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# Polymer



# Synthesis of donor-acceptor-type conjugated polymer dots as organic photocatalysts for dye degradation and hydrogen evolution

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### ABSTRACT

Conjugated polymers (CPs) having various donor-acceptor units in the main chain were synthesized via Suzuki coupling reaction for an organic photocatalyst that can generate reactive oxygen species (ROS) for dye degradation and  $H_2$  evolution under visible-light irradiation. To synthesize four kinds of CPs, two donor units (phenylene and fluorene) and two acceptor groups (benzothiadiazole and bisthienylbenzothiadiazole) were cross-combined. The cyclic voltammograms of the CPs showed their generation ability for ROS, in which the ROS generation efficiency would depend on the main chain structure. Because the CPs are inherently hydrophobic, they were fabricated in nanoparticle (NP) form for convenient use in an aqueous solution. The CP NPs showed repeated uses after simple washing. The ROS generation from CPs played an important role in dye degradation, as well as in  $H_2$  evolution of up to 8.4 mmol/g under visible-light irradiation.

### 1. Introduction

Photocatalysts are one of the important materials that produce useful chemicals using light energy. Among the numerous photocatalysts, various inorganic materials such as TiO<sub>2</sub>, ZnO, CdS, Fe<sub>2</sub>O<sub>3</sub>, and MoO<sub>3</sub>, and organic g-C<sub>3</sub>N<sub>4</sub> are generally used for photocatalysis [1–6]. Electron-hole pairs are generated on the surface of inorganic photocatalysts by light, and react with water molecules to produce reactive oxygen species (ROS) [7]. The ROS generated by photocatalysts are used for dye degradation, organic synthesis, water splitting, and photodynamic therapy [8–13]. However, inorganic photocatalysts have drawbacks such as difficulty in tuning their optical properties, resulting in being activated only by UV light, which limits their versatile use. Therefore, investigations have been conducted to introduce nanomaterials into inorganic photocatalysts for ROS generation in the visible region [14–16]. These techniques, however, need additional synthetic steps and might have a problem at the interface between two materials.

To overcome the disadvantage of inorganic photocatalysts, investigations on the ROS generation using organic conjugated polymers (CPs) have been recently attempted [17–22]. CPs have been used as new types of optoelectronic materials with high light stability, easy surface

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functionalization, and tunable structure and composition [21,22]. By changing the repeat units of the backbone, the CPs have tunable optical absorption, so that absorbance can be obtained in the visible-wavelength region. Because the energy band gap of the CPs can be controlled, the effect of the repeat unit structure on the catalytic activity needs to be understood. Because of the CPs' extended  $\pi$ -conjugation with aromatic groups, CP-based photocatalysts are hydrophobic in nature, resulting in a difficulty in obtaining uniform dispersion in an aqueous solution [23,24]. To enhance photocatalytic activity and avoid inherent hydrophobicity, CPs should be hybridized with inorganic semiconductors. Such hybridization, however, requires proper choice of materials with both well-defined energy levels and improved interfacial interaction for easy carrier transfer [25]. To enhance H<sub>2</sub> production CPs were hybridized with C60, and thus their role in photocatalysis was limited to light harvesting [26]. CPs have been prepared in nanoparticle (NP) form with a size less than 100 nm and, finally, they can be finely dispersed in an aqueous phase, which have been called "polymer dots" (P-dots) [27,28]. P-dots inherit their optical properties from the pristine CPs, and show rapid electron transfer and excellent optical stability [29-33]. In addition, P-dots have been used to generate ROS by light irradiation, resulting in cancer cell apoptosis via photodynamic therapy



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[34,35]. Like CPs, P-dots have an absorption wavelength in the visible region, and their ROS generation under visible-light irradiation is far less restricted than inorganic photocatalysts. P-dots as well as CPs have been used as photocatalysts for H<sub>2</sub> generation [36–38]. P-dots, however, were located on the g-C<sub>3</sub>N<sub>4</sub> surface to assist the H<sub>2</sub> production of the g-C<sub>3</sub>N<sub>4</sub>. In addition, hollow P-dots have been reported to be more efficient in photocatalytic reaction than their pristine polymer [39].

