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# **Synthesis and fluorescence on/off switching of hyperbranched polymers having diarylethene at the branching point**

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## **ABSTRACT:**

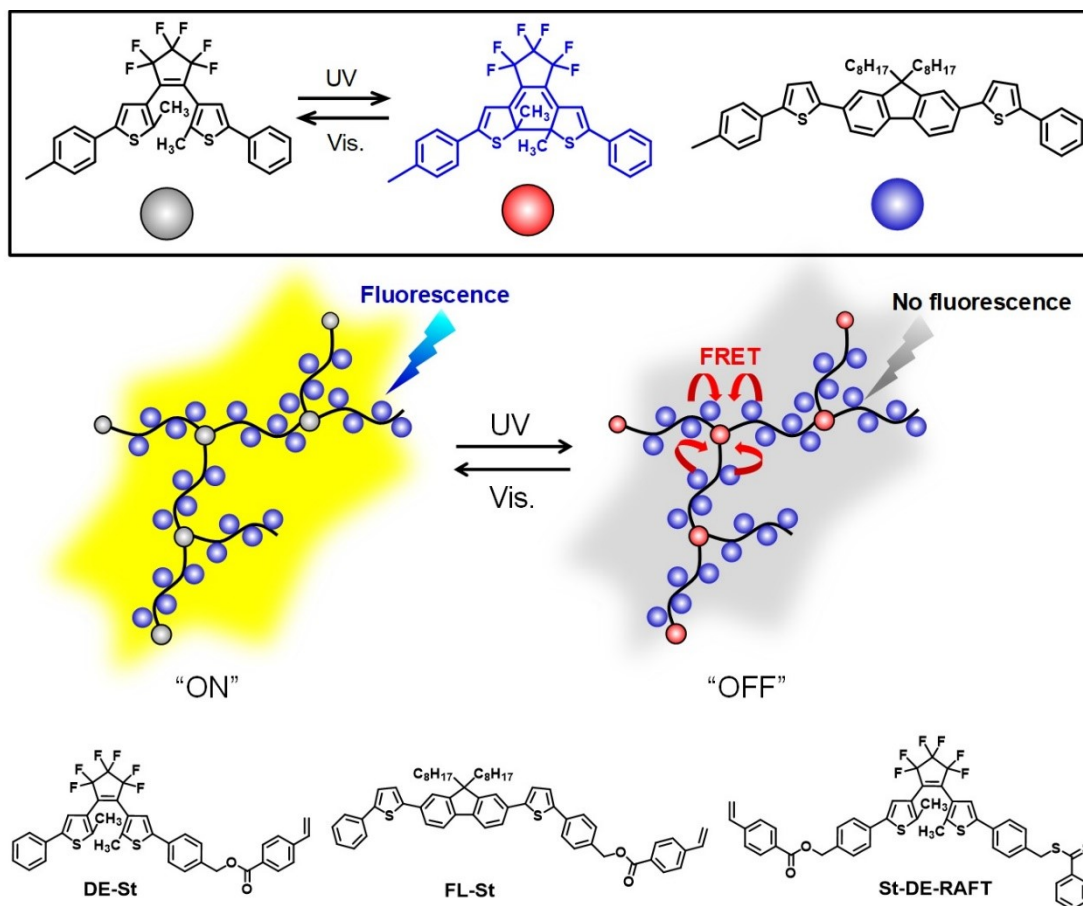
We designed and synthesized hyperbranched polymers (HBPs) having diarylethene (DE) at branching points and having fluorene (FL) and DE derivatives between branching points in order to investigate the effect of the polymer structure to fluorescence on/off switching efficiency induced by the photochromic reaction of DE. First, HBP was synthesized by polymerization of an FL monomer (FL-St) in the presence of a DE monomer with reversible addition-fragmentation chain transfer unit (St-DE-RAFT) in the feed ratio of  $[\text{FL-St}]/[\text{St-DE-RAFT}] = 10$ . The fluorescence intensity of the resulting HBP decreased linearly as a function of the photocyclization conversion of DE. The change in the fluorescence intensity accompanied by the photochromic reactions indicates that one DE closed-ring isomer can quench 16.9 neighboring FL moieties. However, the switching rate and on/off contrast of fluorescence were relatively low because the number of FL in the polymer chain is much larger than that of DE. Therefore, we synthesized two types of HBPs having DE positioned not only at the branching points but also integrated in the polymer chains with different branching degrees. The fluorescence intensity of FL for such HBPs showed a non-linear dependence on the photocyclization conversion of DE, and a significant emission decrease with high on/off contrast even in low conversion was demonstrated. One DE closed-ring isomer quenched 5.4–6.4 FL moieties, whereas the fluorescence quantum yield in the “on” state was found to be around 0.15. The quenching of FL molecules is more pronounced for higher branching degrees in the polymers, indicating that DE closed-ring isomer can quench efficiently FL molecules when located within the polymer chains as well as at the branching points of the polymer.

# 1. Introduction

In recent years, fluorescent switchable materials using photochromic compounds have attracted much attention because of their potential application as fluorescent probes in super-resolution microscopy and optical memory [1–4]. Diarylethenes (DE) are typical P-type photochromic molecules and undergo reversible photochromic reactions between their opening isomer and their closed-ring isomer upon irradiation with ultraviolet (UV) light and visible light [3]. Combining DE with fluorophores, on/off switching of the emission signal can be accomplished. For instance, in the case of a DE molecule directly linked to a fluorophore via covalent bonding, fluorescence is emitted from the fluorophore when DE exists in the opening isomer (DE-o) (“on” state). On the other hand, when DE-o is converted to the closed-ring isomer (DE-c), no fluorescence is emitted because of Förster resonance energy transfer (FRET) from the fluorophore to DE-c (“off” state) [4]. Especially, DE having phenylthiophenes at the aryl groups is promising for fluorescence switching because of the high molar absorption coefficient of the open-ring isomer ( $\epsilon = 35600 \text{ M}^{-1} \text{ cm}^{-1}$ ), high photocyclization quantum yield ( $\Phi_{o \rightarrow c} = 0.59$ ), and relatively low photocycloreversion quantum yield ( $\Phi_{c \rightarrow o} = 0.013$ ) [3]. No significant decrease in the fluorescence intensity at the “on” state was observed even after the repeating cycles of 100 times in the system using DE [5]. In general, the fluorescence intensity is changed in proportion to the photocyclization conversion of DE. For example, the fluorescence intensity decreases to ca. 50% when the photocyclization conversion of DE is 50% because DE-c can quench at most one fluorophore moiety in the system composed of a dyad DE-fluorophore. If one DE-c can quench several fluorophores, high on/off contrast and rapid on/off switching of fluorescence can be achieved and it is not necessary to yield photocyclization conversion of 100% to result in the fluorescence “off” state. To date, various types of switchable fluorescent DE with highly efficient fluorescence switching, high fluorescence quantum yield ( $\Phi_f$ ), and high on/off contrast have been developed [5–15]. Akagi and co-workers reported full-colored fluorescence switching using fluorescent conjugated polymers bearing diarylethene in the side chains, leading to white fluorescence on/off switching by mixing red, green, and blue fluorescent polymer nanoparticles in appropriate ratios [16–18]. We reported fluorescence switching by incorporation of DE and fluorene (FL) derivatives into

