Arylene Ethynylene-Functionalized Bithiazole-Based Zinc Polymers for Ultraefficient Photocatalytic Activity

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Supporting Information

ABSTRACT: Polymers 4 containing poly(arylene ethynylene) were synthesized and characterized systematically. Among them, 4c exhibited a remarkable H2 evolution rate (14.32 mmol h−1 g−1) with visible-light irradiation, lasting 72 h in different water qualities; the corresponding apparent quantum yield was 11.6% at 450 nm.

1. INTRODUCTION

Energy is increasingly in demand around the world.1,2 Hydrogen (H2) is an alternative energy source for fossil fuel.3,4 Numerous inorganic semiconductors work as candidates of photocatalytic H2 production for practical applications.5,6 Nevertheless, there exists low visible-light activity, difficult preparation conditions, and rare low-cost elements among them.7,8

Compared with inorganic photocatalysts, conjugated polymers (CPs) work as semiconductors for photocatalytic H2 production (PHP), thanks to high degree of flexibility, low-price fabrication, bulk synthesis, and multifunctionalization.9,10 Following the pioneer report of various zinc (Zn)-based polymers, such as semi-crystallized bipyridine-based frameworks, poly(arylene ethynylene) (PAE)-covalent organic frameworks and benzothiadiazole-conjugated porous polymers have been further investigating for photocatalysis,11−13 while there exists several shortcomings among them, multistep synthesis or poor quantum efficiency (QE).14,15 In this regard, developing CPs with visible-light photocatalysts still remain an extraordinary challenge currently.16,17 It indicates that metal-binding and visible-light-absorbing polymer with a PAE-backbone show quite interesting building blocks, expected to be novel photocatalytic systems. It also offers to tune the optical properties of the PAE-based ligand, including the catalytic and optical properties of the coordinated metal complexes.18,19

It is necessary for obtaining ideal CPs, including broad wavelength, proper energy levels, and high-efficiency charge transfer.20,21 A variety of building blocks are used for constructing CPs’ aim to realize these desirable properties simultaneously.2,23 Besides, PAE is extraordinary attractive owing to its conjugating plane structure, in favor of charge separation and transport when introduced with PAE.24,25 In addition, bithiazole (BTz)-bridged polymer receives a great deal of uses, including benzothiadiazole moiety, especially for PHP.26−28 Thus, the incorporation of CPs into BTz, and the corresponding polymers were systematically characterized (Scheme 1).29−34 Moreover, these samples were investigated for photocatalytic activity under visible light.

2. RESULTS AND DISCUSSION

The precursor PAE-BTz was then subjected to reaction with zinc chloride, affording the target Zn-COF in over 85% yield (Scheme S1 and Table 1). The optical absorption profile of the

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preparing polymers was determined by diffuse reflectance UV–vis and photoluminescence (PL) spectroscopy. UV–vis spectra show obvious changes between the PAEs (Figure 1), showing a redshift from 420 to 590 nm with increasing BTz content, when moving from 4a to 4e. It is beneficial to adjust the optical properties in the PAE networks, whereas the optical gap is regulated by alternating the molar ratio of the monomer and ZnCl₂ (Table 1). With the help of UV–vis absorption measurements, there exists a distinct bathochromic shift along with the as-grown sample other than monomers, demonstrating the extension of conjugated π system, thanks to alkynyl coupling with electron delocalization.35

The PL spectrum for PAE, the sample without BTz is blue, shows a maximum characteristic emission (445 nm). In contrast, the emission of specimens containing BTz moieties (4a–4e) exhibited a gradual redshift. The polymer 4a reached its peak with a bluish-green emission (465 nm), whereas 4b reached its peak with a saturated green/yellow emission (534 nm), and 4c with a red emission (588 nm) (Figure 2). It is suggested that PAE–BTzs contain cyclic structures, manifesting itself as a redshift in the PL spectrum. Because of its planar nature, an increase was observed for high electric conduction in the copolymer series by the function of PAE.36

