Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 6463–6468 **6463**
DOI: 10.1021/ma100792z

Poly(γ-glutamic acid) Hydrogels with Water-Sensitive Luminescence Derived from Aggregation-Induced Emission of *o*-Carborane

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Received April 12, 2010; Revised Manuscript Received July 2, 2010

ABSTRACT: We demonstrate the synthesis of a novel diglycidyl compound exhibiting aggregation-induced emission (AIE) derived from *o*-carborane, and employed it as a cross-linking reagent to prepare translucent hydrogels consisting of poly(γ-glutamic acid). Swelling ratio of the obtained hydrogels depended on the cross-linking density. Higher cross-linking density of the obtained hydrogels led to stronger emission in the swollen state, and finally the absolute quantum yield reached 0.10, which is directed to that of cross-linker with AIE in water dispersion ($\Phi_F = 0.19$). The luminescence character of lower cross-linked hydrogels was drastically influenced by the gel-shrinkage from the change of ionic strength. Furthermore, these hydrogels showed effective reversible fluorescence switching between the swollen and dried states.

Introduction

Luminescent organic molecules based on π-conjugated systems have been widely studied in the past decade because of their potential applications for organic light-emitting diodes (OLEDs), semiconductor lasers, and fluorescent sensors.[1] Additionally, organic materials with good solubility illustrate promising characteristics for solution-based fabrication, which is an attracting method for the simple and low-cost processing of large-area optoelectronic devices. Since these molecules are practically utilized in solid state such as thin films, many scientists have explored organic solids exhibiting intense emission with high absolute quantum yield.[2] However, the development of organic molecules demonstrating highly efficient solid-state luminescence is still challenging, because the emission from organic luminophores is susceptible to inherent aggregate formation leading to the concentration quenching.

Aggregation-induced emission (AIE), an intriguing phenomenon that nonemissive molecules in the solution state are induced to emit intensely by aggregate or film formation, has become one of the most efficient methods for the construction of solid-state luminescent materials without synthetic efforts and/or elaborate engineering controls, which are essential for chemical and physical approach to avoid the concentration quenching.[3] Recently, we have developed novel AIE system based on three-dimensional aromaticity of *o*-carborane, which is an icosahedral cage compound consisting of 10 boron atoms and 2 carbon atoms.[4] Therein, photoexcitation of π-electrons caused intramolecular charge transfer from electron-donating π-conjugated units to the antibonding orbital of C−C bond in *o*-carborane cage, and the variable C−C bond in *o*-carborane effectively quenches the fluorescence in the solution state.[5]

In order to control the AIE properties, a number of stimuli-responsive AIE systems have been presented until now. For example, Tang and co-workers showed excellent AIE systems responsible to chemicals, pressure, viscosity, and temperature.[6] In principle, the reduction of void or free volume surrounding the AIE-dye restricts the molecular motions giving rise to nonradiative decay, and thus enhances the emission intensity. On the basis of these findings, we focused on a hydrogel consisting of poly(γ-glutamic acid) (γ-PGA), which is a bioproduct secreted by a *Bacillus subtilis* strain.[7] The swelling property of hydrogels is sensitively affected by cross-linking degree or ionic strength, and with more importance, the motions of the swollen gel networks significantly differ from those of dried gel. Moreover, the combination of biodegradable gel and carborane can be attractive for biomedical applications such as HIV protease inhibitor or boron-neutron capture therapy (BNCT).[8] In this article, we designed a diglycidyloxy AIE-dye derived from *o*-carborane, which is connectable to the hydrogels consisting of γ-PGA. Note that the addition of water can quench the emission from AIE-dye in this system due to the increase of free volume or voids for the molecular motions of AIE-dye.

Experimental Section

Materials. γ-PGA (average molecular weight = 200 000−500 000) was purchased from Wako Pure Chemical Industries. Unless stated otherwise, all other reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) and triethylamine were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 1,2-Bis(4-bromophenyl)-ethyne[9] and 4-(*tert*-butoxycarbonyloxy)phenylacetylene[10] were synthesized and characterized according to the literature.