the side chain of a polymer [12]. The switching efficiency for the alternative copolymer is higher than that for the random copolymer because DE and FL alternately exist in the polymer chains. The monomer sequence and molar ratio of fluorescent dye and photochromic dye significantly affect the fluorescence switching efficiency. Moreover, we succeeded in preparing highly efficient switchable fluorescent silica nanoparticles densely covered with random copolymers by thanks to intra-polymer chain and inter-polymer chain FRET processes [13]. The use of FRET between inter-polymer chains is also useful for the improvement of the switching efficiency. However, the influence of the polymer structure and sequence to fluorescence switching efficiency has not been investigated in detail yet, and it is important to examine fluorescence switching of a polymer with a specific structure.

Here, we report on the design and fabrication of a hyperbranched polymer (HBP) having DE at the branching points and having FL in the polymer chain to achieve the efficient fluorescence on/off switching, highlighting the influence of the branching structure to the fluorescence switching, as shown in **Fig. 1**. HBP was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of an FL monomer (FL-St) in the presence of a DE monomer with a RAFT unit (St-DE-RAFT). In this system, St-DE-RAFT plays an essential role as the RAFT agent in the RAFT unit and the polymerizable monomer in the St unit. As a result, the use of St-DE-RAFT in the RAFT polymerization of St can give branched polymers having DE at the branching points. The fluorescence switching behaviors of various types of HBPs including a DE monomer (DE-St) in the polymer chain are also discussed in this study.



**Fig. 1.** Illustration of fluorescence on/off switching of hyperbranched polymers having diarylethene at the branching points.

## 2. Experimental Section

### 2.1. Measurements

Spectroscopic grade solvents used were purified by distillation before use.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. Absorption spectra were measured with a JASCO V-560 absorption spectrophotometer. Fluorescence spectra were measured with a JASCO FP-8300 spectrofluorometer. Fluorescence quantum yields were also determined using a JASCO FP-8300 fluorescence spectrometer equipped with a JASCO ILF-835 integration sphere. Recycling preparative high-performance liquid chromatography (HPLC) was conducted using a JAI LC-908 chromatograph equipped with JAIGEL-1H and 2H columns using chloroform as the eluent. The number- and weight-average molecular weights of polymers ( $M_n$  and  $M_w$ , respectively) were determined by gel permeation chromatography (GPC). GPC was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns and tetrahydrofuran (THF) as the eluent at 40 °C.

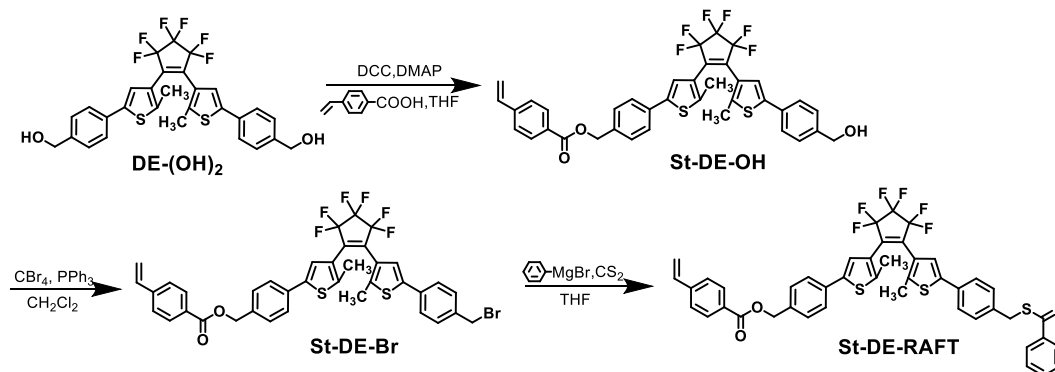
Fluorescence decays were measured by the time-correlated single-photon counting (TCSPC) method using a femtosecond laser excitation composed of a Titanium-Sapphire laser (Tsunami, Spectra-Physics) pumped by a doubled Nd:YVO<sub>4</sub> laser (Millennia Xs, Spectra-Physics). Light pulses at 800 nm from the oscillator were selected by an acousto-optic crystal at a repetition rate of 4 MHz, and then doubled at 400 nm by a nonlinear crystal. Fluorescence photons were detected at 90° through a monochromator and a polarizer at magic angle by means of a Hamamatsu MCP R3809U photomultiplier, connected to a SPC-630 TCSPC module from Becker & Hickl. The fluorescence data were analyzed using Globals software package (Laboratory for Fluorescence Dynamics, University of Illinois at Urbana–Champaign).

### 2.2. Materials

All reagents used for synthesis were commercially available from FUJIFILM Wako Pure Chemical Corporation. 2,2'-Azobis(2,4,4-trimethylpentane) (ATMP) was recrystallized from



*n*-hexane. DE-St and FL-St were synthesized according to a method described in the literature [12,19]. St-DE-RAFT was synthesized according to **Scheme 1**.



