Korean J. Chem. Eng., 34(7), 2092-2095 (2017)
DOI: 10.1007/s11814-017-0083-4

pISSN: 0256-1115
eISSN: 1975-7220

Fabrication of sensory structure based on poly (ethylene glycol)-diacrylate hydrogel embedding polydiacetylene

Jin Hyuk Park* **and Dong June Ahn*,**,†**

*Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea
**KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Korea
(*Received 12 February 2017 • accepted 16 March 2017*)

Abstract−Hydrogel-based sensory structures were developed by embedding polydiacetylene supramolecules into poly-(ethylene glycol)-diacrylate (PEG-DA) to detect chemical gases and cyclodextrin and to determine pH values on the basis of a fluorescence change. We found the optimal condition for patterning-fabrication by controlling the volumetric mixture ratio of the water-soluble PEG-DA and aqueous polydiacetylene vesicle solution. Then, we determined that this hydrogel-based polydiacetylene structure optically responded selectively against vapor-phase targets: ammonia, ethanol, and aldehyde; aqueous solutions with various pH values; and cyclodextrin derivatives. These results could be extended to various label-free sensing applications of hydrogel-based chemo-biosensors.

Keywords: Hydrogel, PEG-DA, Polydiacetylene, Chemo-biosensor

INTRODUCTION

Hydrogels have been widely investigated due to their intriguing properties, namely, their hydrophilicity and biocompatibility [1,2]. They have an ability to absorb large amounts of water and have water content as a result of their three-dimensional network structure consisting of hydrophilic polymer chains. They are also responsive to various stimuli. Therefore, it is essential to fabricate patterned structures for application in biomedical or nanotechnology fields [3-6]. The photopolymerization of water-soluble polyethylene glycol (PEG) macromer, one of the hydrogels, provides stable and biocompatible gels [7-13]. A unique characteristic of PEG-diacrylate (PEG-DA) is that the photopolymerization is propagated by free radicals from the dissociation of the photoinitiator under UV irradiation of 365 nm. During the reaction, the PEG-DA prepolymer can undergo a cross-linking reaction and result in a network structure. Conjugated polydiacetylenes have attracted great interest as a component of sensors due to their bichromatic properties. These polymers are formed via a 1, 4-addition reaction upon exposure to UV light and undergo a transition from a blue, non-fluorescent form to a red, fluorescent form in response to structural changes induced by external stimuli. Therefore, functionalization of the surface of polydiacetylene with molecular receptors has been used to develop label-free biological/chemical sensors [14-25]. In this study, we combined the unique characteristics of polydiacetylene and hydrogels to fabricate new sensory structures by embedding polydiacetylene supramolecules into the PEG-DA hydrogel and realized the detection of three chemical gases (ammonia, ethanol, and formaldehyde) based on the optical and fluorescent changes of the polydiacetylene.

EXPERIMENTAL

1. Materials

PEG-DA (M_n:700), 2-hydroxy-2-methylpropiophenone as the photoinitiator, ammonia anhydrous (≥99.98%), ethanol (95%), formaldehyde solution (36.5-38%), α-cyclodextrin (≥98%), β-cyclodextrin (≥97%), and γ-cyclodextrin (≥98%) were purchased from Sigma-Aldrich. 10,12-Pentacosadiynoic acid (PCDA) and 6,8-heneicosadiynoic acid (HCDA), diacetylene derivatives, were purchased from GFS Chemicals.

2. Preparation of Diacetylene Vesicles

Standard methods were used to transform the diacetylene monomers to diacetylene vesicles in an aqueous solution [15,20]. Diacetylene monomers (PCDA and HCDA) were dissolved in chloroform and the solvent was evaporated by purging with nitrogen gas. Deionized water was then added to yield a total monomer concentration of 1 mM and the solution was hydrated at 80 °C for 15 min. The hydrated suspension was probe-sonicated (Fisher Scientific, Pittsburgh, PA, USA) for 15 min. Following sonication, the solution was filtered through a mixed cellulose ester (MCE) membrane with 0.8 μm pores to remove aggregated supramolecules and then stabilized at 4 °C overnight.

