by a Waters gel permeation chromatography system. THF was used as eluent at a flow rate of 1 mL min⁻¹. A set of monodispersed polystyrenes, covering the $M_w$ range of $10^3$–$10^7$ g/mol, were utilized as standards for molecular weight calibration. The polymers were dissolved in THF (~2 mg mL⁻¹) and filtered through 0.20 μm PTFE syringe-type filters before being injected into the GPC system. The column temperature was maintained at 40 °C and the working wavelength of the UV-vis detector was set at 254 nm. FT-IR spectra and high-resolution mass spectra (HRMS) were recorded on a Bruker Vertex 70 FT-IR spectrometer (KBr disk) and a GCT Premier CAB 048 mass spectrometer, respectively. Kinetic data analysis was obtained through in situ IR technique, and the polymerization spectra were recorded on a ReactIR 15 from Mettler Toledo AutoChem. $^1$H and $^{13}$C NMR spectra were obtained on a Bruker ARX 400 NMR spectrometer using CDCl₃, CD₂Cl₂ or DMSO-d₆ as solvent. Chemical shifts were calibrated using CDCl₃ as internal reference at δ 7.26 ppm ($^1$H NMR) and δ 77.16 ppm ($^{13}$C NMR), CD₂Cl₂ as internal reference at δ 5.32 ppm ($^1$H NMR) and δ 53.84 ppm ($^{13}$C NMR), and DMSO-d₆ as internal reference at δ 2.50 ppm ($^1$H NMR) and δ 39.52 ppm ($^{13}$C NMR).

UV-vis spectra and PL spectra were measured on a Milton Ray Spectronic 3000 Array spectrophotometer and a PerkinElmer LS 55 spectrophotometer, respectively. The photodegradation was conducted using UV flashlight (365 nm) at a distance of 5 cm and the power was 5 W. The stability under white light irradiation was tested using OSRAM LED Lamp (400–780 nm) with maximum luminous flux of 2400 lm with the applied power of 30 W. pH was measured by JENWAY 3510 pH meter. Thin films for refractive index measurement and photopatterning were fabricated by spin-coating the 1,2-
dichloroethane solutions of the polymers (~20 mg mL\(^{-1}\)) on silicon wafers at 600 rpm for 9 s and 1000 rpm for 1 min, and then dried in a vacuum oven at room temperature for two hours. The fluorescent photopatterns were generated by UV irradiating the polymer thin films at 200–400 nm through a photomask in air at room temperature. The photo-irradiation process was conducted using UV light from an Oriel Mercury Arc Lamp at a distance of 8 cm and the applied power of the Mercury Arc Lamp (200–400 nm) was 180 W. The fluorescent photopatterns were taken on a fluorescence optical microscope (Nikon Eclipse 80i) under a UV light source. RI values were determined on a Woollam ellipsometer with a model of Alpha-SE with a wavelength tunability from 380 to 900 nm. The photomask with grid pattern were coated with copper in the square areas whereas the grid lines were transparent glass substrate. The photomask with “QR Code” pattern was printed on a transparent paper by laser printer. The heart-shape photomask was cut out from a piece of black paper. Electron paramagnetic resonance (EPR) spectroscopy experiments were completed using a JES-FA200 EPR spectrometer at room temperature.

For biology experiments, Luria-Bertani (LB) broth, LB agar and normal saline (0.85% NaCl) were purchased from Sigma-Aldrich. All the other chemicals were purchased from Sigma-Aldrich and Sinopharm Chemical Reagent Co., Ltd, and used directly without further purification. Ultrapure water (18.0 MΩ cm) was prepared by a Milli-Q system (Millipore, Germany) and used throughout.

**Sample preparation**

A stock solution of P\(^1\)a/2\(^a\) in THF with a concentration of 100 mg/mL was prepared and stored in the 4 °C fridge. LB broth and LB agar were prepared according to the protocol on the product description. All the mediums were sterilized for 20 min at 121 °C before inoculation with the bacteria.