**Scheme 1.** Synthetic scheme of St-DE-RAFT.

### 2.3. Synthesis of DE having hydroxymethyl and styryl groups (St-DE-OH)

DE having hydroxymethyl groups at both sides (DE-(OH)<sub>2</sub>) was synthesized according to a method described in our previous paper [20]. DE-(OH)<sub>2</sub> (1.12 g, 1.93 mmol), 4-dimethylaminopyridine (DMAP) (236 mg, 1.93 mmol), and dicyclohexylcarbodiimide (DCC) (398 mg, 1.93 mmol) were dissolved in THF (160 mL). Then, to the mixture was added the THF solution (10 mL) containing *p*-vinyl benzoic acid (313 mg, 1.93 mmol). The reaction mixture was stirred for 24 h at room temperature. The reaction mixture was extracted with dichloromethane. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (7:3) as the eluent to give 347 mg of St-DE-OH in 25.3% yield. The <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and IR spectra of the product are shown in **Fig. S1**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ = 1.66 (t, *J* = 5.8 Hz, 1H, OH), 1.96 (s, 3H, CH<sub>3</sub>), 1.97 (s, 3H, CH<sub>3</sub>), 4.72 (d, *J* = 5.8 Hz, 2H, CH<sub>2</sub>), 5.36 (s, 2H, CH<sub>2</sub>), 5.39 (dd, *J* = 0.57 Hz and 11 Hz, 1H, Vinyl H), 5.87 (dd, *J* = 0.57 Hz and 18 Hz, 1H, Vinyl H), 6.76 (dd, *J* = 11 Hz and 18 Hz, Vinyl H), 7.28 (s, 1H, Thienyl H), 7.29 (s, 1H, Thienyl H), 7.39 (d, *J* = 8.3 Hz, 2H, Aromatic H), 7.47 (d, *J* = 8.3 Hz, 4H, Aromatic H), 7.54 (d, *J* = 8.3 Hz, 2H, Aromatic H), 7.56 (d, *J* = 8.3 Hz, 2H, Aromatic H), 8.03 (d, *J* = 8.3 Hz, 2H, Aromatic H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS) δ = 14.7, 65.0, 66.4, 116.8, 122.6, 122.9, 125.9, 125.9, 126.3, 127.7, 129.1, 129.2, 130.2, 136.0, 136.1, 140.8, 141.5, 141.7, 141.9,

142.1, 142.3, 166.3. IR ( $\nu$ , KBr,  $\text{cm}^{-1}$ ): 1508, 1517, 1607, 1716, 2865, 2920, 2952, 3030, 3085, 3410. HR-MS (MALDI)  $m/z = 710.1378$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{38}\text{H}_{28}\text{F}_6\text{O}_3\text{S}_2^+$ : 710.1379.

#### 2.4. Synthesis of DE having bromomethyl and styryl groups (St-DE-Br)

Tetrabromomethane (663 mg, 2.00 mmol) was added to the solution of dichloromethane (100 mL) dissolving St-DE-OH (710 mg, 1.00 mmol) and triphenylphosphine (525 mg, 2.00 mmol). Then, the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was extracted with dichloromethane. The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (8:2) as the eluent to give 532 mg of St-DE-Br in 68.7% yield. The  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and IR spectra of the product are shown in **Fig. S2**.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta = 1.96$  (s, 6H,  $\text{CH}_3$ ), 4.51 (s, 2H,  $\text{CH}_2$ ), 5.37 (s, 2H,  $\text{CH}_2$ ), 5.39 (dd,  $J = 0.57$  Hz and 11 Hz, 1H, Vinyl H), 5.87 (dd,  $J = 0.57$  Hz, 18 Hz, 1H, Vinyl H), 6.75 (dd,  $J = 11$  Hz and 18 Hz, 1H Vinyl H), 7.29 (s, 2H, Thienyl H), 7.3-7.6 (m, 10H, Aromatic H), 8.03 (d,  $J = 8.3$  Hz, 2H, Aromatic H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , TMS)  $\delta = 14.7, 33.2, 66.4, 116.8, 122.8, 123.0, 125.9, 126.0, 126.1, 126.3, 129.1, 129.9, 130.2, 133.4, 133.6, 136.0, 136.1, 137.6, 141.6, 141.9, 142.3, 166.3$ . IR ( $\nu$ , KBr,  $\text{cm}^{-1}$ ): 1508, 1517, 1607, 1716, 2850, 2920, 2955, 3030, 3070. HR-MS (MALDI)  $m/z = 772.0534$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{38}\text{H}_{27}\text{BrF}_6\text{O}_2\text{S}_3^+$ : 772.0535.

#### 2.5. Synthesis of DE having dithiobenzoate and styryl groups (St-DE-RAFT)

Phenylmagnesium bromide was prepared from bromobenzene (1.0 mL, 9.52 mmol) and magnesium turnings (171 mg, 7.03 mmol) in dry THF (10 mL). To the THF solution of the Grignard reagent was slowly added a THF solution (2.0 mL) of carbon disulfide (0.50 mL, 8.28 mmol) at 40 °C. A 1.0 mL aliquot of the total mixture (13.5 mL) was added to a stirred solution of St-DE-Br (300 mg, 0.388 mmol) in dry THF (5 mL). The reaction mixture was stirred for 16 h at room temperature. An adequate amount of ice water was added to the mixture to quench the reaction. The reaction mixture was extracted with ether, washed with brine, dried over  $\text{MgSO}_4$ , filtrated, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane/dichloromethane (1:2) as the eluent to give 306

mg of St-DE-RAFT in 93.0% yield. The  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and IR spectra of the product are shown in **Fig. S3**.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta = 1.96$  (s, 6H,  $\text{CH}_3$ ), 4.61 (s, 2H,  $\text{CH}_2$ ), 5.36 (s, 2H,  $\text{CH}_2$ ), 5.39 (dd,  $J = 0.57$  Hz and 11 Hz, 1H, Vinyl H), 5.87 (dd,  $J = 0.57$  Hz and 18 Hz, 1H, Vinyl H), 6.75 (dd,  $J = 11$  Hz and 18 Hz, 1H Vinyl H), 7.27 (s, 1H, Thienyl H), 7.29 (s, 1H, Thienyl H), 7.3-7.6 (m, 13H, Aromatic H), 7.9-8.1 (m, 4H, Aromatic H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ , TMS)  $\delta = 14.7, 41.8, 66.3, 116.8, 122.8, 125.9, 126.0, 126.0, 126.3, 127.0, 128.5, 129.0, 129.2, 130.1, 130.2, 132.7, 132.9, 133.4, 135.0, 136.0, 136.1, 141.8, 141.9, 142.3, 144.8, 166.3$ . IR ( $\nu$ , KBr,  $\text{cm}^{-1}$ ): 1517, 1608, 1715, 2850, 2912, 2952, 3028, 3054, 3085. HR-MS (MALDI)  $m/z = 846.1184$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{45}\text{H}_{32}\text{F}_6\text{O}_2\text{S}_4^+$ : 846.1184.