3. Fabrication of PEG-DA/Polydiacetylene Hydrogel

The diacetylene vesicle solution was polymerized by exposure to 254 nm UV light at an intensity of 1 mW/cm^2 for 10 min. The polydiacetylene vesicle solution was then mixed with the PEG-DA solution containing 2 vol% photoinitiator. The resultant solution was cast in a chamber (thickness: ca. 5 mm). Overhead projector (OHP) film was first covered on the chamber, and a soda lime glass-photomask then covered the OHP film. The solution was cross-linked by exposure to 365 nm UV light for 2 min. Finally, the pho-

†To whom correspondence should be addressed.
E-mail: ahn@korea.ac.kr
‡This article is dedicated to Prof. Ki-Pung Yoo on the occasion of his retirement from Sogang University.

tomask and OHP film were removed and the resultant hydrogel film was placed in deionized water and stored at room temperature.

4. Optical and Fluorescence Analysis of PEG-DA/Polydiacetylene Hydrogel

We analyzed the fluorescence emission of the PEG-DA/polydiacetylene hydrogel upon exposure to ammonia gas in a gas chamber. The concentration of ammonia gas was monitored using a Gastec standard detector tube system (GV-100 gas sampling pump, No. 3M ammonia detector tube, Gastec, Japan). An optical and fluorescence microscope (Olympus, BX51) equipped with a mercury lamp was used for capturing optical and fluorescence images of the hydrogels. Fluorescence images were captured after excitation by 510-550 nm waves. The filters used ranged from 590 nm-infrared waves. Quantitative fluorescence values were measured using Adobe Photoshop CS3.

RESULTS AND DISCUSSION

To optimize patterning fabrication, the optimal condition was found by controlling the volumetric mixing ratio between the PEG-DA and HCDA vesicle solution. PEG-DA/HCDA solutions (v/v ratio: 0.33/0.67, 0.25/0.75) were crosslinked and patterned, but red fluorescence was observed more strongly in the 0.33/0.67 solution than the 0.25/0.75 solution (Fig. 1(a) and (b), respectively). Interaction with a large amount of PEG-DA was enough to cause a color transition and expression of fluorescence of the HCDA vesicles. Thus, these samples could not be used for detecting chemicals. However, PEG-DA/HCDA solutions (v/v ratio: 0.20/0.80) were well crosslinked and patterned, and fluorescence signal was not expressed in Fig. 1(c) compared with earlier results (0.33/0.67 and 0.25/0.75 (v/v)). PEG-DA/HCDA solutions having water of 82 wt% (0.17/0.83 (v/v)) were unstably crosslinked in this experiment. Previous study has shown that gel fraction was drastically reduced when the water content of the polymerization mixture was greater than 80 wt% [13]. Therefore, the optimal mixing ratio of the PEG-DA/polydiacetylene vesicle solution was found to be 0.20/0.80 (v/v), and this ratio was used for the subsequent sensing experiments.

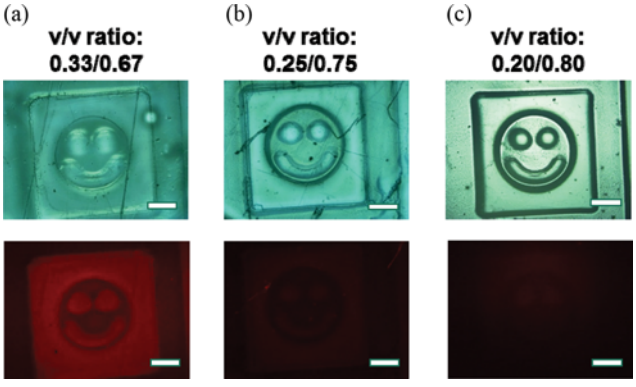

Fig. 1. Optical and fluorescence images of PEG-DA/HCDA hybrid hydrogel. The volumetric ratio of PEG-DA/HCDA was (a) 0.33/0.67, (b) 0.25/0.75, and (c) 0.20/0.80. The upper and lower images were captured using bright-field and fluorescence microscopy, respectively (Scale bar: 500 μm).

This hydrogel-based sensor system was applied to the detection of three chemical gases, namely, ammonia, ethanol, and formaldehyde, as shown in Fig. 2. The sensors were fabricated by using PCDA and HCDA vesicles. They were exposed to sufficient concentration of the gases over a sufficient duration (30 min). A high level of red fluorescence was selectively emitted on reaction with ammonia gas. PCDA and HCDA have carboxyl groups, so these materials could interact via ionic bonding with the amine group of ammonia. However, these could not interact with the hydroxyl group of ethanol and the aldehyde group of formaldehyde.

