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Versatile Route for Preparation of Polydiacetylene/ZnO Nanocomposites and Their Colorimetric Response to pH and Ethanol

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Abstract

This contribution presents a simple method to prepare polydiacetylene(PDA)/ZnO nanocomposites, which can be utilized as active materials in sensing technology. The ZnO nanoparticles, which constitute of Zn-OH$_2^+$, Zn-OH and Zn-O$^-$ groups at their surfaces, function as nano-substrates for self-assembling of diacetylene monomers, 10,12-pentacosadiynoic acid (PCDA), in aqueous medium. Photopolymerization of the assemblies yields poly(PCDA)/ZnO nanocomposites with core-shell structure. Strong interactions between the active groups at ZnO surface and carboxylic head groups of poly(PCDA) promote chain ordering and reduce segmental dynamics of poly(PCDA) in the nanocomposites. The existence of strong interfacial interaction drastically affects the colorimetric response behavior of the nanocomposites upon exposure to external stimuli. The poly(PCDA)/ZnO nanocomposites change color from blue to purple upon increasing pH to ~12.6 while the color transition from blue to red of pure poly(PCDA) vesicles takes place at pH~8. The addition of ethanol into aqueous suspension of pure poly(PCDA) vesicles causes color transition when the ethanol concentration is above ~45 %v/v. However, the addition of ethanol up to 90%v/v into aqueous suspension of the nanocomposites hardly affects their color.

Key words: Polydiacetylene, Nanocomposites, Color transition, Conformation transition, Interfacial effect, pH sensor

Introduction

In recent years, the development of conjugated polymers as sensing materials has gained much attention from scientific community, particularly the polydiacetylene (PDA).(1-14) PDA vesicles are spherical organic nanoparticles with cavity in the center. This class of material has been known to exhibit many interesting properties. The uniqueness of PDA vesicles is the color-transition behavior from blue to red when exposed to environmental perturbations such as the increasing of temperature or pH, addition of alcohols or surfactants, binding with ions or biomolecules.(1-7,13-19) Therefore, PDA vesicles have a potential for being utilized as nano-sensors.

One of the well-known diacetylene monomers, frequently used to prepare PDA vesicles, is the 10,12-pentacosadiynoic acid (PCDA). Its structure consists of hydrophillic head group and hydrophobic tail. The dispersion of PCDA in water, assisted by ultrasonication, leads to the formation of bilayer vesicles.(1-2, 4-6) Poly(PCDA) vesicles can be easily prepared by UV light irradiation of the monomeric vesicles. The unperturbed poly(PCDA) vesicles posses relatively long conjugation length and exhibit a deep blue color. The perturbation of poly(PCDA) vesicles by external stimuli causes the rearrangement of alkyl side chains and hence induces conformational transition of conjugated backbone.(1-5,20) The distortion of conjugated backbone results in the decrease of conjugation length (i.e. wider HOMO-LUMO energy gap). The perturbed poly(PCDA) can exist in different colors such as purple and red, depending on the magnitude of the perturbation.

To control the colorimetric response of PDA vesicles or assemblies upon exposure to external

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stimuli, one can utilize different approaches. Some specific designed molecules can be inserted into layers of PDA assemblies and behave as receptors.(1,4,6,15-16,21) The binding of receptor molecules to ions, biomolecules and other desired materials induces color transition of PDA assemblies. The colorimetric response of PDA assemblies can also be controlled by structural modification. It has been demonstrated by many research groups that the modification of head groups can have major impact on color-transition behaviors.(1,13,17-19,22-29) The increase of interactions between head groups causes the increase of transition temperature. In some cases, where the interactions between head groups are sufficiently strong, the thermochromic transition occurs in a reversible fashion.(1,13,19,24,26) The bonding of head groups by chemical linkers also provides PDA assemblies with reversible thermochromic behavior.(18,27,29)

Although the aforementioned approaches are rather efficient, the chemical modification inevitably involves complicate synthetic methods and requires time-consuming processes. One of other attractive approaches utilizes foreign materials to strengthen the interactions between the head groups of PDA assemblies and hence alter their color-transition behaviors. Different materials have been used such as polymers(Gu et al., 2008 ; Wu et al., 2009), cations (Huang et al., 2005), layered double hydroxide nanosheets(Itoh et al., 2005) and SiO_2 nanoparticles. (33) In this research, we present a simple method to prepare new class of PDA/ZnO nanocomposites. The ZnO nanoparticles are used as nano-substrates for self-assembling of PCDA monomers on their surface (see Figure 1). We have found that the existence of strong interfacial interactions in the nanocomposites largely alters their colorimetric response upon exposure to external stimuli.