Aiming to the excited state dynamics, the fluorescence lifetime of polymers was evaluated. As given in Table 1, the BTz-linked polymer 4c reveals the lowest fluorescence lifetime (τb = 0.54 ns, τc = 3.89 ns, Table 1) in those polymer networks. The decreased fluorescence intensity is obviously combined with localized states in the band gap loaded with BTz moiety.37 It is certainly beneficial to transfer charge carriers in the photocatalytic reactions.38

The porous property of the as-synthesized polymers was determined by N₂ sorption measurements at 77 K. The calculated Brunauer–Emmett–Teller (BET) and Langmuir surface area values for those samples are present in Table 2, varying from 85.4 to 189.3 m² g⁻¹. Among them, the sample 4c exhibits the highest apparent S_BET (189.3 m² g⁻¹, Table 1). N₂ uptake at a low relative pressure (P/P₀ < 0.05) illustrates moderate porous structure, besides having a pore size smaller than 2 nm. The observed hysteresis loop results from the elastic deformation of the cross-linked network in the N₂ atmosphere. The sharp rise at high-pressure regions (P/P₀ = 0.9–1.0) is good for macropores (>50 nm) or absorbance at the external surface area or textural porosity in these materials. It has been demonstrated that the large specific surface area corresponds to more reactive sites in favor of the photocatalysis procedure, thanks to the abundant catalytically active sites, both on the edges and PAE basal planes.39

The structure of the as-prepared PAE sample 4c was measured by transmission electron microscopy (TEM). From Figure 3a, the margin between PAE film and Zn complex is observed. The typical layered structure of the as-obtained PAE can be observed above the interface, demonstrating the π-stacking interlayer distance from two-dimensional layers (Figure 3b). High-resolution TEM (HR-TEM) illustrated curved

### Table 1. Photophysical and Physicochemical Properties of Systems 4a–4e

| polymer | λem (nm) ² | Φ (%) ² | τb (ns) ² | τc (ns) ² | S_BET (m² g⁻¹) ⁵ | pore volume (cm³ g⁻¹) ⁵ | average pore size (nm) ⁵ |
|---------|------------|---------|-----------|-----------|-------------------|--------------------------|--------------------------|
| 4a      | 488        | 91.9    | 4.14      | 8.94      | 88.7              | 0.58                     | 9.8                      |
| 4b      | 521        | 77.6    | 2.83      | 5.18      | 125.5             | 0.99                     | 15.1                     |
| 4c      | 575        | 64.3    | 1.84      | 5.02      | 189.3             | 1.34                     | 21.3                     |
| 4d      | 548        | 78.2    | 3.07      | 6.11      | 103.9             | 0.88                     | 18.6                     |
| 4e      | 516        | 85.7    | 3.98      | 7.08      | 85.4              | 0.76                     | 13.9                     |
| PAE     | 445        | 93.1    | 6.03      | -         | 27.1              | 0.37                     | 5.9                      |

²Recorded at indoor temperature and stimulated at 415 nm. ⁵Solid fluorescence quantum yields (Φ) were evaluated by a calibrated integrating sphere system (λ_em = 415 nm). ⁶Fluorescence lifetime. ⁷Measured from N₂ sorption studies.

### Table 2. Polymer Concentration, H₂ Evolution Velocity, and QE of the As-synthesized Photocatalysts 4a–4e and PAE

| polymer | polymer concentration (mg mL⁻¹) | H₂ (mmol h⁻¹ g⁻¹) ⁶ | QE (%) ⁶ |
|---------|---------------------------------|---------------------|----------|
| 4a      | 17                              | 7.18                | 1.49     |
| 4b      | 13                              | 11.64               | 3.04     |
| 4c      | 11                              | 14.32               | 6.79     |
| 4d      | 12                              | 12.56               | 4.26     |
| 4e      | 15                              | 9.97                | 3.31     |
| PAE     | 56                              | 0.05                | 0.01     |

⁶Reaction was carried out via a 300 W Xe arc lamp without UV light; each catalyst (0.05 g) was dispersed under the upper conditions. QE was evaluated by amounts of H₂ production with a monochromatic light irradiation (λ = 420 nm) in 1 h.