**Bacterial culturing**

A single colony of bacteria (E. coli, S. aureus or P. aeruginosa) on LB agar plate was transferred to 5 mL of LB broth and grown with shaking at 37 °C overnight. The concentration of bacteria was determined by measuring optical density at 600 nm (OD\(_{600}\)). Bacteria were harvested by centrifugation at 7000 rpm for 2 min, and washed with normal saline twice. After removing the supernatant, the remaining bacterial were resuspended with normal saline, and diluted to optical density of 1.0 (OD\(_{600} = 1.0\)) with about 1 × 10\(^9\) CFU/mL.
Antimicrobial assay by plate colony counting method

The harvested bacteria were resuspended with normal saline (OD$_{600} = 1.0$), and diluted for $1 \times 10^3$ fold with normal saline. The resulted bacteria were incubated with P$_{1a/2a}$ (2 mg/mL) for 5 min in the dark. Next, the bacterial suspensions were exposed to UV irradiation at 365 nm (40 mW/cm$^2$) for 30 min. Meanwhile, the bacterial suspensions treated in the absence of P$_{1a/2a}$ or light irradiation were used as control groups. After various treatment, the bacterial suspensions were directly diluted for 100 folds. 50 μL of diluted bacterial cells was spread on the solid LB agar plate, followed by culturing at 37 °C for 14–24 h before colony forming units (CFU) counting and taking photos. The bacterial viability was assessed by the number of colonies of bacteria. Triplicate analyses of each sample were performed and each experiment was carried out in duplicate.

For toxicity tests of P$_{1a/2a}$ to E. coli, S. aureus and P. aeruginosa, the bacterial suspensions were incubated with P$_{1a/2a}$ (2 mg/mL) in natural light for 30 min. and the bacterial viability was assessed by plate colony counting method.

Scanning electron microscopy analysis

Followed by antimicrobial experiments, the resulted cells suspension was dropped onto fresh silicon slices for further drying in air. After drying, 0.1% glutaraldehyde was used to fix bacterial cells for 1 h and the higher concentration of glutaraldehyde (2.5%) was added for further 2 h-fixing. After washing by sterile water, the specimens were dehydrated by addition of ethanol in a graded series (30%, 50%, 70%, 80%, 90%, 95% and 100%) for 6 min each, and then incubated with tert-butanol overnight at 4 °C. After further freeze-drying for 1–2 h, the specimens were coated with gold for SEM analysis by SEM S-4800 (Hitachi, Japan).

Transmission electron microscopy analysis

Followed by antimicrobial experiments, the bacteria were fixed with 2.5% glutaraldehyde for 12 h. The samples were deposited on the copper grid-supported carbon film and characterized by TEM H-7650 (Hitachi, Japan).

Preparation, application and performance evaluation of antibacterial coating

For the preparation of antibacterial coating, a THF solution containing P$_{1a/2a}$ (2 mg/mL) was coated on the glass and dried at room temperature in air. For the antibacterial application, the as-prepared antibacterial coating was coated by living S. aureus suspensions (OD$_{600} = 1.0$), mildly dried at room temperature, and exposed to UV irradiation at 365 nm for 30 min (40 mW/cm$^2$). For comparison, UV irradiations were
performed in humid environment and common environment, respectively. Meanwhile, the glass without P1a/2a coating was also used as a control group. To evaluate the antibacterial performance of the above coating, the residual bacteria were washed into the fresh LB agar plate and incubated at 37 °C for 14–24 h.

**Preparation, application and performance evaluation of antibacterial spray**

The antibacterial spray was obtained by preparing P1a/2a aqueous suspension (2 mg/mL) containing 2% THF. For the antibacterial application, the as-prepared antibacterial spray was sprayed on the glass slide covering living *S. aureus* cells, and then exposed to UV irradiation at 365 nm for 30 min (40 mW/cm²). Meanwhile, the cells treated without spray or UV irradiation were used as control groups. To evaluate the antibacterial performance of the above spray, the residual bacteria were washed into the fresh LB agar plate and incubated at 37 °C for 14–24 h.
Synthesis and Characterization

Monomer Preparation

Synthetic procedure of $\textbf{1a}$ was given below as an example. Into a 100 mL two-necked round-bottom flask equipped with a condenser was placed 1,2-bis(4-bromophenyl)-1,2-diphenylethene (5 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.5 mmol), CuI (0.5 mmol), and PPh$_3$ (0.25 mmol) under nitrogen. Trimethylsilylacetylene (13 mmol), 40 mL of THF and 8 mL of triethyl amine were then injected and the reaction mixture was reflux overnight. Upon completion, the solvent was removed under reduced pressure and the crude product 1,2-diphenyl-1,2-bis(4-((trimethylsilyl)ethyl)phenylethene was purified using hexane as eluent by silica-gel column chromatography in 92% yield.