Materials and Experimental Procedures

PCDA monomer (Fluka) and ZnO nanoparticles (Nano Materials Technology, Thailand) are commercially available. The preparation of pure poly(PCDA) vesicles was as followed. The PCDA monomer was purified by dissolving in chloroform and then filtered through a 0.45 μm nylon membrane to remove polymerized materials. The chloroform was slowly evaporated by heating at ~50°C in water bath. Deionized (DI) water was added into the dried film of PCDA monomers to yield a concentration of 0.5 mM. The sample was sonicated at ~80°C for 30 minutes to disperse the monomers into aqueous medium and then kept in refrigerator (~4°C) over night. The cloudy suspension of PCDA vesicles was irradiated by ordinary UV light (λ~254 nm, 10 watts) for 5 minutes. The samples were filtered through a 0.8 μm cellulose membrane to remove large aggregates. The obtained poly(PCDA) vesicles exhibited a deep blue color. Similar procedure was used to prepare poly (PCDA)/ZnO nanocomposites. However, the ZnO nanoparticles were pre-dispersed in DI water, assisted by probe ultrasonication for 5 minutes, before adding into the dried film of PCDA monomers. Weight ratios of the added ZnO nanoparticles were 5, 9 and 17wt%. We note that these numbers do not necessarily indicate the actual weight ratio of ZnO in the nanocomposites. The pH of nanocomposite suspensions ranges from about 6.5 to 6.8. Figure 1 summarizes the processes that occur during each step of the preparation of the nanocomposites.

Figure 1. Schematic for the preparation of poly (PCDA)/ ZnO nanocomposites dispersed in water.

The size distribution of ZnO nanoparticles was explored by using Transmission Electron Microscopy (TEM, Tecnai 12, D291). The morphology and dimension of pure poly(PCDA) vesicles and poly(PCDA)/ZnO nanocomposites were investigated by using intermittent contact Atomic Force Microscopy (AFM, SPI3800N Nanoscope II, Seiko Instrument Inc., Japan). The cantilever with pyramidal shape Si_3N_4 tip was used. Samples for TEM and AFM measurements were prepared by dropping the aqueous suspensions on Cu grid and polished silicon wafer, respectively. The samples were left to dry in clean atmosphere under ambient conditions.

The absorption spectra of pure poly(PCDA) vesicles and poly(PCDA)/ZnO nanocomposites were measured by using UV/Vis spectrophotometer (Specord S100B, Analytik Jena). The pH of suspensions was varied by adding NaOH aqueous solution. Ethanol was added into the systems by using a micropipette. The magnitude of colorimetric response (%CR) was calculated according to the equation; $\%CR = [(PB_0-PB)/PB_0] \times 100$, where PB_0 is the initial percent blue before exposure to external stimuli and PB is the final percent blue after exposure to external stimuli. The PB value was calculated from $A_{640}/(A_{540}+A_{640})$, where A_{540}, A_{640} were the absorbance at 540 nm and 640 nm, respectively. The PB_0 value was calculated at the initial condition.

Results and Discussion

Morphology and Size Distribution

It has been known that the surface of ZnO nanoparticles in aqueous suspension constitutes of Zn-OH, Zn-OH_2^+ and Zn-O^- groups.(34-36) At low pH region, the ZnO surface is mostly populated by Zn-OH and Zn-OH_2^+ group. Therefore, the acidic PCDA monomers with carboxylic head groups are expected to anchor on the ZnO surface via ionic interaction and/or hydrogen bonding (see Figure 1). The irradiation of the assemblies by UV light results in poly(PCDA)/ZnO nanocomposites where polymeric layers coat on the ZnO nanoparticle. The outer surface of nanocomposites constitutes of hydrophilic layer of carboxylic groups, which favorably interact with aqueous medium. It is important to note that the number of poly(PCDA) layers in the nanocomposites can be higher than two layers.