Measurements. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR measurements were recorded on a JEOL JNM-EX400 instrument. ^{1}H and ^{13}C NMR spectra used 0.05% tetramethylsilane (TMS) as an internal standard and ^{11}B NMR spectra were referenced externally to $BF_3 \cdot Et_2O$ at room temperature. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Fluorescence emission spectra and absolute quantum yield, measured by integrating sphere method, were recorded on a HORIBA JOBAN YVON Fluoromax-4 spectrofluorometer. FT-IR spectra were obtained on a Shimadzu IRPrestige-21 using KBr pellets. The viscosity was measured with a Thermo Haake Viscometer VT550.

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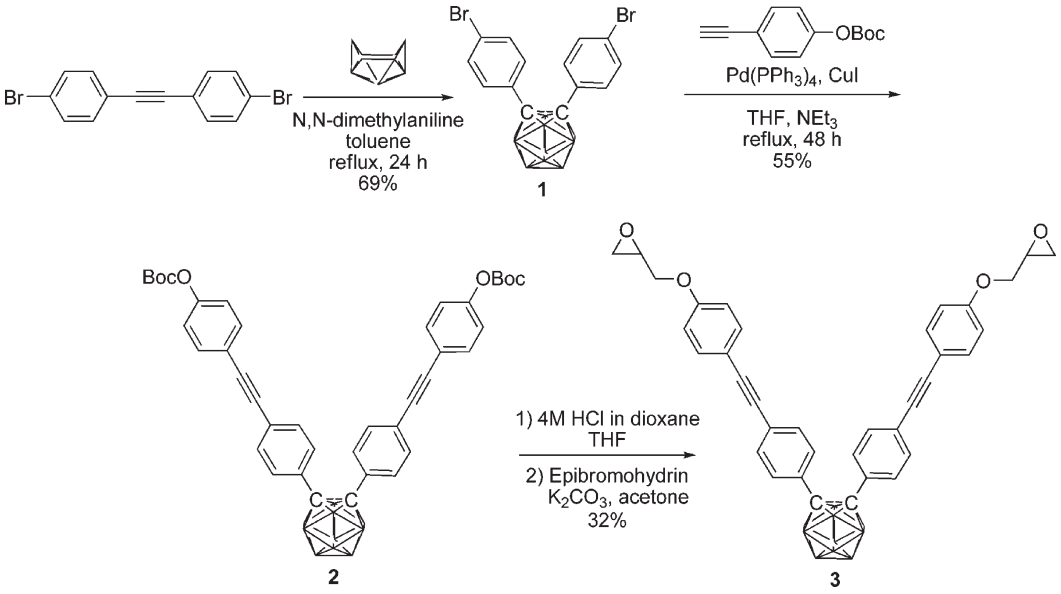
Published on Web 07/14/2010

Scheme 1. Synthetic Route for Diglycidyloxy Cross-Linker 3



Bis(4-bromophenyl)-*o*-carborane (1). 1,2-Bis(4-bromophenyl)ethyne (4.37 g, 13.0 mmol) and decaborane (1.82 g, 15.0 mmol) were dissolved in dry toluene (130 mL) at room temperature under Ar atmosphere. To the reaction mixture was added *N*,*N*-dimethylaniline (2.97 mL, 23.0 mmol), and the mixture was stirred at 120 °C for 24 h. After cooling down, the mixture was decanted from the solid residue and evaporated to dryness. The crude mixture was purified by silica gel column chromatography (hexane/$CHCl_3$ v/*v* = 9/1 as eluent). Recrystallization from chloroform and methanol provided **1** as a colorless crystal (4.05 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 (d, 4H, J = 9.26 Hz, Ar−*H*), 7.28 (d, 4H, J = 9.26 Hz, Ar−*H*). 3.70−1.63 (br, 10H, B-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.0, 131.7, 129.6, 125.4, 84.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −1.1, −2.2, −8.0, −8.8, −10.2, −11.7. HRMS (EI): calcd for $C_{14}H_{18}B_{10}Br_2$, *m*/*z* 454.0706; found, *m*/*z* 454.0705.

