Reactive & Functional Polymers 73 (2013) 451–456

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Fluorescence resonance energy transfer between polydiacetylene vesicles and embedded benzoxazole molecules for pH sensing

Seongwon Seo [a], Daigeun Kim [a], Geunseok Jang [a], Dong-Myung Kim [b], Dong Wook Kim [c], Bum-Kyoung Seo [d], Kune-Woo Lee [d], Taek Seung Lee [a,*]

[a] Organic and Optoelectronic Materials Laboratory, Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, South Korea
[b] Department of Fine Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 305-764, South Korea
[c] Division of Advanced Materials, Korea Research Institute of Chemical Technology, Daejeon 305-343, South Korea
[d] Decontamination and Decommissioning Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, South Korea

ARTICLE INFO

Article history:
Received 16 June 2012
Received in revised form 22 November 2012
Accepted 26 November 2012
Available online 3 December 2012

Keywords:
Polydiacetylene
FRET
Fluorescence
Encapsulation
pH sensor

ABSTRACT

A mixed polydiacetylenes (PDAs) vesicle with a phospholipid unit is functionalized by entrapping fluorescent benzoxazole (BZ) molecules inside the PDA vesicles. Upon photo-polymerization and heat-treatment of the self-assembled vesicles, a weak red fluorescence can be observed. Excitation of BZ molecules enables the amplification of PDA vesicle fluorescence resonance energy transfer (FRET) to more than four times that of the direct excitation of red-phase PDA vesicles. The backbone of the PDA vesicles act as energy acceptors, which absorb energy from embedded BZ donor molecules inside the PDA vesicle, which emit blue fluorescence. The amplified red emission from the PDA vesicle can be altered by pH changes in the aqueous solution and thus the PDA vesicle mixed with a phospholipid and entrapped molecules inside can be a promising candidate as a pH sensor.

1. Introduction

Sensors convert information of target objects into recognizable signals such as color, fluorescence, or electrical signals using chemical and biological elements, enable human determination through the generation of a signal [1]. Sensory systems are being applied and used in various fields, including medical diagnosis, pharmaceutical, food safety testing, drug analysis, and environmental monitoring.

Conjugated polymers have advantages of bringing about changes in conductivity, redox potential, and absorption or emission spectra, according to the changes in the environment [2]. Conjugated polymers with molecular recognition functionalities can bring about characteristic changes in the above properties by recognizing target materials, and hence, they can be utilized as sensory molecules. Compared to low molecular weight sensors, the notable advantage of conjugated polymer sensors is that they are able to amplify their optical signals. In conjugated polymer systems, the signal amplification phenomenon occurs even for low concentration of analytes, because the signals are delivered to the main chain of the conjugated polymers [3].

Among the variety of conjugated sensors, polydiacetylenes (PDAs) have gained special interest because of their ease of synthesis and convenient use [4]. PDAs are prepared by the photopolymerization of self-assembled diacetylene (DA) monomers. When the DA monomers are suitably organized and sufficiently close to each other, 1,4-addition polymerization occurs and PDA is produced by exposure to UV irradiation at 254 nm. Consequently, alternation of double and triple bonds can be observed in the main chain.

It is known that PDA forms a stable vesicle structure that has a double layer in aqueous solutions. Because chemical initiators or catalysts are not required during vesicle formation, additional purification step is not necessary after the synthesis [5]. Once PDA is prepared in aqueous solution, the color of the PDA-dispersed solution turns to blue with a maximum absorption wavelength around 640 nm. Under a variety of external stimuli, the blue-colored PDA solution turns into red with an absorption wavelength about 550 nm. However, the reason for the unique color change is not still clearly understood [4–6].

Utilizing this blue-to-red color transition of PDA vesicles, there have been several reports regarding the detection of various targets, such as external heat (thermochromism) [6a], organic solvent (solvatochromism) [6b], mechanical stress (mechanochromism) [6c], and ligand–receptor interactions (affinochromism or biochromism) [6d]. Among these, studies of ligand–receptor interactions have been pursued most actively, and the primary target molecules

* Corresponding author.
E-mail address: tslee@cnu.kr (T.S. Lee).

1381-5148/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.reactfunctpolym.2012.11.016

are influenza virus [7a], cholera (*Vibrio cholera*) [7b], *Escherichia coli* [7c], ssDNA [7d], glucose [7e], and cyclodextrin [7f].

In addition, PDA does not fluoresce when it is in the blue-phase, however, it shows a weak red fluorescence when in the red-phase [8]. In general, fluorescence turn-on systems such as PDA are very useful in sensing protocols, as detection based on the naked-eye is possible [8].

FRET is a phenomenon in which the fluorescence energy of the donor molecules is delivered to different fluorescent acceptor molecules, which are in close proximity. As such, the acceptor molecule emits amplified fluorescence signal [9]. Conjugated polymer-based biosensors with FRET are useful for the detection of biomaterials such as protein, DNA, and RNA, aboth in solution and on solid substrates [6d,10].