The TEM image of ZnO nanoparticles is illustrated in Figure 2. The ZnO nanoparticles exhibit spherical shape with relatively large size distribution. The diameters of primary particles range from about 20 to 200 nm. The topography AFM images of pure poly(PCDA) vesicles and poly(PCDA)/ZnO nanocomposites are illustrated in Figure 3. It appears that the shape of pure poly(PCDA) vesicles is not spherical. Their height is also quite small, less than 12 nm. This observation is attributed to the interaction between AFM tip and soft vesicles, which may cause the deformation of shape and flatten the vesicles. The diameters of pure poly(PCDA) vesicles range from about 40 to 200 nm. The morphologies and size distribution of poly(PCDA)/ZnO nanocomposites are similar to those of the pure poly(PCDA) vesicles. The variation of ZnO ratios in the preparation of the nanocomposites hardly affects their size. The TEM image of the nanocomposites reveals layers of poly(PCDA) coated on ZnO nanoparticles.(37) The thickness of polymeric layers is about 25 to 30 nm, corresponding to about 6 layers of the poly(PCDA) chains.

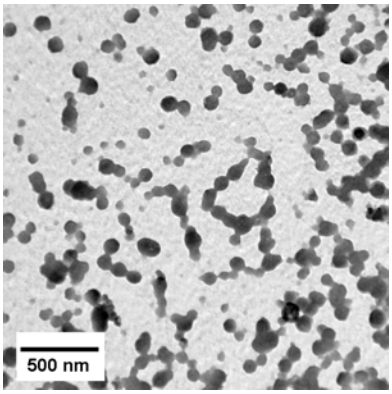

Figure 2. TEM image of ZnO nanoparticles.

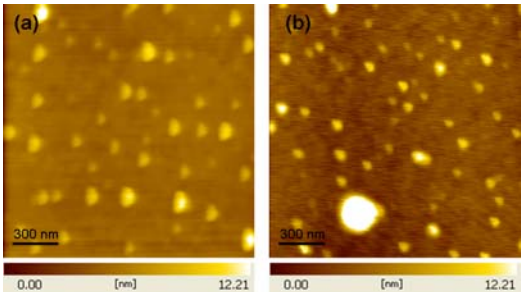

Figure 3. AFM topography images of (a) pure poly(PCDA) vesicles and (b) poly(PCDA)/ZnO nanocomposites on silicon wafer.

Colorimetric Response to pH

The UV/Vis absorption spectra of pure poly (PCDA) vesicles and poly(PCDA)/ZnO nanocomposite aqueous suspensions measured upon increasing pH are shown in Figure 4. The unperturbed state of the vesicles and nanocomposites exhibits maximum absorption band (λ_{max}) at ~640 nm with vibronic shoulder at ~590 nm, corresponding to a deep blue color. We also observe that the full width at half-height maximum of absorption peak of the nanocomposite is much smaller than that of the pure poly(PCDA) vesicles. This indicates higher ordering of backbone and alkyl side chains of poly(PCDA) in the nanocomposites. Detailed discussion on this issue is given in our previous report.(37)

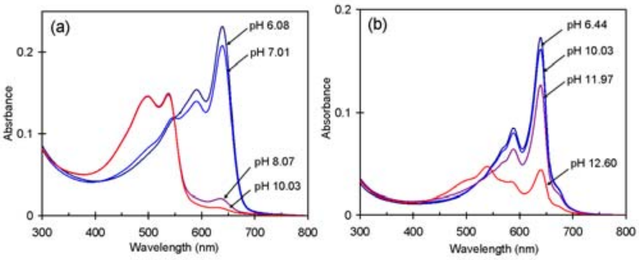

Figure 4. Absorption spectra of (a) pure poly(PCDA) vesicles and (b) poly(PCDA)/ZnO nanocomposites in aqueous suspensions measured at different pH.