In this work, we wanted to elucidate CP-based photocatalysis. ROS generation was investigated by synthesizing four CPs with various backbone structures, followed by fabricating CPs into P-dots. The two main structural advantages of the P-dot form are its high surface area and its good water-dispersibility, resulting from the nanosized spherical shape. This enables the reactants (here, water molecules) and products (here, ROS or H<sub>2</sub>) to easily access and form the catalytic sites on the P-dots. In addition, by careful combination of the donor and acceptor units, it was possible to finely tune the P-dots' optical properties. Most nanosized photocatalysts are only reused with difficulty after the photocatalytic reaction because of their small size and particulate shape. To facilitate reuse after photocatalysis, we used a paper-based photocatalyst containing CPs [40,41].

### 2. Experimental

### 2.1. Materials

2,1,3-Benzothiadiazole, 1-bromooctane, 2-(tributylstannyl)thiophene, tetrahydrofuran (THF), toluene, hydroquinone, N-bromosuccinimide (NBS), N,N-dimethyl-4-nitrosoaniline (RNO), Br<sub>2</sub>, KOH, K<sub>2</sub>CO<sub>3</sub>, 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, methylene blue (MB), and tetrakis(triphenylphosphine) palladium were purchased from Sigma-Aldrich Chemicals. All the reagents and solvents were used without further purification. The compounds 1,4-bis(octyloxy) benzene (1), 1,4-dibromo-2,5-bis(octyloxy) benzene (2), 2,5-bis (octyloxy)phenyldiboronic acid (3), 4,7-dibromo-2,1,3-benzothiadazole (4), 4,7-di-2-thienyl-2,1,3-benzothiadiazole (5), and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (6) were synthesized according to previously reported methods that are briefly described in the Supporting Information [42–44].

### 2.2. Characterization

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Fourier-300 spectrometer at Korea Basic Science Institute (Bruker, MA, USA). Ultraviolet and visible (UV-vis) absorption spectra were recorded on a Lambda 35 spectrometer (PerkinElmer, CT, USA). Fluorescence spectra were obtained using a Cary Eclipse fluorescence spectrophotometer (Varian, CA, USA) equipped with a Xe flash-lamp excitation source. Elemental analysis (EA) was performed on an Elemental Analyzer EA 1108 (Fisons Instruments, UK). The molecular weights (MWs) of polymers were determined by gel-permeation chromatography (GPC), with THF as an eluent with a polystyrene standard (Youngin Scientific, Korea). The nanoparticle images were obtained using a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan), and the size was determined using dynamic light scattering (DLS, Malvern Zetasizer, UK). A solar simulator (PEC-L01, Peccell Technologies, Japan) was used for visible light. The residual Pd catalyst in CPs was determined with an inductively coupled plasma massspectrometer (ICP-MS, ELAN DRC II, PerkinElmer). The contact angles of CPs and their nanoparticles was obtained with a droplet shape analyzer (DSA 100, KRÜSS, Germany) by coating them on glass slides.

# 2.3. Polymerization

Poly(2,5-dioctyloxyphenylene-*alt*-benzithiadiazole) (P8BT) Compounds **3** (0.422 g, 1.0 mmol) and **4** (0.291 g, 1.0 mmol) were dissolved in mixed solvents of THF and toluene. An aqueous solution of 2 M K<sub>2</sub>CO<sub>3</sub> was added slowly, and then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 g, 0.04 mmol) was added and reacted at 80 °C for 72 h. After the reaction, the mixture was poured into methanol to precipitate and the precipitate was isolated by filtration and purified in a Soxhlet apparatus with methanol and acetone (yield 360 mg, 77%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.93 (m), 7.46 (m), 4.03 (m), 1.58 (m), 1.25 (m), 0.86 ppm (m). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 154.39, 150.58, 130.58, 130.13, 127.57, 117.12, 69.52, 31.8, 29.7, 29.37, 29.28,29.25, 29.23, 26, 22.65, 14.11 ppm. Anal. Calcd. for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S: C, 71.75%; H, 8.60%; N, 5.98%; O, 6.83%; S, 6.84%; Found: C, 69.1%; H, 8.50%; N, 4.97%; S, 5.96%.