In this study, PDA vesicles were prepared with 10,12-pentacosadiynoic acid (PCDA) and 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC). BZ molecules have typically been physically entrapped inside the PDA vesicles by means of the double-layered vesicle formation in the presence of BZ molecules. FRET can be accomplished in this system utilizing PDA as an acceptor and the entrapped BZ molecule as a donor. DMPC as a phospholipid is introduced to play a role in pH-sensitive channels in conjugated PDA vesicles, disrupting the vesicle structure and inducing leakage of entrapped BZ molecules. Consequently, this will affect the FRET and changes in the fluorescence due to the greater distance between the donor and acceptor molecules. To our knowledge, the FRET phenomenon involving PDA vesicles and detection of pH change by FRET (with PDA) are here attempted for the first time.

2. Experimental

2.1. Reagents and characterization

PCDA, DMPC, 2-aminophenol, 2,4-diaminophenol dihydrochloride, 4-amino-2-hydroxybenzoic acid, 4-methylsalicylic acid, and polyphosphoric acid (PPA) were purchased from Sigma–Aldrich and were used without further purification. ^{1}H NMR spectra of the polymer were determined using a Bruker DRX-300 spectrometer (Korea Basic Science Institute). UV–vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Fluorescent spectra were measured using a Cary Eclipse spectrofluorometer (Varian).

2.2. Synthesis of 2-(2′-hydroxy-4′-methylphenyl)benzoxazole (BZ 1) [11]

2-Aminophenol (3.57 g, 32.7 mmol) and 4-methylsalicylic acid (4.97 g, 32.7 mmol) were mixed in PPA (150 mL) in a 1 L round-bottomed flask. The reaction mixture was heated to 150 °C and was then stirred for 12 h. The resulting mixture was cooled to room temperature and poured into ice-water with vigorous stirring. The solution was neutralized by adding sodium bicarbonate. The crude product was collected by filtration and was recrystallized in ethanol. Further purification was carried out with column chromatography using an ethyl acetate–toluene mixture as a mobile phase. After chromatography, the product was dried *in vacuo* (yield: 3.23 g, 45%); ^{1}H NMR (300 MHz, $CDCl_3$-d_6): δ = 11.45 (s, OH, 1H), 7.92 (d, Ar—H, 1H), 7.72 (m, Ar—H, 1H), 7.60 (m, Ar—H, 1H), 7.38 (m, Ar—H, 2H), 6.95 (s, Ar—H, 1H),6.84 (d, Ar—H, 1H), 1.56 (s, 3H).

2.3. Synthesis of 5-amino-2-(2′-hydroxy-4′-methylphenyl)benzoxazole (BZ 2) [12]

2,4-Diaminophenol dihydrochloride (6.43 g, 32.7 mmol) and 4-methylsalicylic acid (4.97 g, 32.7 mmol) were mixed in PPA (150 mL) in a 1 L round-bottomed flask. The reaction mixture was heated to 150 °C and was then stirred for 12 h. The resulting mixture was cooled to room temperature and poured into ice-water with vigorous stirring. The solution was neutralized by adding sodium bicarbonate. The crude product was collected by filtration and recrystallized in ethanol. Further purification was carried out with column chromatography using an ethyl acetate–toluene mixture as a mobile phase. After evaporation, the product was dried *in vacuo* (yield: 2.03 g, 26%); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.31 (s, OH, 1H), 7.94 (s, Ar—H, 1H), 6.92 (d, Ar—H, 1H), 6.90 (d, Ar—H, 1H), 6.85 (d, Ar—H, 2H), 6.67 (d, Ar—H, 1H), 4.52 (s, NH, 2H), 2.35 (s, 3H).

2.4. Synthesis of 5-amino-2-(2′-hydroxy-4′-aminophenyl)benzoxazole (BZ 3) [13]

2,4-Diaminophenol dihydrochloride (6.43 g, 32.7 mmol) and 4-amino-2-hydroxybenzoic acid (5.01 g, 32.7 mmol) were mixed in PPA (150 mL) in a 1 L round-bottomed flask. The reaction mixture was heated to 150 °C and was stirred for 12 h. The resulting mixture was cooled to room temperature and poured into ice-water with vigorous stirring. The solution was neutralized by adding sodium bicarbonate. The crude product was collected by filtration and was recrystallized in ethanol. Further purification was carried out with column chromatography using an ethyl acetate–toluene mixture as a mobile phase. After evaporation, the product was dried *in vacuo* (yield: 4.53 g, 37%); ^{1}H NMR (300 MHz, $CDCl_3$-d_6): δ = 11.48 (s, OH, 1H), 7.86 (d, Ar—H, 1H), 7.46 (d, Ar—H, 1H), 6.98 (d, Ar—H, 1H), 6.93 (s, Ar—H, 1H), 6.81 (d, Ar—H, 1H), 6.71 (d, Ar—H, 1H), 3.76 (s, NH, 2H), 1.65 (s, NH, 2H).

2.5. Preparation of vesicles

A mixture of PCDA and DMPC were dissolved in chloroform in a test tube. The solvent was evaporated by a stream of nitrogen gas and deionized water was added to the test tube in order to achieve the desired concentration of DMPC. The resultant suspension was probe-sonicated (Cole-Parmer GEX-130) at 80 °C. After sonication, the solution was filtered with a syringe filter (0.8 μm) to remove dispersed DMPC aggregates and was stored at 4 °C overnight. Polymerization of diacetylene vesicles was performed under UV irradiation at 254 nm for 30 min. To obtain red-phase PDA, blue-phase PDA was heated to 70 °C for 10 min.