Figure 1. UV–vis spectra of samples 4a–4e.

Figure 2. Emission spectra of PAE–BTz–Zn 4a–4e and PAE.

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streaks with a lattice parameter of 0.369 nm that belongs to the interlayer distance of PAE (Figure 3c).41 Meanwhile, selected area electron diffraction (SAED) pattern is shown in Figure 3d as well. The plane (100) is presented in the inset, and its intensity integrates to more than 360°. It is over graphene attribute to a more delocalized system of PAE. The component of sample 4c was further shown for Zn, O, N, S, and C by energy-dispersive X-ray (EDX) spectrum (Figure 3e), which coincides with the result of X-ray photoelectron spectroscopy (XPS) analysis and energy-dispersive system mapping. It implied that the two-dimensional-layered PAE film with good crystallinity was acquired successfully.42

Among them, N and S originated from both PAE and BTz ligands in the system, as confirmed by the XPS data (Figure S14). N (1s) reached its peak at approximately 397.8, 399.7, and 400.7 eV, stating that thiazole coordinated with zinc ions and benzothiadiazole N, respectively.43 In the XPS spectrum of S (2p), a peak was observed at around 163.0 and 164.4 eV attributed to S from carbon sulfur bond, and another peak at around 160.6 and 161.8 eV corresponding to S from thiazole and benzothiadiazole from the catalyst.44

The amount of the corresponding polymers 4a–4e is 11–17 mg mL⁻¹, respectively (Table 2). Increasing the concentration of PAE should be a good strategy to further improve the quantum yield and H₂ generating rate.45 To access the photocatalytic activities of samples 4a–4e, the PHP experiments were carried out when triethanolamine (TEOA) worked as a sacrificial reagent (Table 2, Figure 4). Prior to the actual PHP experiment, control evaluations were measured by a pure TEOA solution with either photocatalysis or irradiation. No apparent H₂ was produced, implying that H₂ comes from the TEOA solution by photocatalysis in these photocatalytic reactions.46

The results show that the ratio between BTz and PAE has an apparent effect on the photocatalytic performance in the system (Figure 4a). The photocatalytic performance of these catalysts increased when the BTz content increases, and the largest activity of H₂ evolution acquired for 4c (14.32 mmol h⁻¹ g⁻¹, QE = 6.79%) far surpasses pure PAE (0.05 mmol h⁻¹ g⁻¹); furthermore, its rate exceeds dramatically that of benzothiadiazole-based complex.41 When the content of Zn increased persistently, the H₂ generation activity of the BTz–PAE specimen obviously decreased, owing to the higher opacity and stronger light scattering from the higher contents of BTz. It is noted that BTz and PAE show positive synergistic effects on the H₂ producing performance of Zn–COF.

The QE of sample 4c was determined under different monochromatic light, as shown in Figure S17. The largest QE of 8.91% was presented at 450 nm. Regarding the remarkable photocatalytic properties, sample 4c demonstrated a great stability after discontinuous photocatalytic measurement and shelved for a month, as illustrated in Figure 4b; only 10% descend of H₂ production can be observed. In addition, sample 4c also exhibits supreme photocatalytic performance under different water qualities (Figure 4c). Although the inorganic salt components are complicated in seawater, a practically identical H₂ generating rate (11.21 mmol h⁻¹ g⁻¹) with that in 3 wt % NaCl was acquired as well.47

Electrochemical impedance spectroscopy (EIS) and transient photocurrent detections evaluated the interface interaction between PAE–BTz and Zn. As shown in Figure 5, from EIS changes of PAE–BTz–Zn 4a–4e electrodes, the highest one was the specimen 4c photoelectrode. This leads to improvements in charge-separation efficiencies, leading to a less curvature radius and a smaller resistance in charge transfer.48 Therefore, sample 4c possesses higher charge-transportation
efficiency than other samples, possessing a similar topology to that coordinated with Zn-oxo clusters.