**Poly(2,5-dioctyloxyphenylene***-alt***-bisthienylbenzithiadiazole)** (**P8BTB**) Compounds **3** (0.422 g, 1.0 mmol) and **6** (0.458 g, 1.0 mmol) were dissolved in THF and toluene. The subsequent procedure was the same as that used for P8BT synthesis (yield 429 mg, 68%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.17 (m), 7.9 (m), 7.6 (m), 7.36 (m), 4.19 (m), 1.61 (m), 1.25 (m), 0.89 ppm (m). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 29.7, 29.29, 22.67, 14.11 ppm. Anal. Calcd. for C<sub>36</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: C, 68.31%; H, 7.01%; N, 4.43%; S, 15.20%; Found: C, 69.1%; H, 8.80%; N, 4.14%; S, 13.4%.

**Poly(9,9-dihexylfluorene-***alt***-benzithiadiazole)** (**F6BT**) 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.502 g, 1.0 mmol) and compound **4** (0.291 g, 1.0 mmol) were dissolved in THF and toluene. The subsequent procedure was the same as that used for P8BT synthesis (yield 0.30 g, 64%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 8.11-7.96$  (m), 2.16 (m), 2.0 (m), 1.54 (m), 1.25 (m), 1.7 (m), 0.80 ppm (m). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 31.55$ , 29.7, 22.64, 14.08 ppm. Anal. Calcd. for C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>S: C, 79.7%; H, 7.34%; N, 6.0%; S, 6.87%; Found: C, 78.1%; H, 7.90%; N, 5.60%; S, 6.18%.

### Poly(9,9-dihexylfluorene-alt-bisthienylbenzithiadiazole)

(**F6BTB**) 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.502 g, 1.0 mmol) and compound **6** (0.458 g, 1.0 mmol) were dissolved in THF and toluene. The subsequent procedure was the same as that used for P8BT synthesis (yield 0.49 g, 78%). <sup>1</sup>H NMR (300 MHz, CDCl3)  $\delta = 8.16$  (m), 8.14 (m), 7.68 (m), 2.03 (m), 1.56 (m), 1.25 (m), 1.1 (m), 0.80 ppm (m). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 31.81$ , 29.71, 29.37, 29.25, 22.7, 22.61, 14.08 ppm. Anal. Calcd. for C<sub>39</sub>H<sub>39</sub>N<sub>2</sub>S<sub>3</sub>: C, 74.1%; H, 6.22%; N, 4.43%; S, 15.2%; Found: C, 72.1%; H, 5.90%; N,4.14%; S, 14.9%.

### 2.4. Removal of Pd catalyst

CP (150 mg) was dissolved in chloroform (50 mL), followed by addition of thiourea (600 mg) and the mixture was stirred for 24 h. The thiourea was removed by filtration and the filtrate was concentrated under reduced pressure; the polymer was then precipitated in methanol and dried in a vacuum oven.

### 2.5. Preparation of P-dots

CP was dissolved in THF and injected into distilled water under sonication. After 30 min sonication, N<sub>2</sub> gas was blown to remove THF for 30 min. Then, a P-dot solution was prepared after filtration with a 0.45  $\mu$ m syringe filter. Four kinds of P-dots (denoted as P8BT-, P8BTB-, F6BT-, and F6BTB-dots) were fabricated from four CPs (P8BT, P8BTB, F6BT, and F6BTB), respectively.

### 2.6. ROS generation of P-dots

To evaluate the ROS generation of the P-dot solution, an RNO dye was used as a ROS indicator. The P-dot solution was mixed with RNO and then irradiated with white light for varying time periods. ROS generation was determined by investigating the changes in UV–vis absorption at 430 nm, resulting from the reduced RNO by ROS.