3. Results and discussion

It has been documented that a fast response time toward external-stimuli can be obtained in the presence of phospholipid in PDA vesicles [14]. Therefore, PCDA vesicles with various compositions of PCDA as a backbone and DMPC as a phospholipid were prepared as illustrated in Table 1. The chemical structures of the PCDA and DMPC used are shown in Fig. 1. General procedures were employed to convert the diacetylene and phospholipid monomers into PDA with BZ dyes in aqueous solution. The size of the PDA vesicle was determined with Dynamic Light Scattering (DLS) and found

Table 1
Feed ratios and amounts of PCDA and DMPC for PDA vesicles.

Entry	PCDA:DMPC	PCDA	DMPC
1	10:0	0.0039 g (10.04 μmol)	0
2	9:1	0.0035 g (9.01 μmol)	0.0007 g (1.03 μmol)
3	8:2	0.0031 g (7.98 μmol)	0.0014 g (2.06 μmol)
4	7:3	0.0027 g (6.94 μmol)	0.0021 g (3.10 μmol)

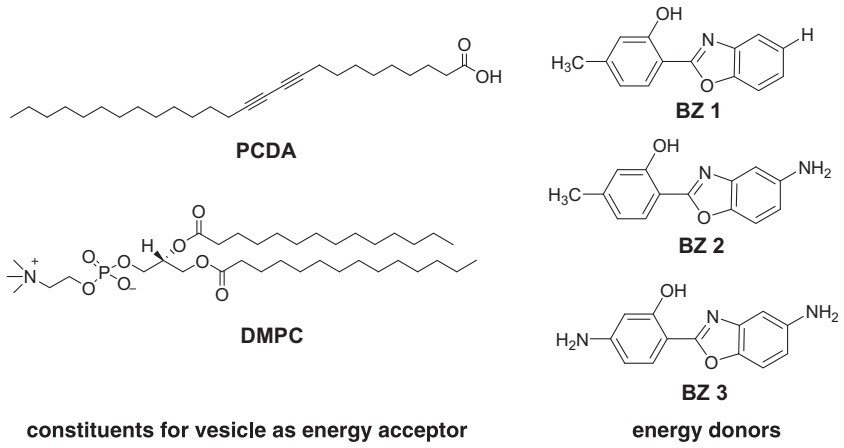


Fig. 1. Chemical structures of PCDA, DMPC, BZ 1, BZ 2, and BZ 3.

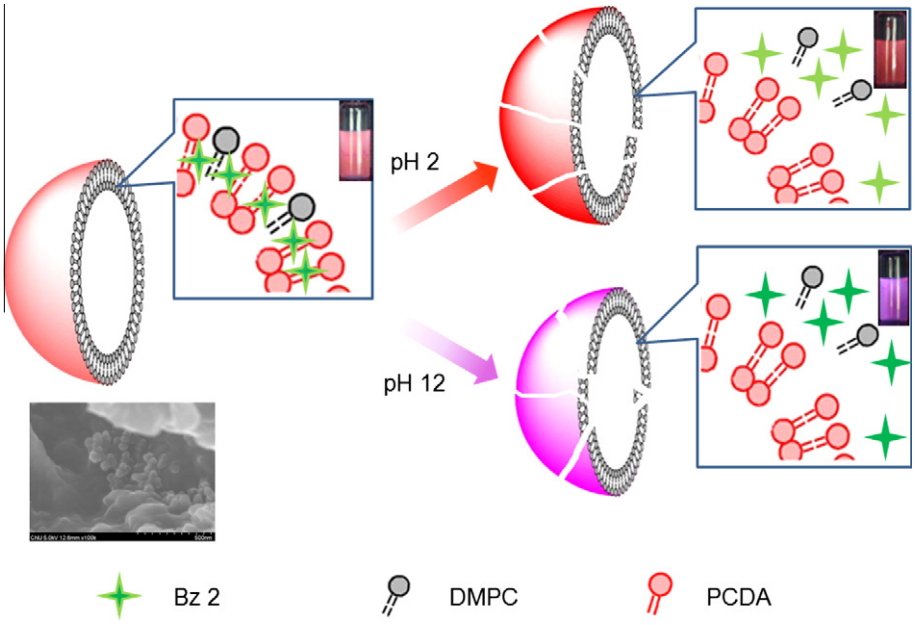
to be 136 nm. The SEM image of the vesicle can be seen in the inset photograph of Scheme 1.

The red-phase PDA is generally known to have weak red fluorescence. In order to amplify this, FRET can be applied to generate a strong red fluorescence by encapsulating a donor molecule inside the acceptor PDA vesicles composed of PCDA and DMPC, inducing FRET between the donor and acceptor molecules. The energy-donating, BZ-based molecules which would be entrapped inside the vesicle were synthesized according to published methods [11–13], and their chemical structures were confirmed with ^{1}H NMR and their structures are illustrated in Fig. 1. UV–vis and fluorescence spectra of the BZ 1, BZ 2 and BZ 3 are shown in Fig. 2.