The addition of NaOH into aqueous suspension of pure poly(PCDA) vesicles causes the growth of new peak at 540 nm while the peak at 640 nm simultaneously drops (see Figure 4(a)). At pH~8, new absorption bands at ~540 nm and ~500 nm are clearly observed. An isosbestic point is detected at ~550 nm, indicating the transition from two distinct electronic species. Further increasing pH hardly affects the pattern of absorption spectrum. The poly(PCDA) vesicles at this state exhibit a red color. The colorimetric response of poly(PCDA)/ZnO nanocomposites to the increasing of pH is rather different. The color transition takes place at much higher pH. The increase of pH to ~12 hardly affects the pattern of absorption spectrum. The growth of new peak at ~540 nm is detected at pH ~12.6, corresponding to the formation of the red phase. However, large fraction of the blue phase (λ~640 nm) still remains in the system at this condition. The nanocomposite at this state exhibits a purple color. The other nanocomposites prepared by using different ratios of ZnO nanoparticles shows color transition at similar pH range. The results are summarized in Figure 5 where the colorimetric response (%CR) is plotted as a function of pH. The sharp increase of the %CR indicates the color transition while the %CR value corresponds to magnitude of the color change. We also observe that the increase of ZnO ratio causes slight increase of pH required for inducing the color transition.

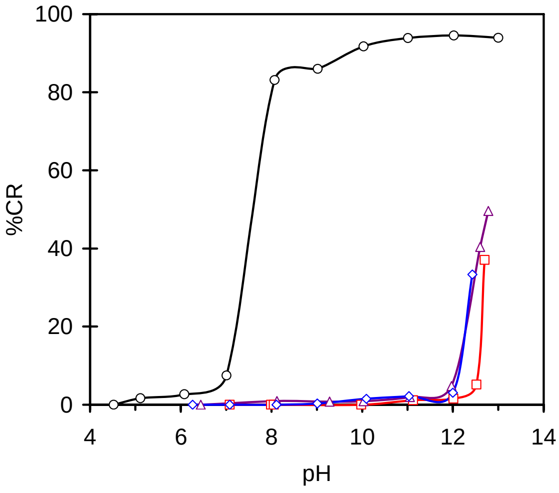

Figure 5. Plots of %CR upon increasing pH of aqueous suspensions of (○) pure poly(PCDA) vesicles, (◊) poly(PCDA)/ZnO5%, (Δ) poly(PCDA)/ZnO9% and (□) (poly)PCDA/ZnO17% nanocomposites.

The mechanism for the color transition of pure poly(PCDA) vesicles and poly(PCDA)/ZnO nanocomposite is proposed in Figure 6. The carboxylic head groups of unperturbed poly(PCDA) vesicles interact with their neighbors via hydrogen bonds. At this initial state (i.e. blue phase), the side chains arrange in an ordered fashion and the conjugated backbone possesses relatively long conjugation length. The increase of pH by adding NaOH into aqueous suspension of pure poly(PCDA) vesicles drastically alters the interactions between their head groups. The OH^- ions can abstract protons from the acidic heads and transform the carboxylic group into the carboxylate one. The strong ionic repulsion between the negatively charged head groups causes the rearrangement of side chains and hence induces the distortion of conjugated backbone. The planarity of π-orbital arrangement in the distorted backbone is reduced significantly, which in turn disrupts the conjugation of π electrons (i.e. decrease of conjugation length). The HOMO-LUMO energy gap of the perturbed poly(PCDA) vesicles becomes wider, resulting in the electronic absorption in higher energy region. The vesicles exhibit red color at this state.

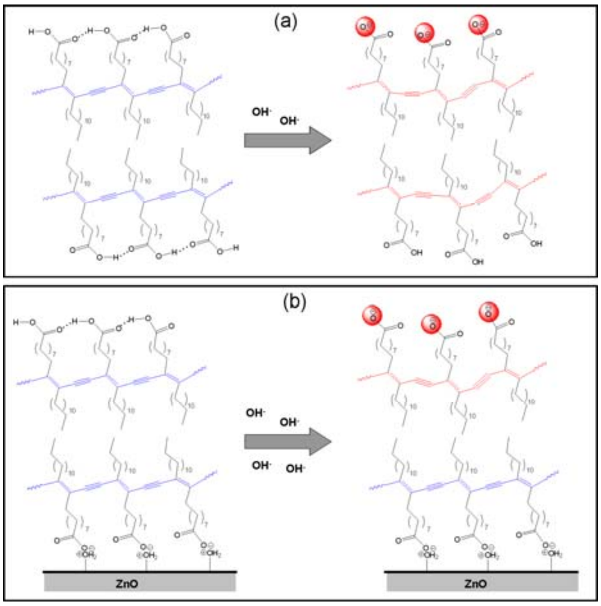

Figure 6. Proposed mechanism for color transition of (a) pure poly(PCDA) vesicles and (b) poly (PCDA)/ZnO nanocomposites upon addition of OH^- ions. The color transition of pure poly(PCDA) vesicles occurs at pH ~8 while the nanocomposites change color at pH ~12.6 (see text).