Bis(4-(4-(*tert*-butoxycarbonyloxy)phenylethynyl)phenyl)-*o*-carborane (2). Bis(4-bromophenyl)-*o*-carborane (**1**) (1.36 g, 3.0 mmol), 4-(*tert*-butoxycarbonyloxy)phenylacetylene (1.44 g, 6.6 mmol), $Pd(PPh_3)_4$ (175 mg, 0.15 mmol), and CuI (29 mg, 0.15 mmol) were placed in a 100 mL round-bottom flask equipped with a magnetic stirrer. The equipment was purged with Ar, followed by adding THF (30 mL) and triethylamine (15 mL). The reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was diluted with $CHCl_3$ and washed with aqueous NH_3 solution, water, and brine. The organic layer was dried over $MgSO_4$. Then, the solvent was removed and the crude mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 v/v = 1/2 as eluent) to provide **2** as a white solid (1.20 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47 (d, 4H, J = 8.77 Hz, Ar−*H*), 7.41 (d, 4H, J = 8.77 Hz, Ar−*H*), 7.29 (d, 4H, J = 8.77 Hz, Ar−*H*), 7.15 (d, 4H, J = 9.02 Hz, Ar−*H*), 3.77−1.79 (br, 10H, B−*H*). 1.55 (18H, s, −C*H*$_3$ (Boc)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 151.2, 132.8, 131.4, 130.5, 130.2, 125.5, 121.4, 120.0, 91.3, 87.9, 84.8, 83.9, 27.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −2.6, −10.3. HRMS (FAB): calcd for $C_{40}H_{44}B_{10}O_6$, *m*/*z* 730.4068; found, *m*/*z* 730.4072.

Bis(4-(4-glycidyloxyphenylethynyl)phenyl)-*o*-carborane (3). A solution of 4 M HCl in dioxane (20 mL) was added to the solution of **2** (1.45 g, 2.0 mmol) in THF (10 mL), and the mixture was refluxed for 3 h. After cooling, the reaction mixture was diluted with $CHCl_3$, and extracted with 1 M NaOH aq. The NaOH solution was then neutralized with dilute HCl in an ice bath. The white precipitate was collected and dried to obtain bis(4-(4-hydroxyphenylethynyl)phenyl)-*o*-carborane. Then, epibromohydrin (1.37 mL, 16.0 mmol) in acetone (2 mL) was added to the mixture of the product and potassium carbonate (1.29 g, 16.0 mmol), and the mixture was refluxed for 12 h. After cooling, the mixture was diluted with CH_2Cl_2, and filtered off, and the filtrate was washed with 1 M NaOH (aq), water, and brine. The solution was dried over $MgSO_4$, and the solvent was removed by rotary evaporator. The crude product was purified by column chromatography to give **4** as a white powder (410 mg, 32%). ^{1}H NMR: δ (ppm) 7.41 (d, 4H, J = 8.77 Hz), 7.39 (d, 8H, J = 8.53 Hz), 7.27 (d, 4H, J = 8.53 Hz), 6.87 (d, 4H, J = 8.77 Hz), 4.24 (dd, 2H, J = 10.96, 3.17 Hz), 3.59−1.75 (br, 10H), 3.94 (dd, 2H, J = 11.20 Hz, 5.60 Hz), 3.40−3.30 (m, 2H), 2.91 (t, 2H, J = 4.51 Hz), 2.75 (dd, 2H, J = 5.04, 2.52 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.8, 133.2, 131.2, 130.5, 129.9, 125.8, 115.2, 114.7, 92.1, 86.9, 85.0, 68.8, 50.0, 44.6. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −2.5, −10.0. HRMS (FAB): calcd for $C_{36}H_{36}B_{10}O_4$, *m*/*z* 642.3544; found, *m*/*z* 642.3563.