The fluorescence characteristics of the PEG-DA/polydiacetylene hydrogel sensor were analyzed according to the concentrations of ammonia gas, as shown in Fig. 3, after 30 min exposure. The fluorescence of the PEG-DA/PCDA hydrogel after exposure to ammonia gas with a concentration of 110 ppm was significantly lower, as shown in Fig. 3(a). In comparison, the fluorescence of the PEG-DA/HCDA hydrogel after exposure to ammonia gas with a concentration of 30 ppm, is shown in Fig. 3(b). Similarly, the quantitative fluorescence intensity of the PEG-DA/HCDA hydrogel was higher than that of the PEG-DA/PCDA hydrogel (Fig. 3(c)). Generally, less thermal energy is required to disturb the organized structure of polydiacetylene with shorter alkyl chains, while more thermal energy is required in the case of longer alkyl chains [26,27]. These results suggest that the interaction with ammonia results in the chemical modification of the diacetylene's head groups; however, there is insufficient energy to perturb the organized structure of

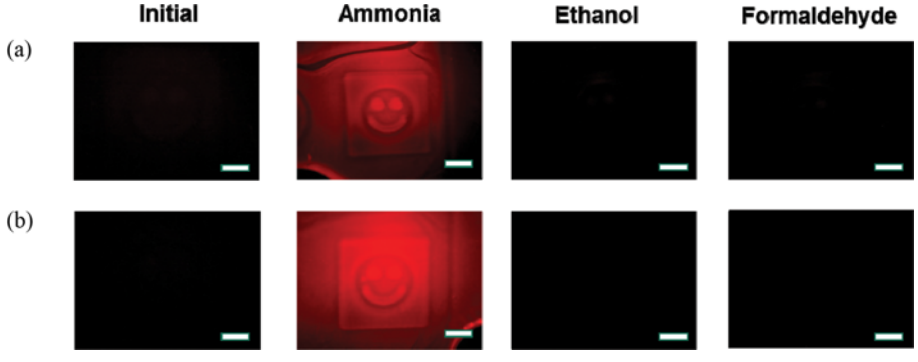

Fig. 2. Fluorescence images of (a) PEG-DA/PCDA and (b) PEG-DA/HCDA hybrid hydrogel. The volumetric ratio of PEG-DA/polydiacetylene was 0.2/0.8. These samples were exposed to ammonia, ethanol, and formaldehyde gases in a gas chamber (Scale bar: 500 μm).

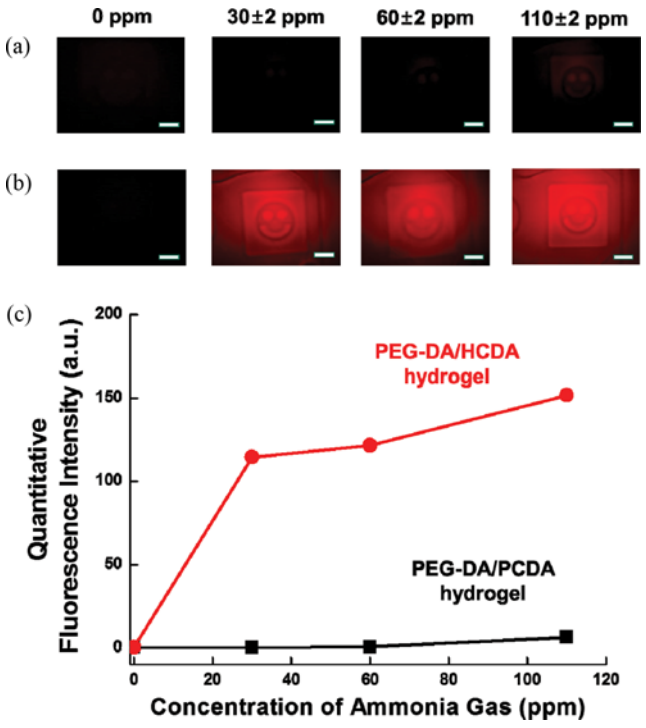

Fig. 3. Fluorescence images of (a) PEG-DA/PCDA and (b) PEG-DA/HCDA hybrid hydrogels after exposure to ammonia gas, and (c) quantitative fluorescence analysis results depending on the concentration of ammonia gas (Scale bar: 500 μm).

polydiacetylene as a result of the PCDA monomer having longer alkyl chains.