Two requirements should be satisfied to attain FRET. Firstly, the donor and acceptor molecules should be in close proximity (~10 nm), and secondly, the emission of the donor molecules and absorption of the acceptor molecule should have good overlap. The emission wavelengths of the donors, BZ 1, BZ 2 and BZ 3, were 484, 474, and 497 nm, respectively, and are in suitable overlap with the absorption wavelengths (500 nm and 543 nm) of the PDA vesicles, which were used as acceptors as shown in Fig. 2b.

Fig. 3 shows the emission changes in blue- and red-phase PDA vesicles with various ratios of PCDA and DMPC, which are loaded with BZ 2 inside the PDA vesicles. Gradual increases in the intensity of emission bands at the long wavelength region (550–700 nm) can be observed, in accordance with an increase in the contents of DMPC in the PDA vesicles at the same concentration of BZ 2 (Fig. 3a–d). In the case of the PDA vesicles composed of 100% PCDA (entry 1), the conjugation length will be extended without interruption by DMPC. As a consequence, it should be noted that the intensity of fluorescence at 650 nm is greater than that at 580 nm (Fig. 3a). In the case of entry 4 (70% PCDA), the conjugation length becomes shortened because of the presence of 30% DMPC. DMPC in the PDA vesicles affects the effective conjugation length of PDA. In addition, emission bands of the PDA vesicles were blue-shifted to 436 nm and 445 nm in Fig. 3c and d compared to the emission band of BZ 2 in chloroform (467 nm, Fig. 2b), presumably due to limited rotation of the phenol ring inside the vesicles [13]. Since the emission band of BZ 2 was not observed in Fig. 3a and b, it is presumed that the disappearance of the emission band of BZ 2 resulted from the tightly and covalently bonded diacetylene units in the vesicles.

The PDA vesicles (entry 2, PCDA:DMPC = 9:1) were prepared to investigate the changes in the fluorescence according to the concentrations and kinds of molecules loaded (Fig. 4). In the cases of



Scheme 1. Working principles of FRET change by pH changes.

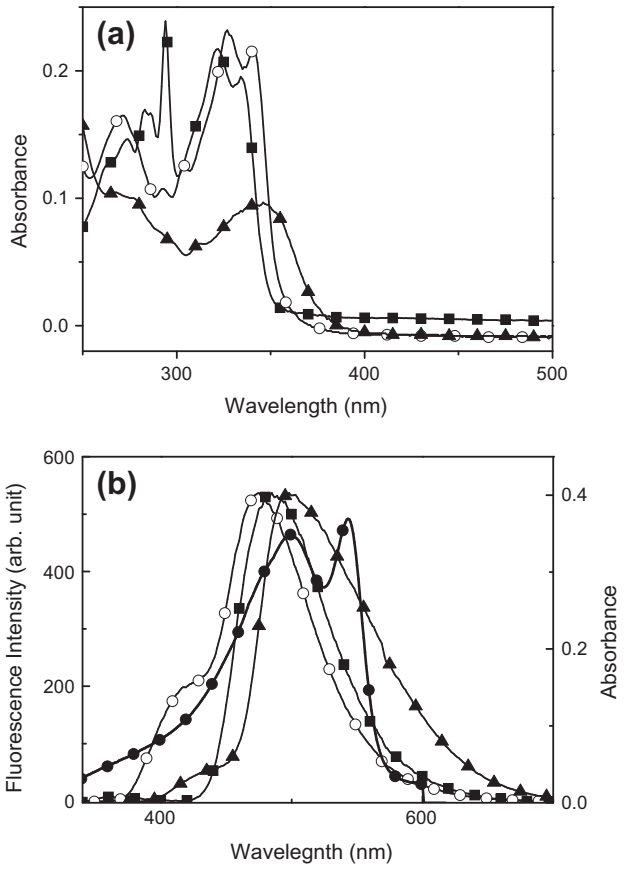


Fig. 2. (a) Absorption and (b) the normalized fluorescence spectra of BZ 1 (■), BZ 2 (○), and BZ 3 (▲) in chloroform; ●: absorption spectrum of red-phase PDA vesicles in deionized water; [BZ 1] = [BZ 2] = [BZ 3] = 1×10^{-4} M; excitation wavelength 350 nm.

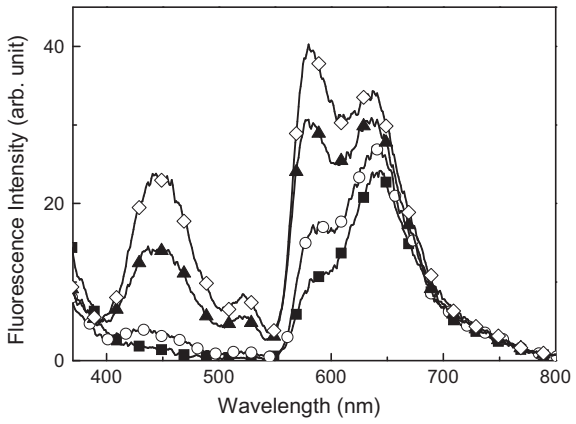


Fig. 3. Fluorescence spectra of PDA vesicles according to the feed ratio of PCDA to DMPC in aqueous solution (entrapped with BZ 2); PCDA: DMPC: (a) 10:0 (■), (b) 9:1 (○), (c) 8:2 (▲), and (d) 7:3 (◇); excitation wavelength 350 nm.