### 2.7. Electrochemical cyclic voltammetry (CV) [45]

The CV of CPs was investigated on a three-electrode electrochemical



Fig. 1. Synthesis of CPs.

system. A 0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> in anhydrous acetonitrile was used as a supporting electrolyte. A Pt wire was used as the counter electrode, and an Ag/Ag<sup>+</sup> electrode (0.01 M AgNO<sub>3</sub> and Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile) was used as the reference electrode, calibrated with the ferrocene/ferrocenium couple (Fc/Fc<sup>+</sup>). The working electrodes were prepared by dropping the polymer solution onto an indium tin oxide (ITO) and then dried in air. The half-wave potential of the Fc/Fc<sup>+</sup> redox couple (E<sub>1/2</sub>, Fc, Fc+) was estimated from E<sub>1/2</sub>, Fc, Fc+ = (E<sub>ap</sub> + E<sub>cp</sub>)/2, where E<sub>ap</sub> and E<sub>cp</sub> are the anodic and cathodic peak potentials, respectively. The redox potential of F<sub>c</sub>/F<sup>+</sup><sub>c</sub> was calibrated under the same conditions, and it was located at +0.42 V from the Ag/AgCl electrode. For the conversion from the Ag/Ag<sup>+</sup> redox couple to the normal hydrogen electrode (NHE), the formula E<sub>NHE</sub> = E<sub>Ag/Ag+</sub> + 0.26 V was applied.

### 2.8. Photocatalysis by paper-based photocatalyst

The paper-based photocatalyst was fabricated by introducing P8BT, P8BTB, F6BT, and F6BTB (0.6 mg) to a filter paper (Whatman No. 2); the samples were denote as P8BT-, P8BTB-, F6BT-, and F6BTB-paper, respectively. After this procedure, the filter paper was immersed in an aqueous RNO solution for various periods of times (0; 30; 60; 90; 120 min). ROS generation was evaluated by the same method used for the P-dot cases. For reusability of the CP-containing photocatalytic paper, regeneration of F6BT-paper was accomplished by washing with water after each photocatalytic cycle.



**Fig. 2.** UV–vis absorption (black) and fluorescence spectra (blue) of (a) P8BT-dot, (b) P8BTB-dot, (c) F6BT-dot, and (d) F6BTB-dot in aqueous solution. Fluorescence spectra were obtained by excitation of corresponding UV–vis absorptions. Photographs of P-dot solutions were taken under ambient (left) and 365 nm UV lights (right). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. SEM images of P-dots (scale bars: 500 nm).



Fig. 4. Proposed electron transfer mechanism of P-dot for photocatalytic ROS generation.

### 2.9. Photocatalytic H<sub>2</sub> evolution [45]

P-dot solution (10 ml) containing 0.2 M ascorbic acid was used as a sacrificial agent. The mixture solution was placed into a vial, bubbled with Ar gas, and ultrasonication was performed for 5 min at ambient temperature. The visible light was generated by a Xe lamp (LSP-X500A, Zolix, China). The incident light wavelength was controlled using an appropriate long-pass cut-off filter (>420 nm) to emit visible white light. The reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved H<sub>2</sub> was analyzed using an online gas chromatograph (GC 7890A, Agilent Instrument Ltd., CA, USA), referencing against a standard gas with a known volume of H<sub>2</sub>.