The mechanism for the color transition of poly(PCDA)/ZnO nanocomposite is similar to that of the poly(PCDA) vesicles. However, the inner layer of poly(PCDA) chain strongly anchors to the surface of ZnO via ionic interaction between carboxylate head and Zn-OH_2^+ group. The FT-IR measurements in our previous report confirm the existence of this type of interfacial interaction.$^{(37)}$ The addition of OH^- ion into aqueous suspension of the nanocomposites mostly affects the interaction between head group of poly(PCDA) chain at the outer layer (see Figure 6(b)). The van der Waals interaction between the alkyl side chains of the outer and inner layers of poly(PCDA) chains is an opposing force that maintains the planarity of conjugated backbone. The perturbation at the head group must be sufficiently strong to overcome the overall interactions between side chains and hence causes the distortion of conjugated backbone. Therefore, it requires higher concentration of OH^- ions (i.e. higher pH) to induce color transition of the nanocomposites. We also suggest that the inner layer of poly(PCDA) in the nanocomposites does not change color as indicated by the results from UV/vis absorption measurements. It is unlikely that the OH^- ions can penetrate through the hydrophobic layer of poly(PCDA) chain into their head groups at the surface of ZnO nanoparticles.

Colorimetric Response to Ethanol

The absorption spectra of pure poly(PCDA) vesicles and poly(PCDA)/ZnO nanocomposite measured upon addition of ethanol are illustrated in Figure 7. At low concentration of ethanol, the absorption pattern of pure poly(PCDA) vesicles is hardly affected. The systematic decrease of absorbance is due to the dilution. A growth of new peak at ~540 nm is detected when the ethanol concentration is higher than 20%v/v. A drastic change occurs in the concentration range of 40 to 50%v/v where the suspension turns from blue to red color. The absorption spectrum of the red phase constitutes of peaks at ~540 nm and ~500 nm. The addition of ethanol into aqueous suspensions of poly(PCDA)/ZnO nanocomposites hardly affects their absorption spectra. It is clear from Figure 7(b) that the increase of ethanol concentration up to 90%v/v does not induce color transition. The comparison of colorimetric response of pure poly (PCDA) vesicles and poly(PCDA)/ZnO nanocomposites are illustrated in Figure 8. The plots of %CR versus ethanol concentration detect a sharp increase at 40 to 50%v/v in the system of pure poly(PCDA) vesicles. The %CR values of the nanocomposites slightly increase at ethanol concentration of 90%v/v. This result shows that the incorporation of ZnO nanoparticles into the core of poly(PCDA) vesicles causes the increase of color stability upon exposure to alcohol.

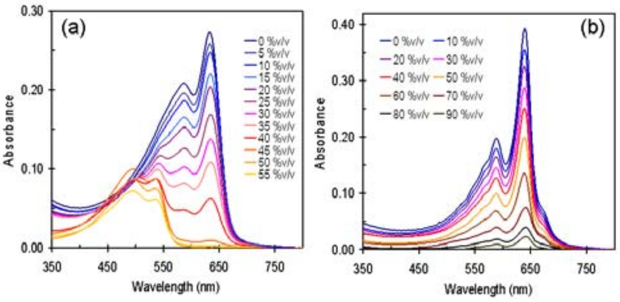

Figure 7. Absorption spectra of (a) pure poly(PCDA) vesicles and (b) poly(PCDA)/ZnO nanocomposites in aqueous suspensions measured upon addition of ethanol.

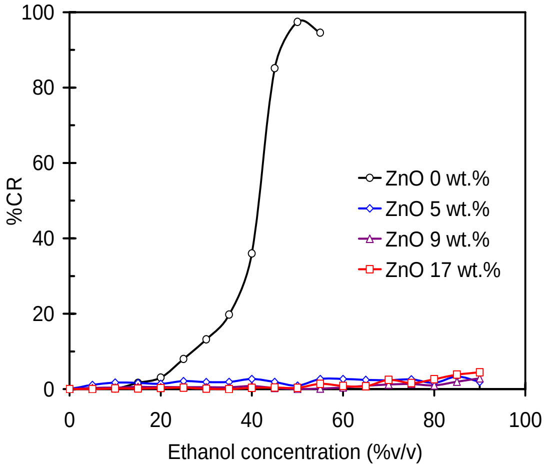

Figure 8. Plots of %CR upon addition of ethanol into suspensions of (○) pure poly(PCDA) vesicles, (◊) poly(PCDA)/ZnO5%, (Δ) poly(PCDA)/ ZnO9% and (□) poly(PCDA)/ZnO17% nanocomposites.