In particular, a drastic shrink of the semicircular Nyquist plots from Figure S18 is observed for sample 4c in the night, revealing that the conjugated structures from the polymeric matrix could efficiently cut down the resistance on the interface, benefiting the photoexcited charge carrier isolation in the photocatalytic process.49

Furthermore, it has an essential effect on the charge dissociation efficiency of PAE–BTz by transient photocurrent tests. These measurements show that PAE–BTz produces a higher photocurrent response than pure PAE, demonstrating that photoinduced electron (e−)–hole (h+) pairs are isolated more effectively (Figure 6). This result further manifests that photoexcited PAE–BTz needs more time to arrive in the balance than pure PAE.50

In the meantime, a similar result was given by the transient photocurrent response test. As illustrated in Figure 6, these as-synthesized photocatalysts’ electrodes show lower photocurrent density, and the specimen 4c has the most outstanding photocurrent density. This demonstrates that 4c is superior to the upper ones in isolating electron–hole pairs, matching with the biggest one for the H2 evolution rate. It implied that pristine PAE played an important role in promoting charge separation and transfer as well.51 However, their photocatalytic activities would decrease when the PAE amount was over 10%, owing to agglomeration and low solubility. The reason may be further explained the enough conductive electron mediator could not connect to the large PAE additive, restricting the isolation of photoexcited electrons and holes.52

After exposure to prolonged visible-light irradiation for as long as 2 days (Figure S20), the photocurrent of sample 4c was beginning to decrease, remained a stable value followed. This phenomenon confirms the prohibition of photocorrosion of PAE planar architecture.53

To further investigate the electronic route for the PHP process, the corresponding mechanism tested the physicochemical behaviors of the photocatalysts (Figure 7).54 In the photocatalytic reaction, the water reduction is the most essential step, where PAE and the (100) crystal plane of Zn are models, respectively. In the photoexcitation of the PAE–BTz–Zn system in the presence of TEOA, the excited state PAE moiety is formed, and it is then quenched by BTz to produce the reduced state Zn moiety. Electrons may be transferred from the PAE unit to zinc sheet through the electron–electron exchange of BTz groups of polymers, and thus, protons are reduced to H2 on the surface of Zn lattice plane.55 This procedure isolated the photogenerated electrons and holes, resulting in improving the photocatalytic performance for H2 generation and efficient photocorrosion inhibition.56

As shown in Figure S21, in both materials, a narrow isotropic electron paramagnetic resonance (EPR) message with a g datum of g = 2.0041 and Lorentzian line shape was tested, even in the night. It showed that the paramagnetic centers were in the PAE framework.57 The g datum revealed that this message was ascribed to surface-trapped electrons, containing preferential carbon character. The conduction band (CB) is generated by carbon 2p orbitals, whereas trapped CB-e− was acquired for analyzing the EPR message intensity with illumination (Figure S21, red spectra).58 The reformation between CB-e− and holes was seen after light burn out (Figure S21, gray spectra). To an extent, conjugation of the upper polymer was influenced by charge separation and transport.59–61

3. CONCLUSIONS

Visible-light-driven H2 generation was realized over novel BTz-based zinc polymers (PAE–BTz:Zn = 1:5) up to 14.32 mmol h−1 g−1. Furthermore, on the basis of the successful electron transfer from the photosensitizer arylene ethynylene to isolated zinc polymers, the resulting new material reaches over 8.91% for QE (λ = 450 nm). It also opens up potential routes for porous organic polymers as candidates to develop the new artificial photosynthesis system, even for using seawater.