### 3. Results and discussion

To synthesize donor-acceptor-type CPs, phenylene and fluorene units were used as electron donors and benzothiadiazole (BT) and bisthienylbenzothiadiazole (BTB) groups were used as electron-accepting units (Fig. 1). Thus, four kinds of CPs were obtained by Suzuki coupling reaction of corresponding monomers. The chemical structures of the polymers were confirmed with <sup>1</sup>H NMR, <sup>13</sup>C NMR (Figs. S1 and S2) and EA. Each polymer had a number-average MW between 8100 and 14,100 (Fig. S3, Table S1). P-dots were obtained from the CPs by the conventional nanoprecipitation technique (Scheme S1) [46]. P-dots fabricated from BT-containing polymers, including P8BT-dot and F6BT-dot showed yellow fluorescence with emission at 575 and 545 nm, respectively, whereas P8BTB- and F6BTB-dot, which contained more extended conjugation of BTB presented a more red-shifted fluorescence at 720 and 660 nm, respectively. In conjunction with the red-shifted fluorescence of P8BTB-dot (720 nm), composed of phenylene and BTB units, it showed a highly red-shifted blue color under ambient light with absorption at 590 nm (Fig. 2 and Table S2). The yellow-colored P-dots (P8BT- and F6BT-dots) and the purple-colored P-dots (F6BTB-dots) exhibited different absorption wavelengths, depending on the acceptor units (BT and BTB) used. The donor moieties (phenylene and fluorene) did not significantly affect the colors of the P-dots (inset photographs in Fig. 2). The shapes and sizes of the P-dots were determined by SEM and DLS, respectively (Fig. 3 and S4), indicating that each P-dot was fabricated with a spherical shape, 50-68 nm in size.

Nanosized P-dots show superior wettability and dispersibility in water than hydrophobic CPs. Therefore, P-dots have an advantage in the catalytic reaction using water as a medium over film shape. To compare CP's water wettability, the contact angles of film and P-dots were investigated (Fig. S5). The contact angle of the F6BT film coated on a glass was determined to be 77.9°, whereas the contact angle of the F6BT-dot was found to be 13.2°. The result indicates that P-dots were more hydrophilic and had better water wettability.

Table 1		
Optical and ele	ectrochemical prope	rties of polymers

Polymer	E <sub>g,opt</sub>	E <sub>red, onset</sub>	LUMO	HOMO	E <sub>g</sub>
	[eV] <sup>a)</sup>	[V] <sup>b)</sup>	[eV] <sup>c)</sup>	[eV] <sup>d)</sup>	[eV] <sup>e)</sup>
P8BT	2.39	-1.04 -1.03	-3.40	-5.79	2.39
P8BTB	1.72		-3.41	-5.13	1.72
F6BT F6BTB	2.37 1.95	-1.20 -1.09	-3.24 -3.35	-5.61 -5.30	2.37 1.95

During the light irradiation of the P-dots, electron-hole pairs were generated, in which the electrons in the highest occupied molecular orbital (HOMO) were excited to the lowest unoccupied molecular orbital (LUMO). The generated electron-hole pairs would react with water molecules to produce ROS (Fig. 4). The LUMO levels of the polymers were associated with the photocatalytic activity of P-dots, and to estimate them the reduction potentials were investigated by CV (Fig. S6). All polymers exhibited well-defined reversible reduction waves. F6BT showed the lowest reduction potential of -1.20 V, and the reduction potentials of P8BT, P8BTB, and F6BTB were determined to be -1.04, -1.03, and -1.09 V, respectively. The HOMO and LUMO levels were determined from the reduction potential and onset absorption wavelength of each polymer (Table 1). From the viewpoint of narrow band gap related to visible light absorption, P8BTB (1.72 eV) and F6BTB (1.95 eV) should be more advantageous than P8BT (2.39 eV) and F6BT (2.37 eV), in which the BTB units in the backbone mainly affected such a narrow band gap. In principle, the narrow band gap contributes the long-wavelength absorption within the visible range, expecting visiblelight-induced generation of electron-hole pairs. By contrast, to achieve an efficient ROS generation, a wide band gap, in which the HOMO-LUMO energy level covers the reduction potential for O2. and oxidation potential for ·OH, is preferred. The energy levels of the polymers were determined; in which the reduction potential was higher than -3.4 eV for all polymers and the oxidation potential was lower than -5.6 eV for P8BT and F6BT (Fig. S7). Thus, in terms of the position and width of the energy level, a more efficient ROS generation was expected from the P8BT- and F6BT-dots.