BZ 1 and BZ 2, increase in the red emission from the PDA vesicles, and increase in blue emission from BZ molecules, can be clearly observed as the concentration of BZ molecules increased. Furthermore, the intensity of the shorter wavelength emission at 581 nm increases noticeably compared to the longer wavelength emission at 632 nm. In the case of BZ 3 (which is more hydrophilic because of the presence of two amino groups), only the intensity at the longer wavelength (637 nm) increases. More hydrophilic molecules such as BZ 3 can penetrate the double-layers of the vesicles. Less hydrophilic molecules, however, such as BZ 1 and BZ 2 move to the middle of the hydrophobic layers, and thus, emit blue and shorter red emissions. Based on this, it can be concluded that the hydrophilicity of entrapped molecules has a great influence on the emission properties of the vesicles.

The FRET efficiency was calculated according to the following equation [15]:

$$E = 1 - F_{DA}/F_D$$

where F_{DA} and F_D are the integrals of the fluorescence in the presence and absence of donor BZ molecules, respectively. The

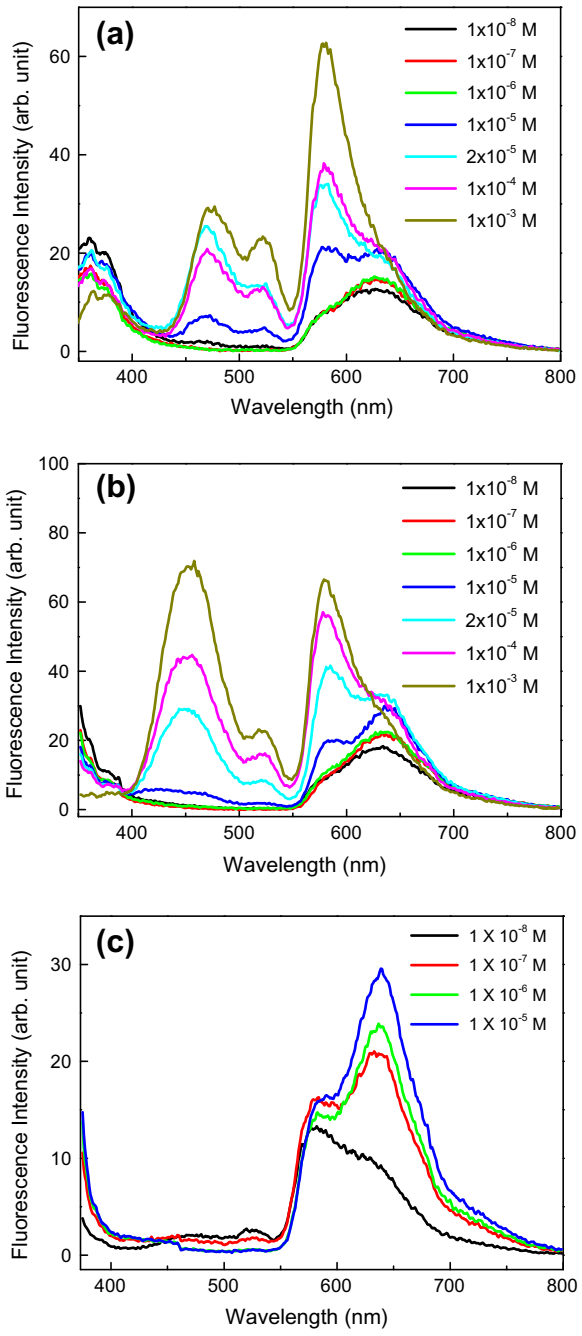


Fig. 4. Fluorescence spectra of red-phase PDA vesicles (entry 3, PCDA:DMPC = 8:2) according to concentrations and kinds of BZ in aqueous solution: (a) BZ 1, λ_{ex} = 322 nm, (b) BZ 2, λ_{ex} = 350 nm, and (c) BZ 3, λ_{ex} = 362 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