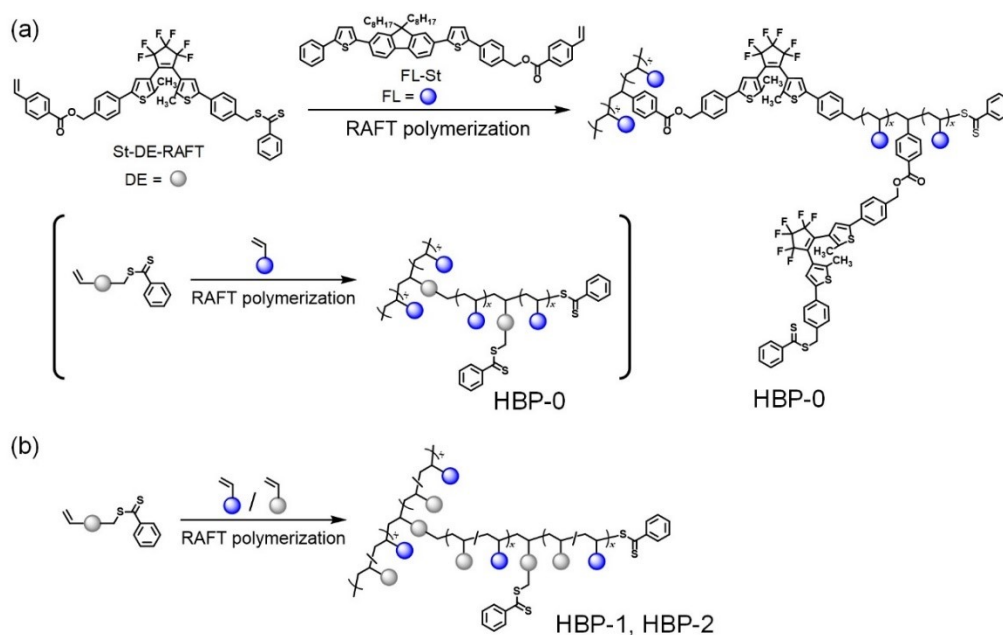
## 2.6. Polymerization

The RAFT polymerization was carried out in a sealed glass tube under a vacuum. Monomer, St-DE-RAFT, ATMP, and toluene were placed in a glass tube. The tube was degassed by several freeze-pump-thaw cycles and sealed under vacuum. The hyperbranched polymer having DE at only branching points (HBP-0) was synthesized using FL-St and St-DE-RAFT in the feed ratio of  $[\text{FL-St}]:[\text{St-DE-RAFT}] = 10:1$ , using ATMP as the initiator in toluene at  $100\text{ }^\circ\text{C}$  for 65 h. The hyperbranched polymers having DE positioned not only at the branching points but also integrated into the polymer chains (HBP-1, HBP-2) were synthesized by adding DE-St under the synthetic condition of HBP-0. The feed ratios for HBP-1 and HBP-2 are conducted on  $[\text{FL-St}]:[\text{St-DE-RAFT}]:[\text{DE-St}] = 5:1:4$  and  $5:2:3$ , respectively. The branching degree of HBP-2 is twice as those of HBP-0 and HBP-1. After the polymerization, the polymers were isolated using the recycling preparative HPLC.

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis and characterization of HBP-0

First, we synthesized HBP incorporating DE only at the branching points. The polymer called HBP-0 was synthesized by polymerization of FL-St in the presence of St-DE-RAFT in the feed ratio of  $[FL-St]/[St-DE-RAFT] = 10$ , using ATMP as the initiator in toluene at 100 °C for 65 h, as shown in **Scheme 2(a)**. After the polymerization, the polymers were isolated using the recycling preparative HPLC and were frozen dry in benzene to obtain powder samples. **Table 1** shows the polymerization conditions and  $M_n$  and  $M_w/M_n$  of the resulting polymers. The color of the polymer in the bulk powder was yellow derived from the FL moiety. The composition of DE and FL was determined by  $^1H$ -NMR spectroscopic analysis of methyl protons for St-DE-RAFT and methylene protons connected to 9-carbon of FL in the polymers. The  $^1H$ -NMR spectrum of HBP-0 is shown in **Fig. S4**. The composition of DE and FL ( $[DE]/([DE]+[FL])$ ) in HBP-0 was estimated to be 9.1 mol% which is almost the same as the feed ratio. This means that ca. 10 FL moieties exist between DE chromophores at the branching points ( $x = \text{ca. } 10$ ).



**Scheme 2.** Synthetic scheme of HBP-0 (a) and HBP-1 and 2 (b).

**Table 1.** Copolymerization of DE-St and FL-St in the presence of St-DE-RAFT in toluene at 100 °C for 65 h.

	[St-DE-RAFT] / M	[DE-St] / M	[FL-St] / M	[ATMP] / mM	[DE]/([DE]+[FL]) in polymer / mol%	$M_n$	$M_w/M_n$
HBP-0	0.020	0	0.20	0.25	9.1	15800	1.47
HBP-1	0.060	0.24	0.30	0.10	50	16700	1.41
HBP-2	0.12	0.18	0.30	0.10	50	14400	1.19