Into a 50 mL round-bottom flask was dissolved 1,2-diphenyl-1,2-bis(4-((trimethylsilyl)ethyl)phenylethene (2 mmol) in acetone (30 mL), and N-Bromosuccinimide (6 mmol) and AgNO$_3$ (0.44 mmol) was added. The reaction mixture was stirred at room temperature under exclusion of light overnight. Upon completion the reaction mixture was concentrated under reduced pressure and the crude product was purified by silica-gel column chromatography using hexane as eluent. Light yellow powder of monomer $\textbf{1a}$ was obtained in 95% yield. $^1$H NMR (400 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 7.22-7.11 (m, 10H), 7.02-6.96 (m, 8H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 144.58, 143.23, 141.39, 131.79, 131.56, 128.30, 128.16, 127.30, 127.17, 121.11, 120.96, 80.29, 50.16. IR (neat): 3057, 3026, 2196, 1596, 1494, 1442, 1404, 1261, 1107, 1074, 1022, 977, 914, 860, 838, 812, 746, 702, 619, 574 cm$^{-1}$.

Model Compound Synthesis and Characterization

To a 10 mL Schlenk tube were added 4-methylbenzenesulfonic acid (0.2 mmol), dihaloalkyne $\textbf{1a}$ (0.1 mmol), and 0.5 mL of HFIP/DCM (v/v, 1:8). The solution turned dark as soon as the addition of HFIP. The resulting solution was stirred at room temperature and monitored by TLC. Upon completion, the solvent was removed under reduced pressure and model compound $\textbf{3}$ was obtained by using silica-gel column chromatography in 76% yield (yellow solid). $^1$H NMR (400 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 7.72-7.63 (m, 8H), 7.28-6.95 (m, 18H), 6.40 (s, 2H), 2.42 (s, 6H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 148.15, 146.17, 145.36, 145.04, 143.14, 142.83, 142.32, 141.49, 132.84, 132.01,
131.53, 131.06, 130.14, 128.76, 128.39, 128.17, 127.57, 127.52, 127.34, 127.20, 101.13, 21.87. IR (neat): 1695, 1679, 1602, 1492, 1442, 1402, 1377, 1305, 1278, 1193, 1178, 1093, 1028, 1006, 850, 812, 761, 732, 700, 663, 565, 549 cm⁻¹. HRMS (CI) calcd for C₄₄H₃₄Br₂O₆S₂: 880.0164, found: 880.0173.

Polymer Characterization

**Characterization Data for P1a/2a**: Yellow powder; 83%. Mₙ: 12,100; Mₘ: 27,600; Mₘ/Mₙ: 2.3 (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1710, 1678, 1664, 1604, 1500, 1492, 1442, 1391, 1240, 1190, 1136, 1047, 1001, 848, 821, 761, 729, 700, 619, 572 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.88, 7.66, 7.30−6.74 (aromatic protons), 6.47 (vinyl proton). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 148.11, 145.18, 144.42, 143.13, 141.78, 141.11, 136.07, 131.67, 131.59, 131.42, 131.13, 129.57, 128.19, 127.34, 121.05, 101.41.

**Characterization Data for P1b/2a**: Yellow powder; 94%. Mₙ: 7,800; Mₘ: 11,900; Mₘ/Mₙ: 1.5 (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1716, 1672, 1629, 1598, 1554, 1494, 1442, 1386, 1267, 1238, 1190, 1138, 1049, 999, 850, 819, 759, 731, 700, 619, 572, 563 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.96, 7.87, 7.62−7.03 (aromatic protons), 6.44 (vinyl proton). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 148.10, 145.18, 144.42, 143.13, 141.78, 141.11, 136.07, 131.67, 131.59, 131.42, 131.13, 129.57, 128.19, 127.34, 121.05, 101.48.