The PEG-DA/polydiacetylene hydrogel was exposed to aqueous solutions with various pH values for 30 min at room temperature. Fluorescence images are shown in Fig. S1. A highly alkaline solution (pH: 12) induced the fluorescence emission of PEG-DA/polydiacetylene hydrogel, as shown in Fig. 4. In particular, an aqueous solution with pH 11 induced the fluorescence emission of the more sensitive PEG-DA/HCDA hydrogel. Previous studies have established that the chromatic change upon adjusting the pH values can be attributed to the repulsive Coulombic interactions during surface ionization, which force adjacent chains apart and trigger a conformational change [28,29]. The acid-base properties of PCDA and HCDA vesicles are confirmed to be those expected for spatially confined interfacial carboxyl groups exhibiting attenuated acidity. In addition, the blue-to-red transition was related to the extent of deprotonation of the interfacial carboxyl groups, which accounts for the occurrence of the blue-to-red response triggered by the high pH range.

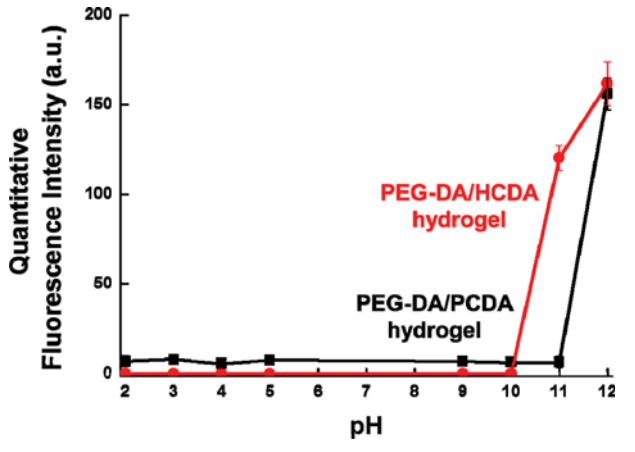

Fig. 4. Quantitative fluorescence analysis results for PEG-DA/PCDA (black line) and PEG-DA/HCDA (red line) hydrogels after exposure to aqueous solutions of various pH values.

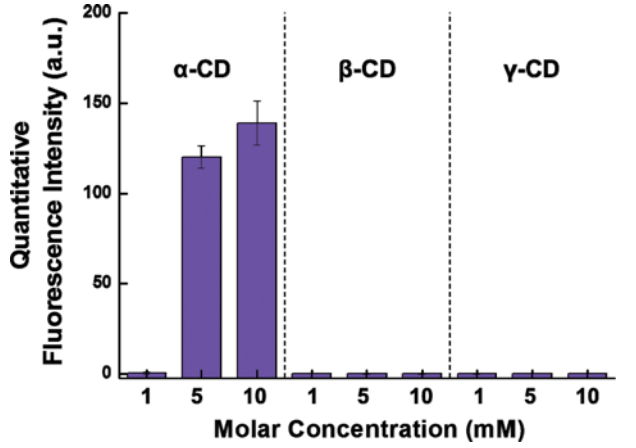

Fig. 5. Quantitative fluorescence analysis results for the PEG-DA/HCDA hydrogel after exposure to various concentration of α-, β-, and γ-cyclodextrin (CD).

Finally, the response of the PEG-DA/polydiacetylene hydrogel to the cyclodextrins (CD) was probed. PEG-DA/polydiacetylene hydrogels were transferred to petri-dishes containing aqueous solutions of α-, β-, and γ-CD. After being left for 2 h at room temperature, the hydrogels were analyzed by using a fluorescence microscope. As shown in Fig. 5, the quantitative fluorescence response established that the PEG-DA/HCDA hydrogel transferred and emitted a high fluorescence signal to solutions containing 5 and 10 mM of α-CD. Previous studies have shown that the inner and outer diameters of the CDs would play a critical role in perturbing the ordered structures of the polydiacetylene vesicles [16]. The approximate inner diameters of the CDs are 0.57, 0.78, and 0.95 nm for α-, β-, and γ-CDs, respectively, and α-CD is more capable of perturbing the ordered structures of the vesicles than β- or and γ-CD. Then PEG-DA/PCDA hydrogel also emitted fluorescence signal to a solution containing 10 mM of α-CD (Fig. S2).