4. EXPERIMENTAL SECTION

4.1. Materials and Equipment. All of the chemical reagents and solvents were commercially available. 2-(5-Bromo-2-(5-bromo-4-(2-hydroxyphenyl)thiazol-2-yl)thiazol-4-yl)phenol (1, Scheme S1) was purchased from Ruiyuan Group Limited (Yurui Chemical Co., Ltd.). 4,7-Diethynyl-5,6-bis-(octyloxy)benzo[c][1,2,5]thiadazole (2, Scheme S1) was synthesized in the lab, starting from rubeanic acid (99.0%), hydroxyacetophenone (99%), iodomethane (CH3I, AR), ethanol (AN, analytical grade) and acetic acid (HAc, AR), copper(II) bromide (CuBr2, 99%), 2’-hydroxyacetophenone (99%), N-bromosuccinimide (99%), tetrakis(triphenylphosphine)palladium (Pd(PPh3)4, Pd ≥ 9.0%), sodium sulfate anhydrous (Na2SO4, 99.99%), zinc chloride (ZnCl2, 99.99%), and sodium carbonate anhydrous (Na2CO3, 99.99%). These raw materials and tetrabutylammonium hexafluorophosphate (TBAPF6, 98%) were purchased from...
Aladdin Co. Ltd. Laboratory deionized water was achieved from an ultrapure water system, resulting in a resistivity >18 MΩ cm⁻¹.

The thermogravimetric analysis (TGA) was performed with a TGA Q600 SDT TA Instruments apparatus (New Castle, DE, USA) at a heating rate of 10 °C/min under dry nitrogen (flow velocity 10 mL/min).

4.2. Synthetic Procedures of Compounds 1–4. Syntheses of compounds 1 and 2 are reported in the literature.

4.3. Preparation of Compound 3. To a 10 mL flask equipped with a rubber seal and a magnetic stirring bar were added PdCl₂(PPh₃)₂ (14.0 mg, 0.02 mmol), 2-(5-bromo-2-(5-bromo-4-(2-hydroxyphenyl)thiazol-2-yl)thiazol-4-yl)phenol 1 (1.1 mmol), and CuI (3.8 mg, 0.02 mmol). Afterward, tetrahydrofuran (3.0 mL) was injected into the flask, and Ar₂ was bubbled into the solution. After the mixture was stirred for 5 min, a solution of 4,7-diethynyl-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole 2 (1.0 mmol) in THF (2.0 mL) was added to the flask successively, and the mixture was stirred under a balloon pressure of Ar₂ at 120 °C for 4 h. The precipitate was filtered, washed with methanol, and then purified by column chromatography (silica gel, petroleum ether—ethyl acetate) to afford compound 3.

4.4. Typical Procedure for the Synthesis of Photocatalyst 4. A mixture of 2-(2-(5-(2-(5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole 2-(4-(2-hydroxyphenyl)thiazol-2-yl))-5-methylthiazol-4-yl)phenol (3, 0.8193 g) and anhydrous ZnCl₂ (0.1363 g) (molar ratio: 1:1) was added into a quartz ampoule inside a glovebox. The ampoule was then evacuated, vacuum-sealed, and then heated at 450 °C for 12 h. The heating rate is 5 °C × min⁻¹. The obtained yellow powder was subsequently ground and washed thoroughly with dilute 2 M HCl, water, acetone, and dichloromethane. The yellow powder was subsequently ground and washed thoroughly with the excitation wavelength of 370 μm. The precipitate was filtered, washed with methanol, and then purified by column chromatography (silica gel, petroleum ether—ethyl acetate) to afford compound 3.

4.5. Steady-State UV–Vis Absorption Measurements. UV absorption peaks were measured by a Hitachi U-3010 absorption spectrophotometer with THF as the solvent. In addition, the corresponding samples were solved in THF to a 10 μM concentration prior to the measurements, unless otherwise stated.

4.6. Steady-State PL Measurements. PL spectra were measured by Hitachi F-4500 fluorescence spectrophotometer, with the excitation wavelength of 370 ± 5 nm. Moreover, the solid fluorescence quantum yield (ϕFL) values were determined, employing a calibrated integrating sphere system (λexc = 370 ± 5 nm).

4.7. PL Lifetime Measurements. Time-resolved PL decay spectra were tested at room temperature with an Edinburgh FLS 920 Fluorescence spectrometer.

4.8. Physicochemical Characterization. Crystallographic information for the as-synthesized samples was obtained on an X-ray diffractometer (Bruker, Germany) with monochromatized Cu Kα radiation (λ = 0.15406 nm).