General Procedure for the γ-PGA Hydrogels. 3 was dissolved in DMF (1.0×10^{-2} M). γ-PGAs were successfully cross-linked with ethylene glycol diglycidyl ether (EGDE) by the following procedure, referred to the reported method by Endo et al.[11] $NaHCO_3$ (50 mol % with respect to the γ-PGA units) was added to a water dispersion (10 mL) of γ-PGA (1.29 g) to solve the polymer by neutralization. EGDE (2−200 mol % with respect to the γ-PGA units) and the solution of AIE-dye (0.1 mL) were added to the homogeneous solution. The solution was heated at 80 °C and kept for 2 h. After cooling down, the hydrogels were purified by immersion in distilled water for 24 h with 50 mol % of $NaHCO_3$ at room temperature to remove the unreacted compounds. The swollen gel was collected by gauze and freeze-dried at room temperature for 72 h to obtain a dry gel.

Swelling Measurements. A 500 mg of dry γ-PGA hydrogel was immersed in 1 L of distilled water, and the beaker covered with aluminum foil was allowed to stand for 24 h. The swollen gel was collected by gauze. After standing for 5 min, the weight of the residual swollen gel was measured. The swelling ratios of the hydrogels (Q) were calculated from the following equation:

$$Q = \frac{W_s - W_d}{W_d}$$

Here W_s is the weight of the equilibrium swollen hydrogel, and W_d is the weight of the dried hydrogel, respectively.

Results and Discussion

Scheme 1 outlines the synthetic route leading to diglycidyloxy cross-linker **3** containing bis(4-phenylethynyl)phenyl-*o*-carborane. Bis(4-bromophenyl)-*o*-carborane **1** was synthesized from 1,2-bis(4-bromophenyl)-ethyne by the addition reaction of decaborane. Then, bis(4-phenylethynyl)phenyl-*o*-carborane derivative **2** was obtained by Sonogashira−Hagihara coupling reaction between **1** and BOC-protected ethynylphenol. Treatment of **2** with 4 M HCl in dioxane resulted in deprotection of BOC groups, followed by Williamson ether synthesis with epibromohydrin gave the desired bis(4-glycidyloxyphenylethynyl)phenyl-*o*-carborane after the purification by flash chromatography. Figure 1 shows the ^{1}H NMR spectrum of **3**. The characteristic broaden peak at around 3.60−1.70 ppm was assigned to the presence of *o*-carborane structure, and the distinctive five peaks at around 4.30−2.70 ppm were assignable to the glycidyloxy groups. Additionally, ^{11}B NMR spectrum also showed the broad peaks at around −2.0 to −11.0 ppm, which were attributed to the boron atoms of *o*-carborane cage. From this result, the *o*-carborane structure is perfectly retained under the basic Williamson ether synthesis condition; i.e., **3** has expected structure with a cross-linker profile.

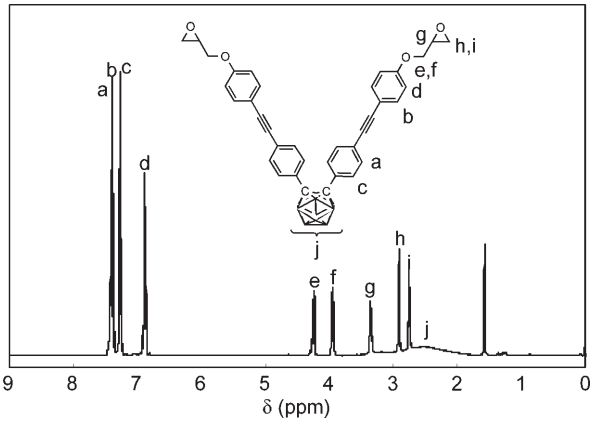


Figure 1. ^{1}H NMR spectrum of **3** in $CHCl_3$ at room temperature.