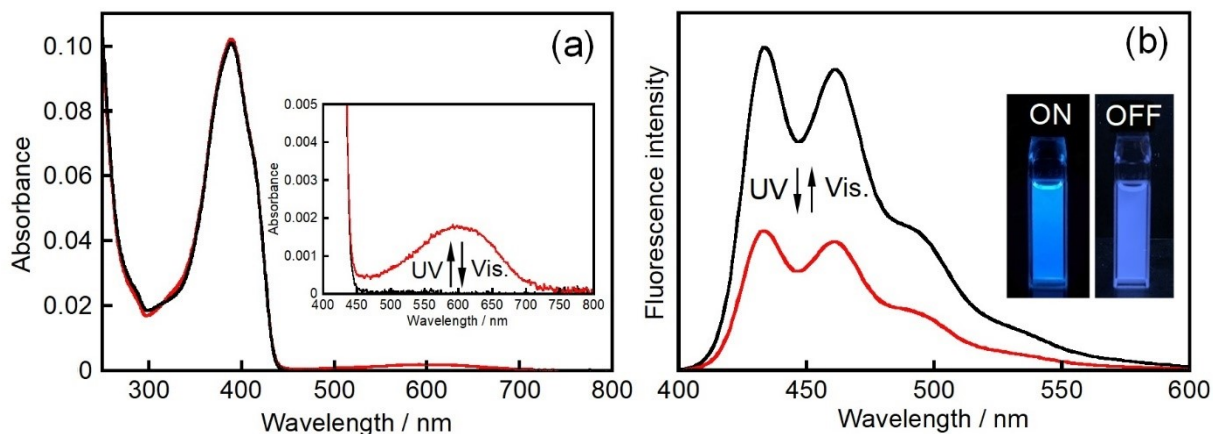
HBP-0 underwent reversible photochromic reactions in THF upon irradiation with UV and visible light, as shown in **Fig. 2(a)**. The main absorption peak at 390 nm is attributable to the FL unit. Upon irradiation with 313 nm light, a new absorption band derived from the  $\pi$ - $\pi^*$  transition of DE-c appeared at 450-700 nm, and the band disappeared upon irradiation with visible light. **Fig. 2(b)** shows fluorescence spectral changes and the fluorescence photographs of HBP-0 that are associated with the photochromic reactions of DE. The fluorescence quantum yield ( $\Phi_f$ ) of HBP-0 in the “on” state was determined to be 0.20. The value is smaller than those of FL-St ( $\Phi_f = 0.70$ ) and a linear polymer (LP) consisting of DE and FL ( $\Phi_f = 0.35$ ) [13]. These results are summarized in **Table 2**. The maximum wavelength of the fluorescence was observed at 434 nm. When DE was converted to DE-c upon irradiation with UV light, the fluorescence intensity decreased due to energy transfer from the FL units (donors) to DE-c moieties (acceptors), as shown in **Fig. 2(b)** since the fluorescence spectrum of FL and the absorption spectrum of DE-c are well-overlapped as shown in **Fig. S5**. However, fluorescence was not completely quenched and 43% of the fluorescence intensity remained at the photostationary state (PSS). The fluorescence intensity gradually decreased with irradiation time, as shown in **Fig. 3(a)**. **Fig. 3(b)** shows the normalized fluorescence intensity relative to the photocyclization conversion of HBP-0 in THF. The fluorescence intensity decreased almost proportionally with increasing photocyclization conversion. In this system, there are 10 equivalents of FL relative to DE in the polymer chain. Therefore, the low on/off contrast of fluorescence means that the energy transfer is not fully effective: a non-negligible fraction of FL fluorophores cannot be quenched by DE-c, probably due to excessive distance between FL units and their closest DE-

c moieties. The number of FL quenched by one DE-c chromophore can be simulated by equations (1) and (2):

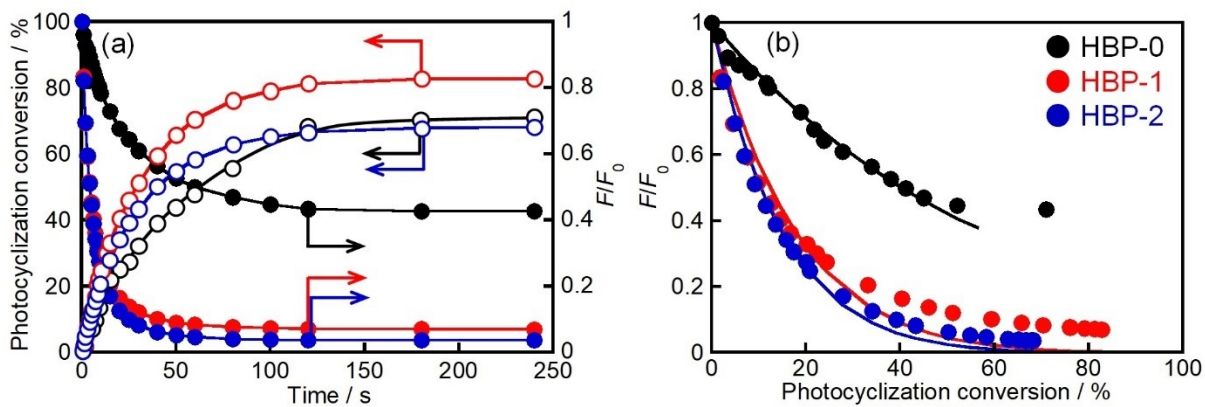
$$F/F_0 = (1 - \beta \alpha)^n \quad (1)$$

$$n' = (1 - \beta) \times n \quad (2)$$

where  $F$  is the fluorescence intensity at an arbitrary conversion,  $F_0$  is the fluorescence intensity in the “on” state,  $\alpha$  is a photocyclization conversion of DE,  $\beta$  is a molar fraction of DE,  $n$  is the number of molecules within the Förster sphere (with a critical radius  $R_0$ ), and  $n'$  is the number of FL molecules quenched by one DE-c chromophore [14]. As a result of the fitting, the  $n'$  value for HBP-0 was determined to be 16.9. To further increase the fluorescence quenching efficiency, the molar fraction of DE in the polymer should be increased. In order to improve the fluorescence switching efficiency, we decided to incorporate DE-St between the branching points by copolymerization of FL-St and DE-St in the presence of St-DE-RAFT. We successfully synthesized two types of HBPs with different branching degrees by controlling the polymerization conditions shown in **Table 1 (Scheme 2(b))**. The resulting polymers were called HBP-1 and HBP-2. The branching degree of HBP-2 is twice as large as that of HBP-1.



**Fig. 2** (a) Absorption and (b) fluorescence spectral changes of HBP-0 ( $1.3 \times 10^{-6}$  M for DE moiety) in THF upon irradiation with 313 nm light. The fluorescence spectra were excited at 390 nm. Inset: Fluorescence photographs in the “on” and “off” states in THF excited with 365 nm light.