The detailed morphology and structure of the products were recorded by TEM, HR-TEM, and SAED, on a JEM-2100 apparatus with an accelerating voltage of 200 kV. EDX spectroscopy was also given from an EDAX detector performed on the same HR-TEM.

The chemical compositions and surface states of those samples were probed with an XPS (Axis Ultra DLD, Kratos) instrument.

The BET specific surface area of as-synthesized photocatalysts was evaluated at 77 K with a Quantachrome NOVA 1200e instrument.

Infrared (IR) spectra were recorded on a Bruker Tensor 27 Fourier transform IR (FT-IR) spectrometer by the KBr salt slice method in the absorption range of 4000–400 cm⁻¹.

Raman spectroscopy was measured using a Renishaw S14.5 nm argon laser.

4.9. Photoelectronic Measurements. Photoelectrochemical and EIS measurements were carried out by an electrochemical analyzer (CHI660C Instruments, Shanghai, China) with a conventional three-electrode system. Prior to these experiments, the film electrodes of sample 4a–4e were prepared at first. The as-prepared sample was employed as the working electrode; the counter electrode and the reference electrode were platinum mesh and an Ag/AgCl (saturated KCl), respectively. TEOA (10%, v/v) was mixed with Na₂SO₄ (0.5 mol xL⁻¹) aqueous solution as the supporting electrolyte.

The measured potentials versus the Ag/AgCl reference electrode were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation

$$E_{RHE} = E_{Ag/AgCl}^0 + E_{Ag/AgCl} + 0.059 \text{pH}$$

where $E_{RHE}$ is the converted potential versus RHE, $E_{Ag/AgCl}$ is the experimental potential measured against the Ag/AgCl reference electrode and is the standard potential of Ag/AgCl (saturated KCl) at room temperature (i.e., 0.197).

Both linear sweep voltammetry and photocurrent-time response ($I$–$t$) experiments were conducted in a three-electrode system, and the scan rate was 20 mV s⁻¹. The photocurrent densities were produced at a bias of −0.4 V versus RHE in the dark and visible-light irradiation (λ > 420 nm, light on/off cycles: 20 s). The photostability measurement was performed under the same condition. Besides, EIS spectrum of the as-prepared samples was measured by following the identical procedure, according to the previous reference.

Electron spin resonance (ESR) spectra were recorded with an ESR spectrometer (Bruker EMX-10). Before testing, the as-synthesized samples, respectively, immersed in an aqueous solution (2 mL) including lactic acid (10%, v/v) were added to the cell, evacuated at 77 K to remove dissolved oxygen, and then illuminated for 30 min under visible light ($λ > 420$ nm, light on/off cycles: 20 s). The photostability measurement was performed under the same condition. Besides, EIS spectrum of the as-prepared samples was measured by following the identical procedure, according to the previous reference.

Cyclic voltammetry was also measured by an electrochemical analyzer (CHI660C Instruments, Shanghai, China) consisting of a standard three-electrode setup, as mentioned above. TBAPF₆ and ferrocenium–ferrocnium (Fc⁺/Fc) worked as the supporting electrolyte and internal standard, respectively. All of the potentials were determined at a scan rate of 100 mV s⁻¹ for oxidation in N₂-purged dichloromethane and 100 mV s⁻¹ for reduction in acetonitrile.

4.9.1. Band Gap Calculation. The energy band gap ($E_g$) of the samples was calculated from the absorption edge of Tauc plot, using the Tauc expression, given below

$$a(hv) = A(hv - E_g)^n$$
where \( \alpha \) is the absorption co-efficient, \( h \) is Planck’s constant, and \( \nu \) is the wavenumber (\( \lambda \)). The value of \( h\nu \) is obtained from the \( \lambda \). \( \Delta H \) is determined from the intercept of the extrapolated linear part of the curve with the energy axis. In another case, the valence band (VB) top position was measured from the VB XPS curve, the actual volume of H\(_2\) for those samples was calculated.

Therefore, the VB and CB potentials of samples get the H\(_2\) peak area. On the basis of the previous calibration photocatalytic measurement was injected into the online GC to determine the water-soluble M. Therefore, the VB and CB potentials of samples 4a–4e are listed in Table 3.