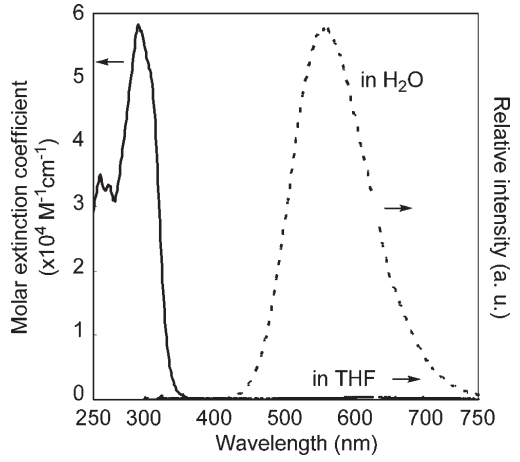


Figure 2. UV−vis and fluorescence spectra of **3** in THF (1.0×10^{-5} mol/L, solid line) and in the mixed solvent of THF/H_2O = 1/99 (v/v) (1.0×10^{-5} mol/L, dashed line).

Information for the optical properties of the cross-linker **3** was given by the UV−vis absorption and fluorescence measurements (Figure 2). In the UV−vis absorption spectrum, the absorption maximum was observed at 310 nm with high extinction coefficient ($\varepsilon_{\lambda_{max}}$ = 57900 M^{-1} cm^{-1}), corresponding to $\pi \rightarrow \pi^*$ transition of *p*-phenylene-ethynylene moieties. The cross-linker **3** exhibited yellow emission (absolute fluorescence quantum yield (Φ_F) = 0.19) at 551 nm with large Stokes shifts (241 nm) in the mixed solvent of THF/H_2O = 1/99 (dashed line), whereas no emission was observed in THF solution (Φ_F < 0.01). Analogously, alternating polymers with *o*-carborane and *p*-phenylene−ethynylene segments showed no luminescence in dissolved states and characteristic AIE behavior, presumably because of intramolecular charge transfer from electron-donating *p*-phenylene-ethynylene units to the antibonding orbital of C−C bond in *o*-carborane cage, which led to nonradiative quenching process due to the variable C−C bond.[4,5] These findings suggest that **3** having cross-linkable diglycidyloxy groups exhibits AIE property. Actually, **3** readily underwent the ring-opening reaction of two epoxides, and gave a diacetoxy compound **4** (see Supporting Information). Compound **4** also exhibited typical AIE property such as cross-linker **3**, representing that the ring-opening reaction caused no damage on the photoluminescence properties (Figure S1a). The fluorescence quantum yield of **4** displayed slower response to water fraction (Figure S1b), presumably due to the improvement of solubility in water.

Scheme 2 shows the cross-linking process of γ-PGA with EGDE as the cross-linker. Generally, γ-PGA is soluble in water (pH > 3). On the other hand, the addition reaction of carboxylate anion to epoxy group is inactive under a basic condition (pH > 7). Thus, the cross-linking reactions were carried out at pH = 4 water adjusted using $NaHCO_3$ (50 mol % with respect to the γ-PGA units). The AIE-dye **3** was dissolved in DMF (1.0×10^{-2} M), and 0.1 mL of the solution was added to a 100 times amount of water solution (10 mL) of γ-PGA. γ-PGAs were successfully cross-linked with ethylene glycol diglycidyl ether (EGDE) with 2 h stirring at 80 °C as previously reported by Endo et al.[11] Table 1 summarizes the results of cross-linking reaction with different ratio of cross-linker EGDE (2−200 mol % with respect to the γ-PGA units for **PGAOCB1**−**7**, i.e., [EGDE]/[**3**] = 2.0×10^2−2.0×10^4). Gel formation was observed with more than 5 mol % cross-linker ratio. After the freeze-drying stage described in the Experimental Section, the obtained hydrogels were immersed in deionized water for the measurements of swelling ratio and specific viscosity. Hydrogels with higher cross-linker content