a) Optical band gap determined by the absorption onset ( $E_{g,opt}=1240/\lambda_{onset}$ ). b) vs. Ag/Ag<sup>+</sup> in acetonitrile solution with 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte at a scan speed of 50 mV s<sup>-1</sup>,  $E_{1/2,Fc,Fc+}=0.36$  V. c) The LUMO levels of polymers were calculated according to the formula: LUMO =  $-(E_{red, \, onset} - E_{1/2,Fc,Fc+} + 4.8) = -(E_{red, \, onset} + 4.44)$  eV, where  $E_{red, \, onset}$  was determined from the onset potentials of the reduction waves. d) Estimated from  $E_{HOMO} = E_{LUMO} - E_{g,opt.}$  e)



**Fig. 5.** Changes in the absorption of RNO dye at 430 nm in each P-dot solution upon white-light irradiation. A<sub>o</sub> and A correspond to UV–vis absorption of RNO dye at 430 nm before and after white-light irradiation, respectively.

### Table 2

MB degradation in the presence of P-dot after white-light irradiation.

P-dots	MB Degradation (%) <sup>a)</sup>		
	10 min	240 min	
P8BT-dot	22	84	
P8BTB-dot	13	33	
F6BT-dot	43	90	
F6BTB-dot	27	81	

a) MB degradation was determined by following equation.

### Energy band $gap = E_{LUMO} - E_{HOMO}$

The RNO dye has an absorption wavelength at 430 nm, and in the presence of ROS its absorption decreases. Therefore, the RNO dye is generally used to investigate ROS generation [47]. The RNO dve was photostable enough to maintain its chemical structure without degradation during prolonged white-light irradiation up to 240 min (Fig. S8). The changes in the RNO dye absorption in P-dot solutions were investigated to estimate the relative amounts of ROS produced, according to the chemical structure of the P-dots (Fig. S9). After the addition of RNO dye to each P-dot solution, it was shown that the absorption at 430 nm was reduced by white-light irradiation. Because we already found that the RNO absorption was not varied by the light, decrease at 430 nm clearly indicated RNO degradation by ROS. Also, considering that the UV-vis spectra of P-dots were not changed by light irradiation (at other ranges except around 430 nm), the decrease in the spectra around 430 nm clearly resulted from the RNO degradation. The ROS generation was quantified in terms of RNO decomposition of each P-dot; the RNO decomposition was determined to be 46.6%, 43.3%, 68.4%, and 68.2% for P8BT-, P8BTB-, F6BT-, and F6BTB-dots, respectively, after irradiation for 240 min (Fig. 5). The results show that the acceptor unit (BT or BTB) did not affect ROS generation, while the ROS generation was highly dependent on the donor group (phenylene or fluorene). In particular, the F6BT- and F6BTB-dots, which contained fluorene as a donor showed а more effective ROS generation than phenylene-containing P8BT- and P8BTB-dots. Therefore, ROS generation was strongly affected by the donor unit in the backbone, regardless of the UV-vis absorption spectra of the polymers.

For practical photocatalysis, the photocatalytic activity of P-dots was investigated via MB dye degradation. Similar to the RNO dye, MB could be degraded by ROS generated from P-dots upon light irradiation. The MB degradation was evaluated by determining changes in the UV–vis absorption of MB (Fig. S10). For RNO dye cases, a more efficient ROS generation was observed for the F6BT- and F6BTB-dots that contained fluorene units. A significant photocatalytic degradation of MB was found for the F6BT-dot, in which 90% MB degradation was observed (Table 2). The low MB degradation by the P8BTB-dot (33% after 240 min irradiation) was presumed to result from the overlap of the UV–vis absorption spectra of the P8BTB-dot and MB at around 665 nm. We believe that



Fig. 7. Light-driven hydrogen evolution of P-dots at ambient temperature. [ascorbic acid] = 0.2 M, pH 4.0 (adjusted with 1 M NaOH).

more MB was decomposed, but further decrease in the MB absorbance was limited because of the spectral overlap. The MB degradation by photocatalytic activity of P-dots was clearly observed by the naked eye (Fig. S11). The color of each P-dot became a green or dark violet color in the presence of MB, but the original colors of the P-dot solutions were recovered as the irradiation time increased (except for the P8BTB-dot), indicating the MB was degraded and lost its original color.