**Characterization Data for P1c/2a**: Yellow powder; 91%. Mₙ: 7,400; Mₘ: 9,500; Mₘ/Mₙ: 1.3 (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1716, 1674, 1627, 1600, 1558, 1490, 1442, 1384, 1267, 1238, 1190, 1137, 1049, 999, 860, 819, 761, 731, 700, 621, 574, 563 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.96, 7.85, 7.61−6.93 (aromatic protons), 6.56 (vinyl proton). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 149.70, 145.18, 144.42, 143.99, 141.51, 136.08, 131.57, 131.42, 129.56, 128.57, 128.29, 127.19, 101.48.

**Characterization Data for P1d/2a**: Yellow powder; 80%. Mₙ: 7,500; Mₘ: 12,800; Mₘ/Mₙ: 1.7 (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1595, 1558, 1485, 1465, 1413, 1382, 1305, 1267, 1238, 1190, 1157, 1137, 1097, 1047, 1014, 1001, 869, 819, 729, 619, 578, 543 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.81−6.80 (aromatic protons), 6.59 (vinyl proton), 1.55−1.11 (CH₃). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 154.55, 154.26, 153.91.
149.05, 148.70, 148.53, 144.92, 141.01, 139.88, 135.90, 135.72, 131.63, 130.72, 129.89, 129.43, 128.99, 135.72, 131.63, 130.72, 129.89, 129.43, 128.99, 128.74, 128.29, 126.91, 126.69, 123.58, 123.30, 120.47, 103.79, 102.18, 47.36, 26.88.

**Characterization Data for P**1e/2a**: Yellow powder; 88%. \( M_n: 5,100 \); \( M_w: 11,500 \); \( M_w/M_n: 2.3 \) (GPC, polystyrene calibration). IR (KBr), \( \nu \) (cm\(^{-1}\)): 1683, 1597, 1558, 1485, 1448, 1384, 1303, 1238, 1190, 1132, 1037, 1016, 999, 962, 864, 837, 821, 759, 729, 617, 572 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) (ppm): 7.96–6.60 (aromatic protons), 6.40–6.30 (vinyl proton). \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) (ppm): 149.61, 147.78, 145.07, 142.25, 135.70, 132.03, 129.43, 128.51, 128.36, 127.78, 124.69, 124.04, 120.91, 120.42, 104.27, 101.97, 66.18.

**Characterization Data for P**1b/2a**: Yellow powder; 75%. \( M_n: 8,700 \); \( M_w: 27,000 \); \( M_w/M_n: 3.1 \) (GPC, polystyrene calibration). IR (KBr), \( \nu \) (cm\(^{-1}\)): 1710, 1679, 1656, 1598, 1500, 1442, 1402, 1274, 1244, 1226, 1190, 1151, 977, 908, 794, 769, 698, 661, 613, 568, 528, 466 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) (ppm): 7.88, 7.64, 7.30–6.99 (aromatic protons), 6.47 (vinyl proton). \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) (ppm): 143.40, 142.00, 141.28, 131.64, 128.91, 128.18, 127.24, 100.54.

**Characterization Data for P**1c/2a**: Yellow powder; 69%. \( M_n: 8,500 \); \( M_w: 16,200 \); \( M_w/M_n: 1.9 \) (GPC, polystyrene calibration). IR (KBr), \( \nu \) (cm\(^{-1}\)): 1679, 1597, 1494, 1442, 1400, 1276, 1180, 1163, 1107, 1072, 1018, 856, 837, 815, 759, 698, 621, 574 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) (ppm): 7.73, 7.46–7.06 (aromatic protons), 6.75 (vinyl proton), 4.45. \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) (ppm): 148.55, 143.09, 141.31, 132.03, 131.54, 128.66, 128.31, 127.48, 101.81, 31.98.