Scheme 2. Cross-Linking Process of γ-PGA Hydrogel Using EGDE as a Cross-Linker

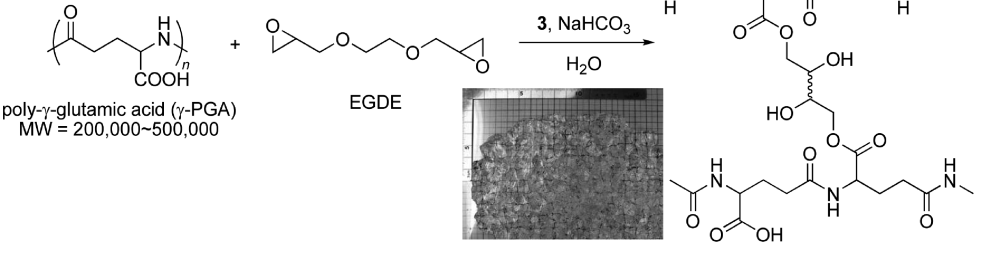


Table 1. Cross-Linking Results[a]

sample	EGDE/GA ratio (mol/mol)	gelation	Q[b] (g/g)	specific viscosity[c] (cP)
PGAOCB1	0.02	−		
PGAOCB2	0.05	○	280	900
PGAOCB3	0.10	○	170	1300
PGAOCB4	0.20	○	90	5400
PGAOCB5	0.50	○	20	41 700
PGAOCB6	1.00	○	17	
PGAOCB7	2.00	○	10	

[a] The initial concentration of **3** was 1.0×10^{-4} M. [b] Equilibrium swelling ratio of hydrogels in deionized water (100 mL per 50 mg of dry gel for 24 h). [c] Determined by a cone and plate viscometer at 25 °C.

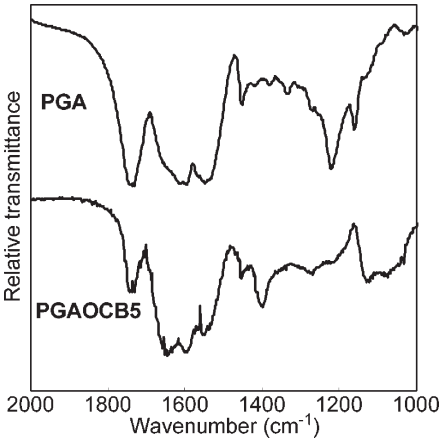


Figure 3. FT-IR spectra of γ-PGA and cross-linked γ-PGA (**PGAOCB5**) with EDGE.

exhibited lower value of Q as shown in Table 1. Furthermore, specific viscosities of swollen **PGAOCB2**−**5** measured by a cone and plate viscometer increased gradually with the amount of cross-linker, meaning the increase of cross-linking point in the hydrogel. Actually, addition of excess cross-linking reagent resulted in the formation of brittle hydrogels such as vegetable gelatin which were inadequate for the viscosity measurement.

The FT-IR spectra of γ-PGA were recorded before and after the cross-linking reaction using KBr pellets (Figure 3). The characteristic absorption band at 1730 cm^{-1} assignable to carboxylic acid diminished, and the bands at 1650 and 1400 cm^{-1}, which are attributed to carbonyl stretching of ester and carboxylate groups, respectively, increased upon the cross-linking reaction. This result clearly illustrates that the cross-linking reaction efficiently proceeded through the addition of carboxylate anion to epoxy groups.

Absolute fluorescence quantum yields of **PGAOCB2**−**7** in swollen state, and that of **3** in THF or mixed solvent of THF/H_2O = 1/99 (v/v) are shown in Figure 4. **PGAOCB2** exhibited higher fluorescence quantum yield (0.02) as compared to that of **3** in dissolved state in THF ($\Phi_F < 0.01$), suggesting that the hydrogel formation gave the enhancement of fluorescence quantum yields probably due to the existence of insoluble parts of **3** under the reaction condition. However, the addition of **3** to swollen gels consisting of γ-PGA and EGDE resulted in the comparable fluorescence quantum yield (0.20) to that of **3** in aggregated state (0.19) in the mixed solvent of THF/H_2O = 1/99 (v/v), indicating that covalent linkage of **3** to the hydrogel is responsible for the low fluorescence quantum yield of **PGAOCB2**−**4** (0.02) in the swollen state. Above 20 mol % of cross-linking reagent, the fluorescence quantum yields of the hydrogels (**PGAOCB5**−**7**) increased ($\Phi_F = 0.03 \rightarrow 0.11$) with rise of cross-linker content, while those of **PGAOCB2**−**4** were maintained constant at around 0.02. These results represent that increasing of cross-linking point