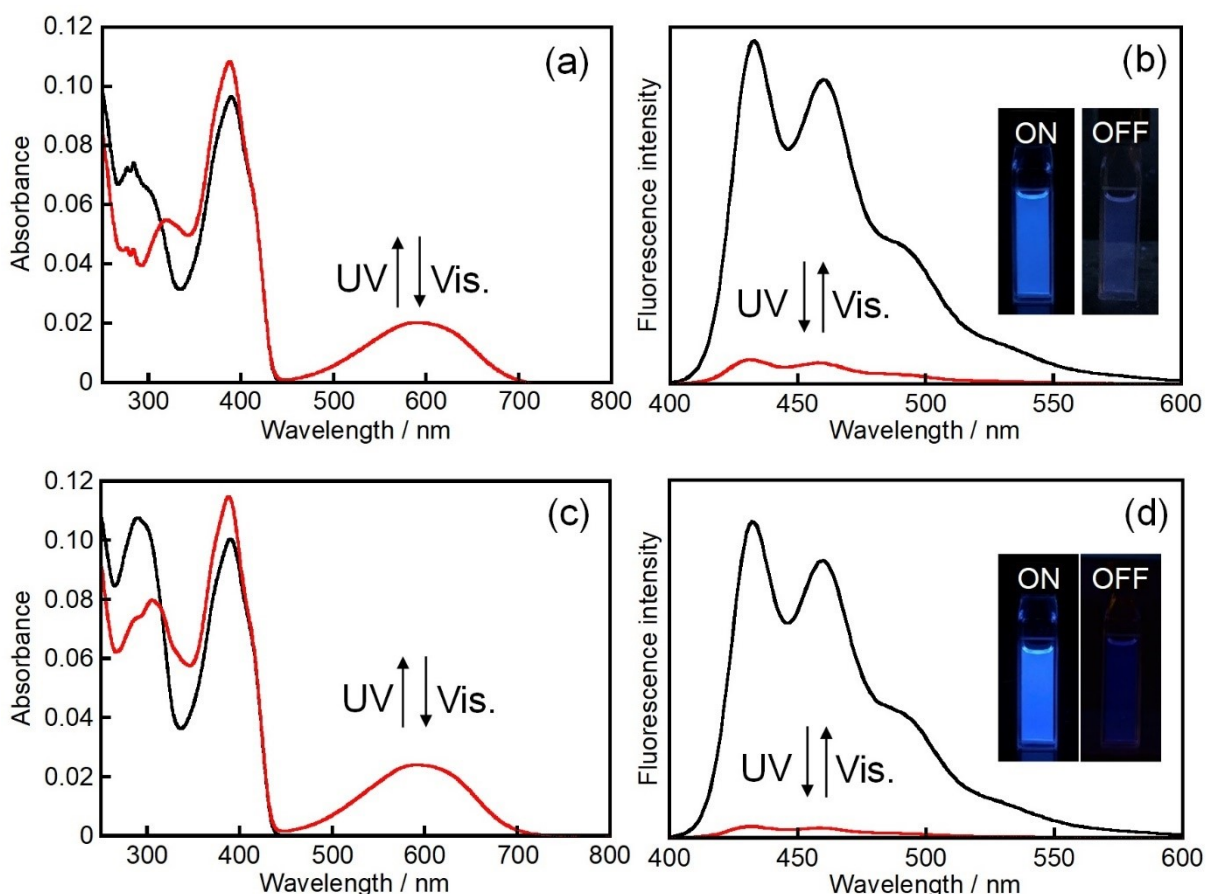
**Fig. 3.** (a) Photocyclization conversion upon irradiation with 313 nm light ( $0.25 \text{ mW cm}^{-2}$ ) and normalized fluorescence intensity of HBP-0 (black mark), HBP-1 (red mark), and HBP-2 (blue mark) in THF, excited at 390 nm. (b) Normalized fluorescence intensity relative to the photocyclization conversion of HBP-0 (black mark), HBP-1 (red mark), and HBP-2 (blue mark). Black, red, and blue lines are fitting curves of the fluorescence intensity changes using eq (1).

### 3.2. Characterization and optical properties of HBP-1 and HBP-2

The polymerization results for HBP-1 and HBP-2 are also summarized in **Table 1**. The copolymer compositions were determined by  $^1\text{H-NMR}$  spectroscopic analysis as mentioned above. The  $^1\text{H-NMR}$  spectra of HBP-1 and HBP-2 are shown in **Figs. S6 and S7**. The copolymer composition of DE in both HBP-1 and HBP-2 was estimated to be 50 mol%, which is comparable to the feed ratio. **Fig. 4** shows absorption and fluorescence spectral changes and fluorescence photographs of HBP-1 and HBP-2 in THF as a function of the photochromic reactions of DE. Upon irradiation with 313 nm light, a new absorption band appeared at 450–700 nm and disappeared by irradiation with visible light. The photocyclization conversions of DE in their polymers are shown in **Fig. 3(a)**. The conversion of HBP-2 at PSS is lower than that of HBP-1. The difference is possibly due to a more efficient FRET process from FL to DE-c in more highly branched polymer for HBP-2, compared with HBP-1. Therefore, the excited state of DE-c produced by the FRET process promotes the photocycloreversion reaction to result in the lowering of the photocyclization conversion. Moreover, the reason why the conversion of HBP-0 is lower than that of HBP-1 is also due to the efficient FRET process from FL to DE-c following the photocycloreversion reaction in the polymer HBP-0 having an excess amount of

the FL units relative to the DE units. The fluorescence intensities of HBP-1 and HBP-2 decreased with increasing absorption bands of DE-c. Their changes are photoreversible and similar to those of HBP-0 and LP. **Table 2** also summarizes the optical properties of photochromic-fluorescent polymer samples in THF. The fluorescence quantum yield in the “on” state was lowered with the increasing branching degree (from 0.35 for LP to 0.14 for HBP-2) because of locally aggregation caused quenching. However, the fluorescence was significantly decreased with irradiation time and increasing photocyclization conversion, as shown in **Fig. 3**. This finding indicates that one DE-c molecule can switch off the fluorescence of several FL moieties. As a result of the simulation using eqs (1) and (2), one DE-c molecule in the branched polymer chain of HBP-1 and HBP-2 was able to quench the fluorescence of 5.4 and 6.4 FL moieties, respectively. Although these quenching numbers are lower than that of HBP-0, the on/off contrast was dramatically improved and the change in the fluorescence intensity relative to the photocyclization conversion was noticeably increased. 70% and 80% of the initial fluorescence were quenched in the photocyclization conversion of 20% in HBP-1 and HBP-2, respectively.





**Fig. 4.** (a) Absorption and (b) fluorescence spectral changes of HBP-1 ( $1.3 \times 10^{-6}$  M for DE moiety) and (c) absorption and (d) fluorescence spectral changes of HBP-2 ( $1.3 \times 10^{-6}$  M for DE moiety) in THF upon irradiation with 313 nm light. The fluorescence spectra were excited at 390 nm. Inset: Fluorescence photographs in the “on” and “off” states in THF excited with 365 nm light.