**4.10. Photocatalytic Experiments.** Typical photocatalytic experiments were set up as follows. Photocatalytic performances of as-synthesized samples were evaluated in a closed gas circulation system equipped with a Pyrex glass reactor cell. Briefly, a total of each photocatalyst (0.05 g) was, respectively, loaded into a mixture of lactic acid (10 mL) and water (90 mL) in the reactor under magnetic stirring. The reactor was placed in a thermostated and irradiated using a high-pressure Xe lamp (300 W) with a UV cutoff filter. In addition, high purity (99.999%) N\(_2\) carrier gas was employed.

**4.11. H\(_2\) Detected by Online Gas Chromatography.** Generated H\(_2\) was characterized by gas chromatography (GC) analysis (GC7900, Tian Mei, Shanghai), equipped with a 5 Å molecular sieves column and a thermal conductivity detector. The retention time of H\(_2\) was approximately 0.9 min under the same condition. First of all, a H\(_2\) calibration curve was obtained by high purity (99.999%) H\(_2\). Then, the evolved H\(_2\) from the photocatalytic measurement was injected into the online GC to get the H\(_2\) peak area. On the basis of the previous calibration curve, the actual volume of H\(_2\) for those samples was calculated.

**4.12. Determination of QE Values.** QE was measured using various monochromatic lights with different band-pass filters (\( \Delta \lambda = 240, 450, 480, 510, 540, 570, 600, 630, 660, \) and 690 nm) and an irradiation meter. The QE was then estimated by the following formula.

\[
\text{QE} = 1 - \epsilon \cdot (1 - e^{-\alpha d})
\]

**4.12.1. 4,7-diethynylbenzo[c][1,2,5]thiadiazole-5,6-diol (1).** Pale white solid, yield 89%; UV–vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} \) 382 nm; \(^1\text{H}\) NMR (400 MHz, DMSO-TMS): \( \delta \) 3.329–3.485 (m, 2H, 2CH\(_2\)), 5.066–5.182 (s, 2H, 2OH) ppm; \(^{13}\text{C}\) NMR (100 MHz, DMSO-TMS): \( \delta \) 67.894, 79.750, 83.343, 84.336, 102.790, 103.921, 148.138, 148.421, 153.756, 154.414 ppm; IR (KBr) \( \nu \): 3061, 3045, 3028, 2858, 1589, 1656, 1559, 1512, 1494, 1363, 1255, 1159, 1081, 1034, 981, 769, 699 cm\(^{-1}\); ESI-MS \( m/z \) (%): 239 ([M + Na]\(^+\), 100); Anal. Calculated for C\(_{10}\)H\(_9\)N\(_2\)O\(_2\)S: C, 55.55; H, 1.86; N, 12.66. Found: C, 55.48; H, 1.72; N, 13.05.

**4.12.2. 4,7-Diethynyl-5,6-bis(octoxy)benzo[c][1,2,5]thiadiazole (2).** Yellow solid, yield 92%; UV–vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} \) 390 nm; \(^1\text{H}\) NMR (400 MHz, DMSO-TMS): \( \delta \) 1.629–1.650 (m, 6H, 2CH\(_3\)), 1.715–1.768 (m, 4H, 2CH\(_2\)), 1.905–2.007 (m, 8H, 4CH\(_2\)), 2.061–2.147 (m, 8H, 4CH\(_2\)), 2.330–2.433 (m, 4H, 2CH\(_2\)), 2.851–3.006 (m, 2H, 2CH\(_2\)), 4.246–4.338 (m, 4H, 2CH\(_2\)) ppm; \(^{13}\text{C}\) NMR (100 MHz, DMSO-TMS): \( \delta \) 14.168, 15.008, 22.411, 22.901, 26.486, 26.971, 29.328, 29.511, 29.737, 29.942, 30.291, 30.594, 31.355, 31.959, 69.193, 78.327, 79.361, 82.937, 83.494, 101.912, 102.563, 147.236, 148.239, 153.378, 153.571 ppm; IR (KBr) \( \nu \): 3074, 3061, 3037, 2952, 2923, 2851, 2815, 1780, 1565, 1524, 1499, 1479, 1456, 1438, 1422, 1389, 1292, 1262, 1223, 1192, 1179, 1159, 1137, 1087, 1049, 985, 876, 768 cm\(^{-1}\); ESI-MS \( m/z \) (%): 463 ([M + Na]\(^+\), 100); Anal. Calculated for C\(_{26}\)H\(_{36}\)N\(_2\)O\(_2\)S: C, 70.48; H, 8.78; N, 6.07. Found: C, 70.48; H, 8.78; N, 6.07.