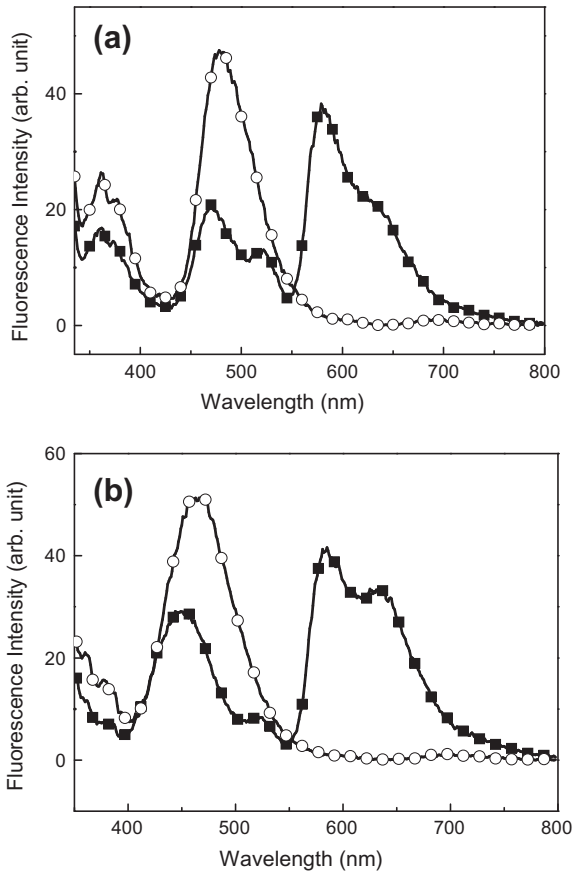


Fig. 5. Fluorescence change of PDA vesicles (PCDA:DMPC = 8:2) by FRET from: (a) [BZ 1] = 1×10^{-4} M, λ_{ex} = 322 nm and (b) [BZ 2] = 2×10^{-5} M, λ_{ex} = 350 nm (■: red-phase PDA; ○: blue-phase PDA).

optimized concentrations of BZ 1 and BZ 2 are found to be 1×10^{-4} M and 2×10^{-5} M, respectively. As a result, the FRET efficiencies were calculated to be 55.6% and 45.7% for BZ 1 and BZ 2, respectively (Fig. 5).

The intensity of red fluorescence of PDA vesicles via energy transfer from BZ 2 (excitation at 350 nm) can be amplified to more than four times that of direct excitation at 500 nm, as shown in Fig. 6a. Considering this large amplification in intensity, it can be confirmed that the FRET occurred from the donor molecule BZ 2 to the acceptor species of red-phase PDA vesicles, as clearly seen in Fig. 6b. The FRET phenomenon cannot be observed unless the phospholipid DMPC is used. That is, energy transfer is not facilitated when PDA vesicles composed of 100% PCDA (entry 1) are used. It can be thought that the DMPC in the vesicles act like a channel for excitation energy to activate BZ molecules.

In addition, the changes in emission of PDA vesicles (PCDA:DMPC = 8:2, entry 3) were observed under pH change as shown in Fig. 7. There were negligible changes in the fluorescence between pH 4 and 10, while considerable changes in emission were observed at strong acidic and strong basic conditions. This is attributed to the facts that depending on both destruction of the vesicle structure and the molecular characteristics of the BZ 2 loaded inside, the pH significantly affects the fluorescence intensity of the donor (BZ 2). At pH 2, intramolecular tautomerism is prevented in BZ 2, and as a result, the fluorescence is considerably quenched. The decrease in donor fluorescence causes a subsequent decrease in acceptor fluorescence and, thus, amplified, red fluorescence is weakened. In contrast, at pH 12, it can be seen that the blue fluorescence increases remarkably, presumably due to spontaneous tautomerism. Thus, the increase in donor fluorescence

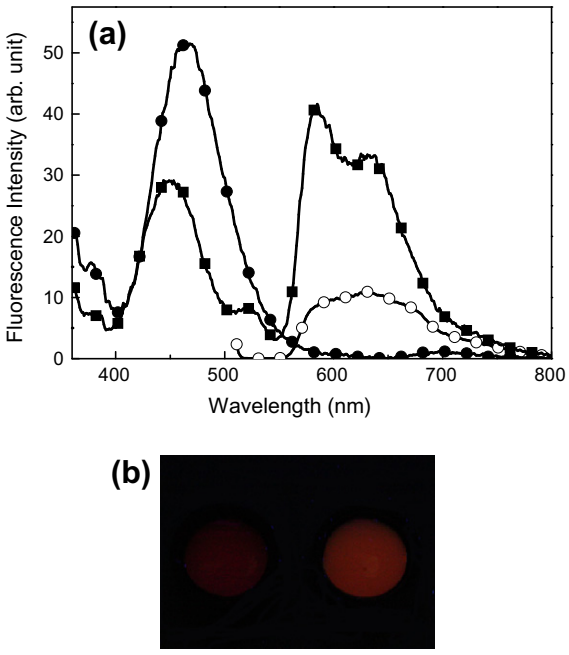


Fig. 6. (a) Fluorescence intensity change of PDA vesicles (PCDA:DMPC = 8:2) via FRET from BZ 2 to PDA (○: red-phase PDA with excitation wavelength 500 nm; ■: red-phase PDA with excitation wavelength 350 nm; ●: blue-phase PDA with excitation wavelength 350 nm, (b) photographs of red-phase PDA under different excitation wavelength (left: λ_{ex} = 500 nm; right: λ_{ex} = 350 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

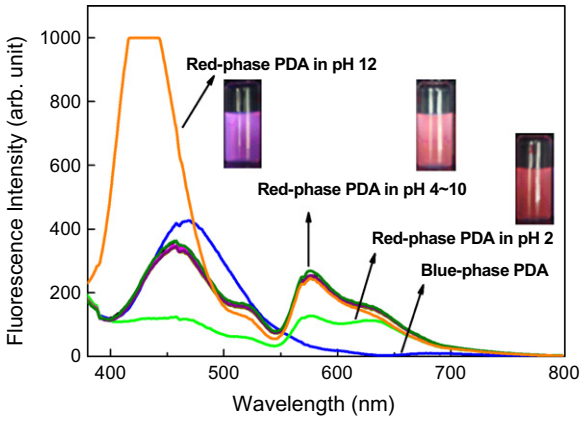


Fig. 7. Emission intensity change of blue- and red-phase PDA vesicles (PCDA:DMPC = 8:2) under various pH in aqueous solution (excitation wavelength 350 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

causes an increase in acceptor fluorescence, as illustrated in Scheme 1. However, because part of DMPC in the vesicle is locally destroyed due to the high pH, the efficiency of FRET is dramatically reduced [16]. In contrast, for PDA vesicles composed of PCDA alone (entry 1), the fluorescence spectrum remained almost unchanged, demonstrating that the presence of DMPC is essential for emission change under various pH (data not shown here).