**Table 2.** Optical properties of LP, HBP-0, HBP-1, and HBP-2 in THF.

	$\lambda_{\text{abs}}$ / nm	$\lambda_{\text{flu}}$ / nm	Conversion / %	$\Phi_{\text{E.open}}$	$(1 - F/F_0) \times 100$ / % <sup>a</sup>	$R_0$ / nm	Quenching number
LP <sup>b</sup>	390, 592	434	94	0.35	98	3.80	6.3
HBP-0	389, 593	434	71	0.20	57	3.46	16.9
HBP-1	390, 593	433	83	0.16	93	3.34	5.4
HBP-2	390, 589	432	68	0.14	96	3.26	6.4

<sup>a</sup> At the PSS upon irradiation with 313 nm light.

<sup>b</sup> Ref. 13

### 3.3. Förster distance and fluorescence lifetime

To evaluate the fluorescence switching efficiency quantitatively, we calculated Förster distances ( $R_0$ ) between FL and DE-c for HBP-0, HBP-1, and HBP-2 from eq (3) [21,22],

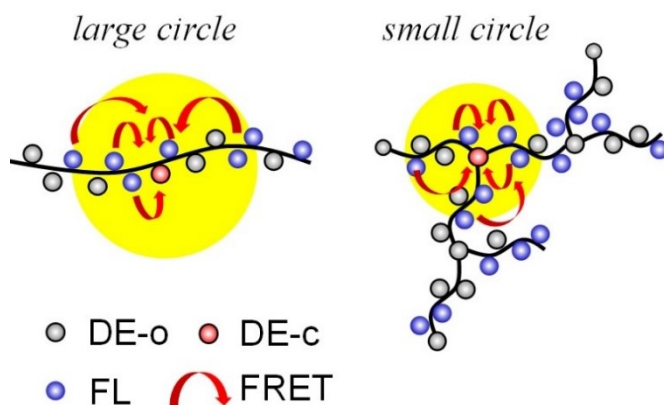
$$R_0^6 = \frac{9\Phi_0(\ln 10)\kappa^2 J}{128\pi^5 c^4 N_A} \quad (3)$$

where  $\Phi_0$  is the fluorescence quantum yield of a donor,  $\kappa^2$  is the dipole orientation factor,  $c$  is the refractive index of the solvent,  $N_A$  is the Avogadro's number, and  $J$  is the spectral overlapping between the fluorescence spectrum of FL and the absorption spectrum of DE-c. Using the values previously reported in our paper [13], all of the values except for fluorescence quantum yield  $\Phi_0$  are the same for HBP-0, HBP-1, and HBP-2 in this case. As a result of the calculation, the  $R_0$  values for HBP-0, HBP-1, and HBP-2 were determined to be 3.46, 3.34, and 3.26 nm, respectively, as shown in **Table 2**. We calculated the Förster's volume ( $v$ ) and the quenching number per Förster's sphere ( $n'/v$ ), as shown in **Table S1**. The Förster's volume for LP is 1.6 times larger than that of HBP-2, which means that one DE-c molecule in LP could quench the fluorescence of FL moieties in a larger area compared with HBP-2. In contrast, the  $n'/v$  values for LP, HBP-1, and HBP-2 were 0.027, 0.035, and 0.044 nm<sup>-3</sup>, respectively. Thus, the quenching ability of HBP-1 and HBP-2 is higher than that of LP, indicating that the branching structure affects the switching behavior significantly: the highest the branching degree, the most efficient the fluorescence photoswitching performances. These results indicate that DE-c can quench FL molecules when incorporated in the polymer chains but also at the branched positions. The fluorescence photoswitching ability ( $n'/v$ ) of HBP-2 is 1.6 times higher than that of LP.

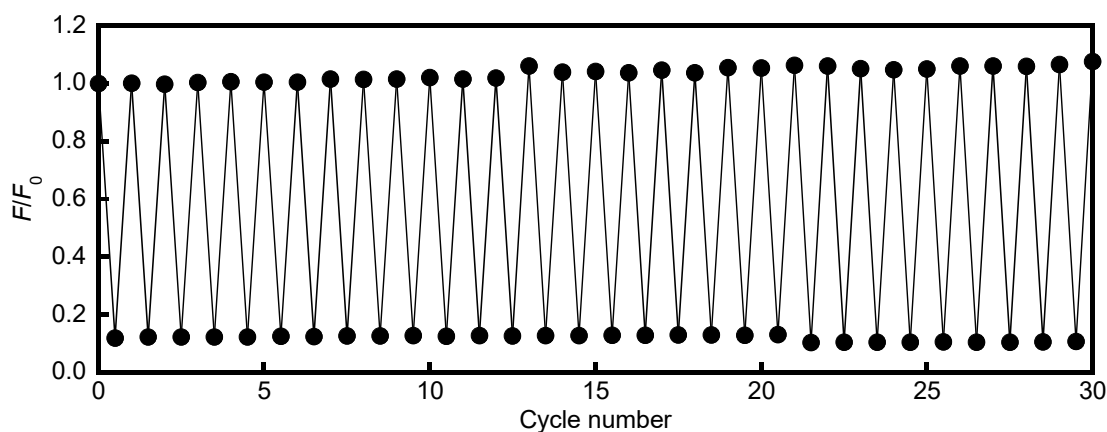
The quenching number of LP and HBP-2 are almost the same, but HBP-2 exhibited highly efficient fluorescence switching despite low Förster distance, as shown in **Fig. 5**. These results demonstrate that the highly branched polymer structures can bring excellent performance in terms of fluorescence switching.

**Fig. 6** shows repeating cycles of the fluorescence on/off switching of HBP-2 upon alternating irradiation with UV and visible light, which could be repeated more than 30 times without significant changes in the fluorescence intensity in the "on" and "off" states. It indicates

that HBP we prepared is promising for fluorescence switching materials with fatigue resistance in both photochromic and fluorescent dyes.