The molecule of ethanol constitutes of hydrophilic head and hydrophobic tail similar to the structure of normal surfactants. The addition of ethanol into aqueous suspension of poly(PCDA) vesicles perturbs the organization of head group and alkyl side chain as illustrated in Figure 9(a). The ethanol molecules can swell the outer layer of poly(PCDA) vesicles, which in turn breaks the hydrogen bonds between carboxylic head groups. When magnitude of the swelling is sufficiently large, the rearrangement of side chains occurs, leading to the distortion of conjugated backbone. The strength of inter- and intrachain interactions within the layers of poly(PCDA) dictates the quantity of ethanol required for inducing the color transition. For pure poly(PCDA) vesicles, the presence of ~50%v/v of ethanol in the system causes color transition from blue to red. In the systems of poly(PCDA)/ZnO nanocomposites, the swelling of ethanol at the outer layer is expected to occur in a similar fashion (see Figure 9(b)). However, strong ionic interaction between carboxylate heads and Zn-OH_2^+ groups at ZnO surface strengthens layered structure of the poly(PCDA). The van der Waals interaction between alkyl side chains of the inner and outer layers also resist the distortion of conjugated backbone in the outer layer. Therefore, the presence of ~90%v/v of ethanol in aqueous suspensions of the nanocomposites still does not induce color transition of poly(PCDA). However, the swelling of other solvents or surfactants may cause color transition of poly(PCDA) in the nanocomposites. This issue is currently being carried out in our laboratory.

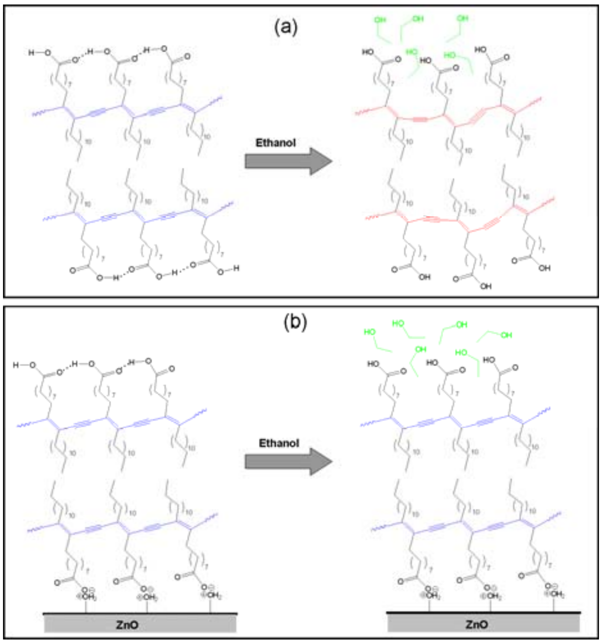

Figure 9. Proposed mechanism for color transition of (a) pure poly(PCDA) vesicles and (b) poly (PCDA)/ZnO nanocomposites upon addition ethanol. The color transition of the pure poly (PCDA) vesicles occurs at ethanol concentration of about 50%v/v while the nanocomposites do not change color upon addition of ethanol up to 90%v/v (see text).

Conclusions

In this research, we present a simple method to prepare poly(PCDA)/ZnO nanocomposites with core-shell structure. The incorporation of ZnO nanoparticles into the core of poly(PCDA) vesicles strengthens their layered structure, which results in the increase of color stability upon exposure to OH^- ion and ethanol. The nanocomposites exhibit color transition at much higher pH compared to the system of pure poly(PCDA) vesicles. The addition of ethanol does not induce color transition. Our preparation method of the nanocomposites is very simple and inexpensive. In addition, it does not require a time-consuming purification process. This approach offers a new route for controlling the colorimetric response behavior of polydiacetylene-based materials to external stimuli, which is important for the development of nano-sensor technology.

Acknowledgements

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