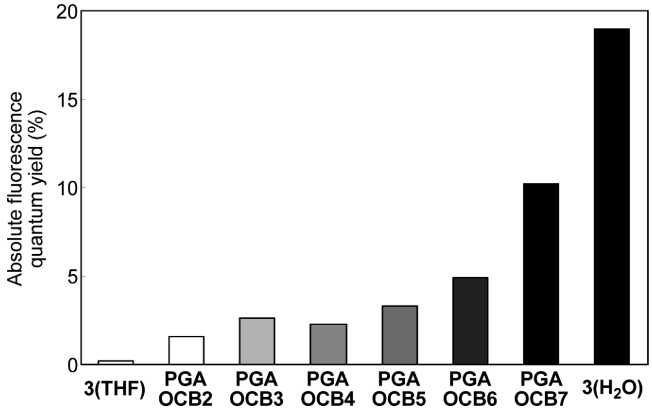


Figure 4. Absolute fluorescence quantum yields of hydrogels **PGAOCB1**−**7** in swollen state in deionized water, and the cross-linker **3** dissolved in THF (1.0×10^{-5} M) or mixed solvent of THF/H_2O = 1/99 (v/v) (1.0×10^{-5} M).

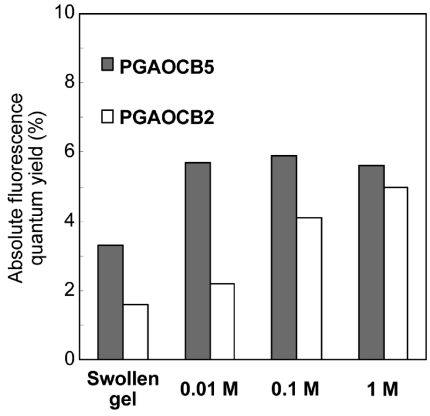


Figure 5. Absolute fluorescence quantum yields of **PGAOCB2** and **PGAOCB5** in NaCl solution (0.01, 0.1, 1.0 M). The swollen hydrogels were immersed in the salt solution for 1 h.

effectively limits the free volume to quench the emission from AIE-dye in the hydrogel with more than 20 mol % of cross-linker content. In other words, with less than 20 mol % of EGDE content, the fluorescence quantum yields are almost unrelated to the cross-linker content because of the enough free volume to quench the emission from AIE-dye.

Generally, the swelling ratio of hydrogels are dramatically dependent on the ionic strength of the medium.[7] Therefore, the fluorescence quantum yields of hydrogels (**PGAOCB2** and **PGAOCB5**, Figure 5) were measured by using NaCl (aq) with different concentration (0.01, 0.1, and 1.0 M). The hydrogel with higher cross-linking degree (**PGAOCB5**) showed slight rise of fluorescence quantum yield ($\Phi_F = 0.03 \rightarrow 0.06$) when the hydrogel was immersed in 0.01 M NaCl (aq). The fluorescence quantum yield was maintained constant with higher concentration of NaCl. On the other hand, the hydrogel with lower cross-linking degree (**PGAOCB2**) exhibited gradual increase of fluorescence quantum yield ($\Phi_F = 0.02 \rightarrow 0.05$) with rise of NaCl concentration. This finding reveals that the hydrogel with less cross-linking points is more susceptible to the ionic strength which is responsible for gel-shrinkage and subsequent AIE-enhancement.