**Postfunctionalization**

**P**1c/2a/3a** was synthesized by Suzuki reaction of **P**1c/2a** and 4-hexylphenylboronic acid in the presence of Pd(PPh\(_3\))\(_4\). 0.06 mmol of **P**1c/2a**, 0.15 mmol of 4-hexylphenylboronic acid, 0.006 mmol of Pd(PPh\(_3\))\(_4\), 0.3 mmol of K\(_2\)CO\(_3\) were added into the Schlenk tube, and charged with nitrogen. Then 2 mL THF and 0.2 mL H\(_2\)O were injected. The resulting solution was refused for 24 h. After solvent evaporation in *vacuo*, 2 mL of DCM was added to the crude product, and then filtered. The filtrate was added dripwisely into 100 mL of hexane, and the precipitate was finally collected after filtration, washing
with hexane and dried under vacuum at room temperature to a constant weight. Dark Orange powder, yield: 79%, conversion: 88% (according to integrates of the $^1$H NMR peaks). $M_n$: 6,800; $M_w$: 10,400; $M_w/M_n$: 1.5 (GPC, polystyrene calibration). $^1$H NMR (400 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 8.12–7.07 (m, 41H), 2.70–2.61 (4H), 1.58–0.88 (22H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$), $\delta$ (ppm): 136.23, 135.59, 135.09, 134.04, 132.35, 131.72, 131.05, 128.97, 128.60, 128.08, 115.30, 32.15, 29.41, 23.00, 14.24.
**Scheme S1.** Synthetic routes to monomers 1a–c.

**Scheme S2.** Synthetic routes to monomers 1d–e.
Scheme S3. Synthetic route to model compound 3.
Figure S1. FT-IR spectra of (A) 1a, (B) 2a, (C) model compound 3, and (D) P1a/2a.

Figure S2. FT-IR spectra of (A) P1b/2a, (B) P1c/2a, and (C) P1d/2a.
Figure S3. IR spectra of (A) P1e/2a, (B) P1a/2b, and (C) P1a/2c.

Figure S4. HRMS (CI) spectrum of model compound 3.
Figure S5. $^1$H NMR spectrum of model compound 3 in CD$_2$Cl$_2$.

Figure S6. $^{13}$C NMR spectrum of model compound 3 in CD$_2$Cl$_2$. 
Figure S7. $^1$H NMR spectrum of P1a/2a in CD$_2$Cl$_2$.

Figure S8. $^{13}$C NMR spectrum of P1a/2a in CD$_2$Cl$_2$. 
Figure S9. $^1$H NMR spectrum of P1b/2a in CD$_2$Cl$_2$.

Figure S10. $^{13}$C NMR spectrum of P1b/2a in CD$_2$Cl$_2$.
Figure S11. $^1$H NMR spectrum of $\text{P1c/2a}$ in CD$_2$Cl$_2$.

Figure S12. $^{13}$C NMR spectrum of $\text{P1c/2a}$ in CD$_2$Cl$_2$. 
Figure S13. $^1$H NMR spectrum of P1d/2a in CD$_2$Cl$_2$.

Figure S14. $^{13}$C NMR spectrum of P1d/2a in CD$_2$Cl$_2$. 

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Figure S15. $^1$H NMR spectrum of P1e/2a in CD$_2$Cl$_2$.

Figure S16. $^{13}$C NMR spectrum of P1e/2a in CD$_2$Cl$_2$. 
Figure S17. $^1$H NMR spectrum of P1a/2b in CD$_2$Cl$_2$.

Figure S18. $^{13}$C NMR spectrum of P1a/2b in CD$_2$Cl$_2$. 
Figure S19. $^1$H NMR spectrum of P1a/2c in CD$_2$Cl$_2$.

Figure S20. $^{13}$C NMR spectrum of P1a/2c in CD$_2$Cl$_2$. 
Figure S21. $^1$H NMR spectrum of P1c/2a/3a in CD$_2$Cl$_2$.

Figure S22. $^{13}$C NMR spectrum of P1c/2a/3a in CD$_2$Cl$_2$.
Figure S23. $^1$H NMR spectra of (A) 2a, (B) HFIP, (C) a 1:10 mixture of 2a: HFIP, and (D) 1-D gradient NOE with $T_{\text{mix}} = 800$ ms for a 1:10 mixture of 2a: HFIP when irradiated $H_a$ in DMSO-$d_6$.

Figure S24. NOESY spectrum of a 1:10 mixture of 2a: HFIP in DMSO-$d_6$. 
Proposed polymerization mechanism:

Scheme S4. Proposed mechanism for the polymerization of disulfonic acids and dihaloalkynes to polysulfonates.
Figure S25. Absorption spectra of P1/2 in THF solution. Concentration: 40 μM.

Figure S26. Emission spectra of P1/2 in THF solution. Concentration: 40 μM. Excitation wavelength: 350 nm.
Figure S27. Emission spectra of P1a/2a in hexane/DCM mixtures with different hexane fractions. Excitation wavelength: 350 nm. Inset: Photographs of P1a/2a in hexane/DCM mixtures with different hexane fractions (f_H) taken under 365 nm UV irradiation from a handheld UV lamp. Concentration: 40 μM.