CONCLUSIONS

PEG-DA hydrogels with embedded carboxyl group-functionalized polydiacetylene vesicles were developed and used to detect ammonia gas selectively. The PEG-DA/HCDA hydrogel was more sensitive than PEG-DA/PCDA hydrogel to external stimuli because the alkyl chain of HCDA is shorter than that of PCDA. This hydrogel sensor also exhibited a selective fluorescence change in a highly alkaline solution and aqueous solutions of α-CD. These results could be extended to various sensing applications of hydrogel-based

chemo- and bio-sensors.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation (MSIP 2014023305, MSIP 2015M3C1A3002152), Ministry of Trade, Industry and Energy (MOTIE 10033477-2012-21), and the Korea University Grant. This paper was submitted for dedication to professor Ki-Poong Yoo, Sogang University.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

REFERENCES

1. S. Nayak and L. A. Lyon, *Angew. Chem. Int. Ed.*, **44**, 7686 (2005).
2. N. A. Peppas, J. Z. Hilt, A. Khademhosseini and R. Langer, *Adv. Mater.*, **18**, 1345 (2006).
3. K. Y. Lee and D. J. Mooney, *Chem. Rev.*, **101**, 1869 (2001).
4. M. B. Mellott, K. Searcy and M. V. Pishko, *Biomaterials*, **22**, 929 (2001).
5. T. Schmidt, J. I. Mönch and K.-F. Arndt, *Macromol. Mater. Eng.*, **291**, 755 (2006).
6. T. A. Asoh, M. Matsusaki, T. Kaneko and M. Akashi, *Adv. Mater.*, **20**, 2080 (2008).
7. R. P. Witte, A. J. Blake, C. Palmer and W. J. Kao, *J. Biomed. Mater. Res.*, **71A**, 508 (2004).
8. M. S. Hahn, L. J. Taite, J. J. Moon, M. C. Rowland, K. A. Ruffino and J. L. West, *Biomaterials*, **27**, 2519 (2006).
9. M. S. Hahn, J. S. Miller and J. L. West, *Adv. Mater.*, **18**, 2679 (2006).
10. B. Cho, D. H. Kim, H. Lee and B. Na, *Korean J. Chem. Eng.*, **24**, 1037 (2007).
11. J. J. Moon, M. S. Hahn, I. Kim, B. A. Nsiah and J. L. West, *Tissue Eng. Part A*, **15**, 579 (2008).
12. Z. Sui, W. J. King and W. L. Murphy, *Adv. Funct. Mater.*, **18**, 1824 (2008).
13. Y. Wu, H. B. Park, T. Kai, B. D. Freeman and D. S. Kalika, *J. Membr. Sci.*, **347**, 197 (2010).
14. S. Y. Okada, R. Jelinek and D. Charych, *Angew. Chem. Int. Ed.*, **38**, 655 (1999).
15. H. Y. Shim, S. H. Lee, D. J. Ahn, K. Ahn and J.-M. Kim, *Mater. Sci. Eng. C*, **24**, 157 (2004).
16. J.-M. Kim, J. Lee, J. Lee, S. Woo and D. J. Ahn, *Macromol. Chem. Phys.*, **206**, 2299 (2005).
17. J.-M. Kim, Y. B. Lee, D. H. Yang, J. Lee, G. S. Lee and D. J. Ahn, *J. Am. Chem. Soc.*, **127**, 17580 (2005).
18. J.-M. Kim, S. K. Chae, Y. B. Lee, J. Lee, G. S. Lee, T. Kim and D. J. Ahn, *Chem. Lett.*, **35**, 560 (2006).
19. D. J. Ahn and J.-M. Kim, *Acc. Chem. Res.*, **41**, 805 (2008).
20. S. Park, G. S. Lee, C. Cui and D. J. Ahn, *Macromol. Res.*, **24**, 380 (2016).
21. J. Y. Hyun, G. S. Lee, T. Y. Kim and D. J. Ahn, *Korean J. Chem. Eng.*, **14**, 533 (1997).
22. E. K. Ji, D. J. Ahn and J.-M. Kim, *B. Korean. Chem. Soc.*, **24**, 667 (2003).
23. S. K. Kwak, G. S. Lee, D. J. Ahn and J. W. Choi, *Mat. Sci. Eng. C*, **24**, 151 (2004).
24. K. W. Kim, H. Choi, G. S. Lee, D. J. Ahn, M. Oh and J.-M. Kim, *Macromol. Res.*, **14**, 483 (2006).
25. K. W. Kim, H. Choi, G. S. Lee, D. J. Ahn and M. Oh, *Colloids Surface B*, **66**, 213 (2008).
26. N. Charoenthai, T. Pattanatornchai, S. Wacharasindhu, M. Sukwattanasinitt and R. Traiphol, *J. Colloid Interface Sci.*, **360**, 565 (2011).
27. H. Tachibana, N. Hosaka and Y. Tokura, *Polymer*, **42**, 8311 (2001).
28. S. J. Kew and E. A. H. Hall, *Anal. Chem.*, **78**, 2231 (2006).
29. D. L. Giokas and A. G. Vlessidis, *Anal. Chim. Acta.*, **683**, 156 (2011).