As shown in the TEM images, the destruction of the vesicle structure and formation of aggregation can be observed in Fig. 8 with increase in the size measured by DLS (136 nm in pH 7; 7215 nm in pH 2; 1875 nm in pH 12). It can be concluded that the vesicles are extremely unstable in high and low pH with

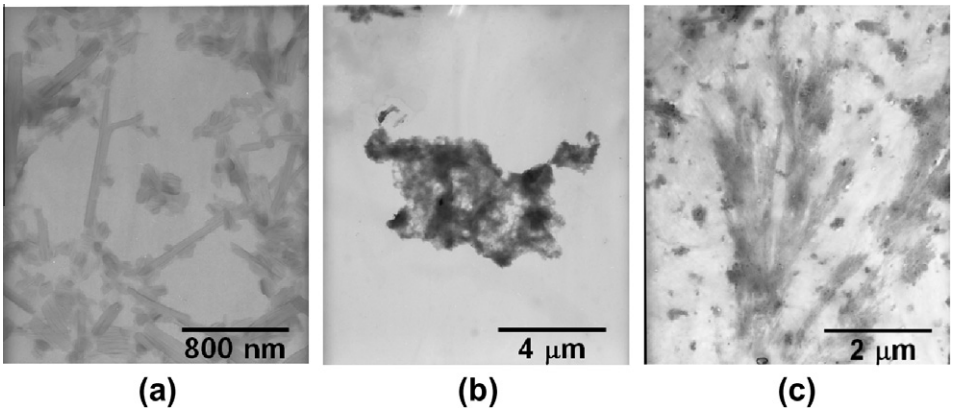


Fig. 8. TEM images of the red-phase PDA vesicles (PCDA:DMPC = 8:2) under: (a) pH 7 (size 136 nm with DLS), (b) pH 2 (7215 nm), and (c) pH 12 (1875 nm) in aqueous solution.

destruction of the vesicle structure, exuding BZ molecules into the solution.

4. Conclusion

We have prepared PDA vesicles comprising PCDA and DMPC monomers. Three kinds of BZ molecules with different hydrophilicity were synthesized to be entrapped inside the vesicles. The emission of BZ molecules (the donors) has a suitable overlap with the absorption of PDA vesicles (the acceptors), which is an essential requirement for FRET. The PDA vesicles containing BZ molecules showed FRET with 45–55% efficiency, depending on the structure of the BZ molecules. It was found that DMPC played an important role as a phospholipid, in transporting the excitation energy from donor to acceptor molecules. FRET can be modulated via variation in pH, and thus, this system can be used for sensing the pH of solutions.

Acknowledgment

This work was supported by the Ministry of Education, Science and Technology (MEST) of the Republic of Korea under the Nuclear R&D Project and Human Resource Training Project for Regional Innovation (2012H1B8A2025978).