The nanosized, spherical shape of the P-dots resulted in difficulty of separation from the solution for further reuse. To achieve a reusable photocatalyst, the use of a substrate that accommodates CPs was necessary. Therefore, a paper-based photocatalyst was fabricated by introducing a CP to a filter paper. P8BT, P8BTB, F6BT, or F6BTB was incorporated in a conventional filter paper by immersing the paper in the polymer solution. Then the filter paper was exposed to an aqueous solution of RNO dye. The light source was the same as that used for the photodegradation of RNO and MB in the P-dot solution. The RNO decomposition efficiency of the paper-based photocatalysts was similar to that of the P-dot solution, in which the F6BT-paper showed better photocatalytic activity over other papers (Fig. 6a). It was concluded that the CPs maintained photocatalytic activity, even when they were located in the substrate. The F6BT-paper-based photocataly showed an advantage in reusability over the particle-based one in terms of simple regeneration of the paper by washing and, subsequently, the photocatalytic efficiency was maintained even after being used four times. (Fig. 6b).

MB degradation (%) =  $(A_0 - A)/A_0 \times 100$ 



**Fig. 6.** (a) Changes in the UV–vis absorption of RNO dye at 430 nm by paper-based photocatalysts containing CPs.  $A_o$  and A correspond to UV–vis absorption of RNO dye at 430 nm before and after white-light irradiation, respectively. (b) Repeated uses of F6BT-paper over 4 cycles.

where  $A_0$  and A correspond to UV–vis absorbance at 665 nm before and after white-light irradiation, respectively.

# The CPs were synthesized via the Suzuki coupling polymerization, in which the use of a Pd catalyst was inevitable. It has been reported that the residual Pd catalyst in CP affects the photocatalytic H<sub>2</sub> evolution and the amount of generated H<sub>2</sub> is dependent on the residual Pd concentration [48]. Thus, residual Pd was removed by thiourea treatment and 0.12 wt% of Pd was found in F6BT determined with ICP. To quantify the performance of P-dots for light-driven H<sub>2</sub> evolution, ascorbic acid and P-dots were used as a sacrificial electron donor and photocatalyst, respectively. The comparative dynamics curve of H<sub>2</sub> evolution was investigated (Fig. 7). The amounts of H<sub>2</sub> generated were found to be 8.4 mmol/g for F6BT-dot and 0.07 mmol/g for F6BTB-dot. However, no noticeable H<sub>2</sub> evolution was observed for the P8BT-, F6BTB-, and P8BTB-dots. It is presumed that H<sub>2</sub> evolution was strongly dependent on the chemical structures composed of fluorene and BT, the same as in the cases of ROS generation in paper-embedded as well as particle forms.

### 4. Conclusions

Four CP combinations of donors and acceptors were synthesized to explore the relationship between chemical structure and photocatalytic activity, including ROS generation, dye degradation, and  $H_2$  evolution. The chemical structures of the polymers affected the absorption wavelength and energy band gap, which were important in visible-light absorption and ROS generation, respectively. To facilitate the access of water molecules to the hydrophobic CPs, the latter were fabricated as uniformly dispersed NPs in an aqueous solution. The ROS generation was investigated in terms of degradation of RNO and MB dyes. A more effective ROS generation was obtained when fluorene and BT were used as donor and acceptor units in the polymer backbone, respectively, and a higher efficiency of dye degradation with reusability and  $H_2$  evolution was observed. The results indicate that the CPs are potentially more effective for use as an organic photocatalyst.

### CRediT authorship contribution statement

Yougjin Gwon: Validation, Investigation, Writing – original draft. Seonyoung Jo: Investigation, Writing – review & editing. Hyun-Jun Lee: Validation, Investigation. Soo Young Park: Validation. Taek Seung Lee: Conceptualization, Supervision, Validation, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2021.124004.

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