Supporting Information

Fabrication of sensory structure based on poly (ethylene glycol)-diacrylate hydrogel embedding polydiacetylene

Jin Hyuk Park* and Dong June Ahn*,,†**

*Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea
**KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Korea
(*Received 12 February 2017 • accepted 16 March 2017*)

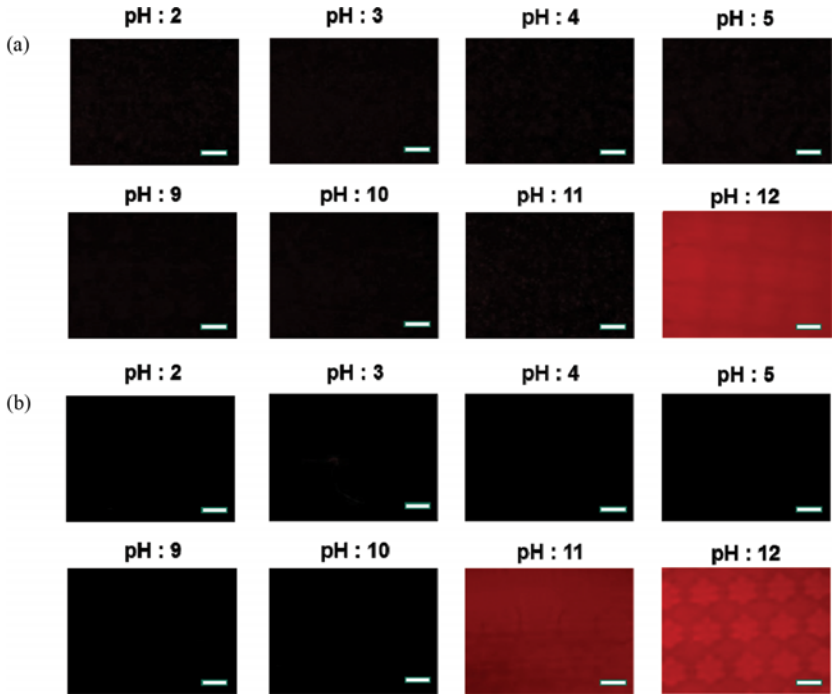

Fig. S1. Fluorescence images of (a) PEG-DA/PCDA and (b) PEG-DA/HCDA hybrid hydrogel after reaction with various pH of aqueous solution (Scale bar: 500 μm).

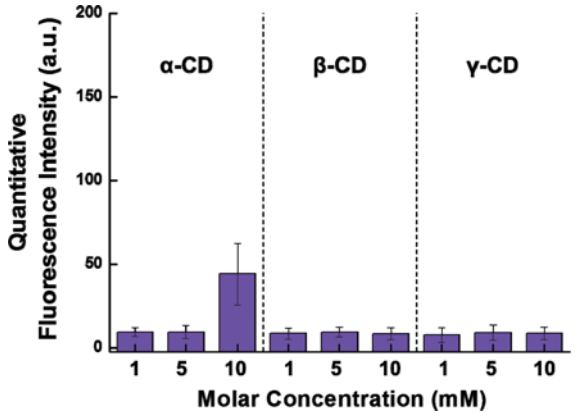

Fig. S2. Quantitative fluorescence analysis of PEG-DA/PCDA hydrogel after reaction with various concentration of α-, β-, and γ-cyclodextrin (CD).