References

[1] (a) S. Okada, S. Peng, W. Spevak, D.H. Charych, Acc. Chem. Res. 31 (1998) 229–239;
(b) B. Wang, M.R. Wasielewski, J. Am. Chem. Soc. 119 (1997) 12–21.
[2] (a) A. Ojida, Y. Miyahara, J. Wongkongkatep, S. Tamaru, K. Sada, I. Hamachi, Chem. -Asian J. 1 (2006) 555–563;
(b) H.A. Ho, M. Leclerc, J. Am. Chem. Soc. 125 (2003) 4412–4413.
[3] (a) D.T. McQuade, A.H. Hegedus, T.M. Swager, J. Am. Chem. Soc. 122 (2000) 12389–12390;
(b) S.W. Thomas III, G.D. Joly, T.M. Swager, Chem. Rev. 107 (2007) 1339–1386;
(c) T.M. Swager, Acc. Chem. Res. 31 (1998) 201–207;
(d) U.H.F. Bunz, Chem. Rev. 100 (2000) 1605–1644.
[4] (a) R. Jelinek, S. Kolusheva, Biotechnol. Adv. 19 (2001) 109–118;
(b) H. Bader, H. Ringsdorf, J. Skura, Angew. Chem. Int. Ed. Engl. 20 (1981) 91–92;
(c) R.R. Chance, Macromolecules 13 (1980) 396–398.
[5] E.-K. Ji, D.J. Ahn, J.-M. Kim, Bull. Korean Chem. Soc. 24 (2003) 667–670.
[6] (a) A. Singh, R.B. Thompson, J.M. Schnur, J. Am. Chem. Soc. 108 (1986) 2785–2787;
(b) J. Yoon, S.K. Chae, J.-M. Kim, J. Am. Chem. Soc. 129 (2007) 3038–3039;
(c) R.A. Nallicheri, M.F. Rubner, Macromolecules 24 (1991) 517–525;
(d) D.H. Charych, J.O. Nagy, W. Spevak, M.D. Bednarski, Science 261 (1993) 585–588;
(e) D.H. Kang, H.-S. Jung, J. Lee, S. Seo, J. Kim, K. Kim, K.-Y. Suh, Langmuir 28 (2012) 7551–7556.
[7] (a) A. Reichert, J.O. Nagy, W. Spevak, D. Charych, J. Am. Chem. Soc. 117 (1995) 829–830;
(b) J.J. Pan, D. Charych, Langmuir 13 (1997) 1365–1367;
(c) Z. Ma, J. Li, M. Liu, J. Cao, Z. Zou, J. Tu, L. Jiang, J. Am. Chem. Soc. 120 (1998) 12678–12679;
(d) C. Wang, Z. Ma, Anal. Bioanal. Chem. 382 (2005) 1708–1710;
(e) Q. Cheng, R.C. Stevens, Adv. Mater. 9 (1997) 481–483;
(f) Y. Okawa, M. Aono, Nature 409 (2001) 683–684.
[8] (a) J.-M. Kim, J.-S. Lee, J.-S. Lee, S.-Y. Woo, D.J. Ahn, Macromol. Chem. Phys. 206 (2005) 2299–2306;
(b) E.Y. Park, J.W. Kim, D.J. Ahn, J.-M. Kim, Macromol. Rapid Commun. 28 (2007) 171–175;
(c) J.-M. Kim, J.-S. Lee, H. Choi, D. Sohn, D.J. Ahn, Macromolecules 38 (2005) 9366–9376.
[9] (a) E.A. Jares-Erijman, T.M. Jovin, Nat. Biotechnol. 21 (2003) 1387–1395;
(b) B.S. Gaylord, A.J. Heeger, G.C. Bazan, Proc. Natl. Acad. Sci. USA 99 (2002) 10954–10957;
(c) H.A. Ho, K. Doré, M. Boissinot, M.G. Bergeron, R.M. Tanguay, D. Boudreau, M. Leclerc, J. Am. Chem. Soc. 127 (2005) 12673–12676;
(d) S.K. Dishari, Macromol. Rapid Commun. 30 (2009) 1645–1650;
(e) K. Lee, K. Maisel, J.M. Rouillard, E. Gulari, J. Kim, Chem. Mater. 20 (2008) 2848–2850;
(f) K.-Y. Pu, K. Li, B. Liu, Adv. Mater. 22 (2010) 643–646;
(g) J. Wang, B. Liu, Chem. Commun. (2009) 2284–2286;
(h) F. He, Y. Tang, S. Wang, Y. Li, D. Zhu, J. Am. Chem. Soc. 127 (2005) 12343–12346;
(i) K. Lee, J.-M. Rouillard, B.-G. Kim, E. Gulari, J. Kim, Adv. Funct. Mater. 19 (2009) 3317–3325;
(j) C.-C. Pun, K. Lee, H.-J. Kim, J. Kim, Macromolecules 39 (2006) 7461–7463.
[10] H.-J. Kim, J. Lee, T.-H. Kim, T.S. Lee, J. Kim, Adv. Mater. 20 (2008) 1117–1121.
[11] T.H. Kim, N.Y. Kwon, T.S. Lee, Tetrahedron Lett. 51 (2010) 5596–5600.
[12] T.H. Kim, D.G. Kim, M. Lee, T.S. Lee, Tetrahedron 66 (2010) 1667–1672.
[13] (a) T.H. Kim, M.S. Choi, B.-H. Sohn, S.-Y. Park, W.S. Lyoo, T.S. Lee, Chem. Commun. (2008) 2364–2366;
(b) T.H. Kim, M. Lee, T.S. Lee, J. Nanosci. Nanotechnol. 10 (2010) 6929–6934.
[14] (a) S.Y. Okada, R. Jelinek, D. Charych, Angew. Chem. Int. Ed. 38 (1999) 655–659;
(b) S. Kolusheva, L. Boyer, R. Jelinek, Nat. Biotechnol. 18 (2000) 225–227;
(c) D.J. Ahn, S. Lee, J.-M. Kim, Adv. Funct. Mater. 19 (2009) 1483–1496.
[15] C.K. Kwak, D.M. Kim, C.–S. Lee, M. Lee, T.S. Lee, J. Nanosci. Nanotechnol. 10 (2010) 6920–6924;
(b) C.K. Kwak, D.G. Kim, T.H. Kim, C.-S. Lee, M. Lee, T.S. Lee, Adv. Funct. Mater. 20 (2010) 3847–3855;
(c) T.H. Kim, H.J. Kim, C.G. Kwak, W.H. Park, T.S. Lee, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 2059–2068.
[16] (a) S. Kim, S.Y. Park, Adv. Mater. 15 (2003) 1341–1344;
(b) S. Park, S. Kim, J. Seo, S.Y. Park, Macromolecules 38 (2005) 4557–4559.