Figure S28. Plot of relative emission intensity (I/I_0) versus the composition of a hexane/DCM mixture of P1a/2a. Concentration: 40 μM. I_0 = PL intensity in pure DCM solution.
**Table S1.** Quantum yield ($\Phi_{\text{solid}}$) of the polymer powder.

| Polymer     | P1a/2a | P1b/2a | P1c/2a | P1d/2a |
|-------------|--------|--------|--------|--------|
| $\Phi_{\text{solid}}$ (%) | 1.4    | 1.3    | 0.9    | 0.6    |

| Polymer     | P1e/2a | P1a/2b | P1a/2c |
|-------------|--------|--------|--------|
| $\Phi_{\text{solid}}$ (%) | 0.5    | 1.2    | 1.3    |

**Table S2.** Photophysical properties of P1a/2a in THF/H$_2$O mixture (v/v, 1/99) before and after irradiation at 365 nm for 40 min. Concentration: 100 $\mu$M. $^a$

| P1a/2a     | $\lambda_{\text{abs}}$ (nm) | $\lambda_{\text{em}}$ (nm) | $\Phi_{\text{aggre}}$ (%) |
|------------|-----------------------------|-----------------------------|---------------------------|
| before     | 357                         | 498                         | 1.3                       |
| after      | 253                         | 427                         | 4.0                       |

$^a$Abbreviation: $\lambda_{\text{abs}}$ = absorption maximum; $\lambda_{\text{em}}$ = emission maximum; $\Phi_{\text{aggre}}$ = fluorescent quantum yield of the polymer suspension.

**Figure S29.** GPC curves of P1a/2a in (A) THF or (B) H$_2$O/THF mixture (v/v, 1/99) before and after UV irradiation at 365 nm.
Figure S30. Change of pH of P1a–1e/2a (1.17 mM) in H2O/THF mixture (v/v, 1/99) at different irradiation time.

Table S3. Change of molecular weight of P1a–1e/2a (1.17 mM) in H2O/THF mixture (v/v, 1/99) after 365 nm irradiation for 20 min.

| Polymer   | Before UV irradiation | After UV irradiation |
|-----------|------------------------|----------------------|
|           | $M_n$ | $M_w$ | $M_n$ | $M_w$ |
| 1a/2a     | 12,100 | 27,600 | 1,900 | 5,100 |
| 1b/2a     | 7,800  | 11,900 | 2,500 | 3,900 |
| 1c/2a     | 7,400  | 9,500  | 2,200 | 3,200 |
| 1d/2a     | 7,500  | 12,800 | 2,300 | 3,200 |
| 1e/2a     | 5,100  | 11,500 | 2,800 | 7,800 |
**Figure S31.** Electron paramagnetic resonance (EPR) spectra of P1a/2a powder in the presence or absence of UV irradiation at room temperature. (g-factor = 2.0039)

**Figure S32.** HRMS (MALDI-TOF) spectrum of the photodegradation product of 3.
Figure S33. $^1$H NMR spectrum of (A) $p$-Toluenesulfonic acid, (B) model compound 3, and (C–F) photodegradation product of 3 at different irradiation time in DMSO-$d_6$. The photodegradation was conducted in $\text{H}_2\text{O}/\text{THF}$ (v/v, 1/99) mixture under 365 nm irradiation of 40 mW cm$^{-2}$, and then the solvent was removed under reduced pressure. $S_a$ and $S_b$ are the area of peak “a” and “b”, respectively.
Figure S34. $^{13}$C NMR spectrum of (A) $p$-Toluenesulfonic acid, (B) model compound 3 and (C) photodegradation product of 3 in DMSO-$d_6$. 
Figure S35. Wavelength-dependent refractive index of thin films of P1/2.