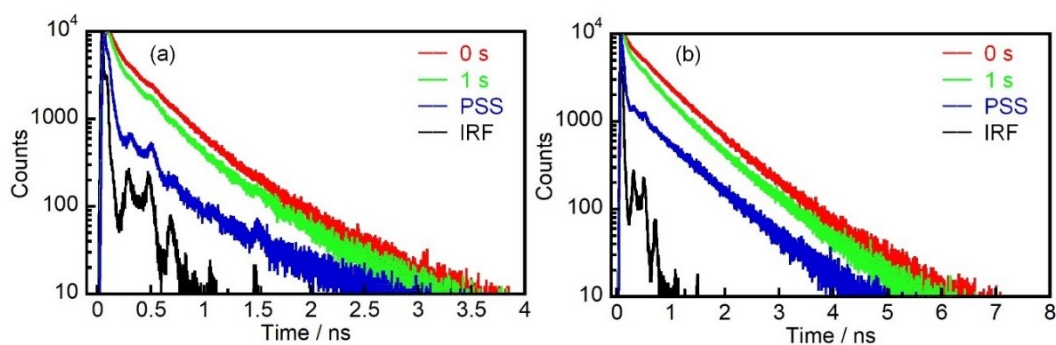
**Fig. 5.** Illustration of FL fluorescence quenching by one DE-c molecule in LP (left) and HBP-1 and 2 (right).



**Fig. 6.** Reversible fluorescence on/off switching of HBP-2 ( $1.3 \times 10^{-6}$  M for DE moiety) in THF upon alternating irradiation with 313 nm light ( $0.28 \text{ mW cm}^{-2}$ ) for 1 min and visible light ( $> 500 \text{ nm}$ ) for 3 min.

To further investigate the fluorescence properties of HBPs, the fluorescence decay curves of HBP-1 and HBP-2 were measured before irradiation (0 s), after 1 s of irradiation at 313 nm, and at the PSS, as shown in Fig. 7. The resulting decay times are summarized in Table 3. The decays were found to show multi-exponential behaviors. In our previous paper [12], we reported that FL-St has  $\tau$  of 0.75 ns with a single component, whereas poly(FL) shows two-

component decays with  $\tau$  of 0.32 (16%) and 1.1 ns (84%). Moreover, poly(DE'-co-FL) shows multi-component decays with  $\tau$  of 0.10 (59%), 0.43 (31%), 1.1 (7%), and 3.6 ns (2%), as shown in **Table S2**, where DE' represents a molecular structure different from DE in this study. Before photoirradiation, HBP-1 and HBP-2 have multi-component lifetimes similar to poly(DE'-co-FL) despite the different molecular structures of diarylethene. For both HBP-1 and HBP-2, the main decay-component of the FL moiety is around 0.5-1.3 ns. However, upon irradiation at 313 nm, very fast decay-times are observed, associated with large fractions of intensity. Indeed, for HBP-1 at the PSS, both  $\tau_1$  and  $\tau_2$  decay times (< 10 ps and 40 ps, respectively) represent 71% of the emission, whereas they were absent before irradiation (*cf.* **Table 3**). The fast lifetime components in the polymers are actually due to an energy transfer from the excited state of FL to neighboring DE-c moieties. This result confirms the presence of very fast FRET processes from FL fluorophores to DE-c units in the polymer systems. Such conclusions are confirmed for both HBP-1 and HBP-2, and fully compatible with the steady-state experiments detailed above.



**Fig. 7.** Fluorescence decay curves of HBP-1 (a) and HBP-2 (b) monitored at 430 nm.

**Table 3.** Fluorescence lifetimes, fluorescence quantum yields, and radiative and non-radiative rate constants in THF.

compound	Irradiation time / s <sup>a</sup>	$\tau_1$ / ns	$\tau_2$ / ns	$\tau_3$ / ns	$\tau_4$ / ns	$\tau_{ave}$ / ns <sup>b</sup>	$\chi^2$	$\Phi_f$	$k_f$ / ns <sup>-1</sup> <sup>c</sup>	$k_{nr}$ / ns <sup>-1</sup> <sup>d</sup>
HBP-1	0	0.06 (15%)	0.21 (55%)	0.58 (30%)	—	0.18	1.15	0.16	0.89	4.67
HBP-1	1	0.04 (21%)	0.17 (50%)	0.58 (30%)	—	0.11	1.20	—	—	—
HBP-1	PSS	<0.01 (50%)	0.04 (21%)	0.18 (12%)	0.79 (17%)	0.02	1.12	—	—	—
HBP-2	0	0.11 (10%)	0.51 (46%)	1.02 (44%)	—	0.45	1.16	0.14	0.31	1.91
HBP-2	1	0.03 (5%)	0.15 (18%)	0.55 (44%)	1.06 (33%)	0.22	1.08	—	—	—
HBP-2	PSS	<0.01 (27%)	0.09 (7%)	0.74 (54%)	1.26 (12%)	0.05	1.05	—	—	—

<sup>a</sup> Irradiation wavelength: 313 nm (0.28 mW cm<sup>-2</sup>).

<sup>b</sup> Average fluorescence lifetime:  $\tau_{ave} = \sum c_i \tau_i / \sum c_i$ .  $\tau_i$ : decay times.  $c_i$ : decay components expressed as  $c_i = a_i \tau_i / \sum a_j \tau_j$  where  $a_i$  are the pre-exponential factors.

<sup>c</sup>  $k_f = \Phi_f / \tau_{ave}$ .

<sup>d</sup>  $k_{nr} = (1 - \Phi_f) / \tau_{ave}$ .

## 4. Conclusion

We synthesized three kinds of hyperbranched polymers (HBP-0, HBP-1, and HBP-2), and investigated the fluorescence on/off switching behavior of the fluorene moiety accompanied by the photochromic reaction of diarylethene in the polymers. The fluorescence intensity of HBP-0 decreased linearly with increasing photocyclization conversion of the diarylethene. On the other hand, the fluorescence intensity of HBP-1 and HBP-2 significantly decreased in a non-linear fashion with increasing photocyclization conversion of the diarylethene. Interestingly, the fluorescence quenching ability of HBP-2 is higher than that of HBP-1 and a linear polymer (LP) consisting of fluorene and diarylethene derivatives. The number of FL quenched by one DE-c molecule per unit Förster's volume ( $n'/v$ ) increased with the following order: LP < HBP-1 < HBP-2. We have demonstrated the interest of the branched polymer structure and high branching degrees to improve the fluorescence switching efficiency because the  $n'/v$  value of HBP-2 is higher than those of HBP-1 and LP.

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Graphical Abstract

## Fluorescence Switchable Hyperbranched Polymer