Under the dry condition, these hydrogels showed intense emission as can be seen in water dispersion of **3**. Figure 6a illustrates the fluorescence quantum yields of the hydrogel **PGAOCB5** in swollen and dried states. The emission of AIE-dye was apparently recovered upon drying ($\Phi_F = 0.03 \rightarrow 0.39$), presumably due to the fixation of molecular motion of AIE-dye

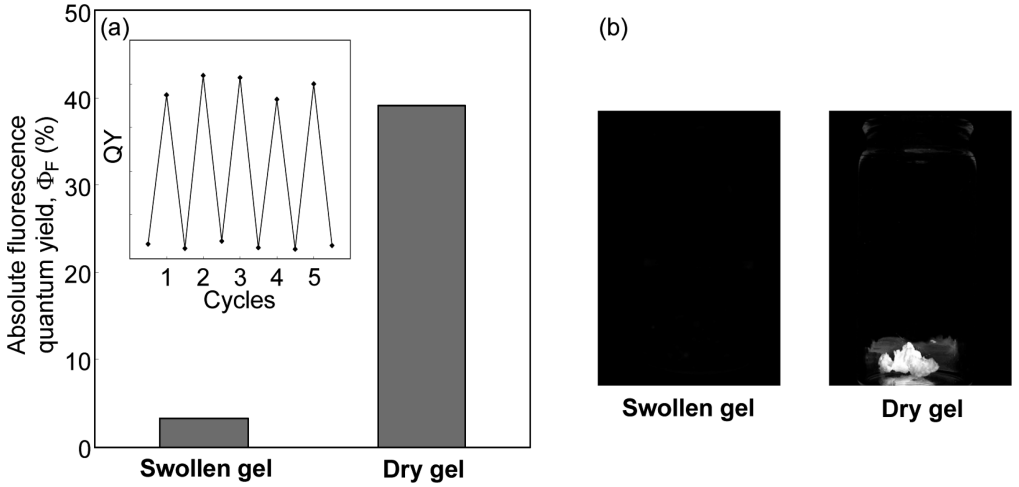


Figure 6. (a) Absolute fluorescence quantum yields of **PGAOCB5** in swollen and dry state. The inset shows the switching of absolute fluorescence quantum yields of **PGAOCB5** in swollen and dry state. (b) Photographs of **PGAOCB5** in swollen and dry state under UV lamp irradiation.

in the dried state. The inset of Figure 6a presents the reversible fluorescent cycles of **PGAOCB5** between swollen and dried condition. The optical switching of fluorescence can be repeated five times without any apparent fatigue and hysteresis. Additionally, the photographs of **PGAOCB5** can directly see the effective reversible decrease and increase of emission under UV irradiation on swollen and dried states, as shown in Figure 6b.

Conclusion

To summarize, we have successfully synthesized a novel diglycidyl compound exhibiting aggregation-induced emission (AIE) derived from *o*-carborane, and the incorporation of the AIE-dye into hydrogels consisting of poly-γ-glutamic acid was examined. With the higher cross-linking density, the hydrogels exhibited stronger emission in the swollen state, and finally the absolute quantum yield reached 0.10, which is dominated to that of AIE-dye in water dispersion ($\Phi_F = 0.19$). The luminescence property of lower cross-linked hydrogels were drastically influenced by the gel-shrinkage from the change of ionic strength. Furthermore, hydrogels containing the AIE-dye exhibited effective reversible fluorescence switching between the swollen and dried states. More research work is in progress to design an indicating system for water content by AIE phenomenon.

Acknowledgment. This study was supported by a Grant-in-Aid for JSPS Fellows (No. 09J01013) and Global COE Program "Integrated Materials Science", MEXT, Japan.

Supporting Information Available: Text detailing supplementary procedures for ring-opening reaction of compound **3** and optical properties of compound **4**, a scheme showing the ring-opening reaction of **3**, and a figure showing UV−vis and fluorescence spectra of **4** and dependence of quantum yields of **3** and **4** on solvent compositions. This material is available free of charge via the Internet at http://pubs.acs.org.

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