Table S4. Refractive indices and chromatic dispersions of polymers.

| Polymer   | $n_{632.8}$ | $\nu_D$ | $D$ |
|-----------|-------------|--------|-----|
| P1a/2a    | 1.770       | 13.444 | 0.074 |
| P1b/2a    | 1.685       | 13.598 | 0.073 |
| P1c/2a    | 1.714       | 19.947 | 0.050 |
| P1d/2a    | 1.742       | 18.623 | 0.054 |

*Abbreviation: $n$ = refractive index, $\nu_D$ = Abbé number = $(n_D - 1)/(n_F - n_C)$, where $n_D$, $n_F$, and $n_C$ are the $n$ values at wavelengths of Fraunhofer D, F, and C spectral lines of 589.2, 486.1, and 656.3 nm, respectively; $D$ = chromatic dispersion = $1/\nu_D$. 
Table S5. Refractive indices and chromatic dispersions of P1a/2a upon different UV irradiation time.\textsuperscript{a}

| Entry | Time (min) | $n_{632.8}$ | $\nu_D$ | $D$   |
|-------|------------|-------------|---------|------|
| 1     | 0          | 1.770       | 13.444  | 0.074|
| 2     | 10         | 1.721       | 14.057  | 0.071|
| 3     | 20         | 1.687       | 15.628  | 0.064|
| 4     | 30         | 1.676       | 13.960  | 0.072|
| 5     | 40         | 1.669       | 14.136  | 0.071|

\textsuperscript{a}Abbreviation: $n$ = refractive index, $\nu_D$ = Abbé number = $(n_D - 1)/(n_F - n_C)$, where $n_D$, $n_F$, and $n_C$ are the $n$ values at wavelengths of Fraunhofer D, F, and C spectral lines of 589.2, 486.1, and 656.3 nm, respectively; $D$ = chromatic dispersion = $1/\nu_D$. The definition of $\nu_D$ and $D$ can be found in literatures.\textsuperscript{5}
**Figure S36.** The effect of irradiation time on pH of *S. aureus* solution in the presence of P1a/2a (2 mg/mL).

**Figure S37.** Toxicity tests of P1a/2a to *E. coli*, *S. aureus* (SA) and *P. aeruginosa* (PA) in natural light.
Survival rates of *E. coli* and *S. aureus* in the presence of P1a/2a (2 mg/mL) at different irradiation time. (365 nm, 40 mW cm$^{-2}$)

Photographs of the agar plates of *E. coli*, *S. aureus* and *P. aeruginosa* in the presence or absence of P1a/2a (2 mg/mL) or light irradiation at 365 nm (40 mW cm$^{-2}$) for 30 min.
Figure S40. Photographs of the agar plates from two antimicrobial methods upon diverse treatments. Irradiation time: 30 min.
**Figure S41.** Absorption spectrum of P\textsubscript{1c}/2a/3a in THF solution. Concentration: 20 \( \mu \text{M}. \)

**Figure S42.** Emission spectrum of P\textsubscript{1c}/2a/3a in THF solution. Concentration: 20 \( \mu \text{M}. \) Excitation wavelength: 350 nm.
Figure S43. GPC curves of P1c/2a/3a (1 mg/mL) in H₂O/THF mixture (v/v, 1/99) before and after UV irradiation at 365 nm.

Figure S44. Change of molecular weight of P1c/2a/3a (1 mg/mL) in H₂O/THF mixture (v/v, 1/99) at different UV irradiation time.
References

1. Pigulski, B. et al. Transition-Metal Free Mechanochemical Approach to Polyyne Substituted Pyrroles. *J. Org. Chem.* **81**, 9188-9198, (2016).

2. Zhang, J., Sun, J. Z., Qin, A. & Tang, B. Z. Transition-Metal-Free Polymerization of Bromoalkynes and Phenols. *Macromolecules* **52**, 2949-2955, (2019).

3. Katoono, R., Tanaka, Y., Kusaka, K., Fujiwara, K. & Suzuki, T. Dynamic Figure Eight Chirality: Multifarious Inversions of a Helical Preference Induced by Complexation. *J. Org. Chem.* **80**, 7613-7625, (2015).

4. Bowles, D. M. & Anthony, J. E. A Reiterative Approach to 2,3-Disubstituted Naphthalenes and Anthracenes. *Org. Lett.* **2**, 85-87, (2000).

5. Jim, C. K. W. et al. Metal-Free Alkyne Polyhydrothiolation: Synthesis of Functional Poly(vinylenesulfide)s with High Stereoregularity by Regioselective Thioclick Polymerization. *Adv. Funct. Mater.* **20**, 1319-1328, (2010).