**4.13. Characterization Discussion.** The structures of product 4 (Scheme S1) are characterized by gel permeation chromatography (GPC), IR, differential scanning calorimetry (DSC), and TGA. The following discussions on the features reveal that these polymers are obtained indeed as expected.

All of the samples are well-soluble in common solvents such as THF, DMF, and DMSO, owing to the presence of ether and flexible side chains, along the macromolecular chains. As
determined by GPC (Figure S10), the number-average molecular weight \( (M_n) \) and polydispersity index (PDI) values of those specimens are in the modest ranges of 1.84–4.14 kDa and 1.05–1.18, respectively (Table 3). Similarly, the reason is derived from the enhanced reactivity of long-chain ester groups as well as good solubility of the polymer in the reaction solution.

According to upper FT-IR analysis, two peaks were at 1251 and 1451 cm\(^{-1}\), which may be assigned to C–N and C=O bonds, respectively. The band observed at 1060 cm\(^{-1}\) could be attributed to the stretching vibration of the C–O bond. The band of 2191 cm\(^{-1}\) is the typical C≡C stretching vibration, that is in agreement with the result of the below Raman spectrum. The stretching vibration strength of C/N double bond in the BTz ring located at 1456 and 1563 cm\(^{-1}\) gradually increases as the BTz content increases for all of the samples, indicating that the chemical composition of the as-prepared polymers was fine-tuned by changing the PAE/BTz ratio.

The thermal properties of the polymers were characterized by TGA and DSC. The five polymers show good thermal stability with a 5 wt % weight loss for decomposition temperatures \( (T_d) \) over 250 °C (Table 3, Figures S11 and S12). DSC curves clearly exhibited endothermic peaks at 143–190 °C while being heated, and the corresponding exothermic peaks at 90–121 °C were also observed during cooling. These five polymers exhibited similar transitional temperatures which may be attributed to the phase transition of the long alky1 chains.

Meanwhile, the C (1s) peak in the XPS spectra of the PAE photocatalyst can be deconvoluted into two peaks, accounted for sp\(^2\) and sp (C=C) hybridized carbons at 284.1 and 285.9 eV, respectively (Figure S14). No surface oxygen-containing groups are evident in the C 1s peak, validating the vacancy of oxidized carbons in backbones. Overall, the \( E_g \) for 4a–4e ranges from 2.56 to 3.42 eV (Table 3).

Raman spectra as a sensitive technique is used to investigate the uniformity and quality of the PAE-based polymer 4c. As exhibited in Figure S15, the peak at 1520 cm\(^{-1}\) coincides with the stretching vibration of sp\(^2\) carbon domains in the aromatic rings. The peak at 2910 cm\(^{-1}\) can be attributed to the stretching vibration of conjugated alkyne links. As shown in the Raman spectrum, two dominant peaks appeared at 1605 and 1360 cm\(^{-1}\), belonging to G- and D-band in the PAE system, respectively. That is, it contains abundant BTz rings from 4c and edges and defects of PAE. Besides, peaks at around 2610 cm\(^{-1}\) are attributed to N in zinc nitron bond of sample 4c that coordinate with zinc ions.

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**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02382.

Full synthetic details; detection and analysis for the polymers, including DSC, Raman, TGA, IR, and additional photocatalytic measurements; XPS measurements; and EPR spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

**Author Contributions**

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