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Aqueous sols of oligo(ethylene glycol) surface decorated polydiacetylene vesicles for colorimetric detection of Pb^{2+}

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ABSTRACT

A series of ethylene glycol (EG), triethylene glycol (3EG) and pentaethylene glycol (5EG) esters of 10,12-pentacosadiynoic acid (PCDA) are synthesized. The glycol ester lipids can be hydrated and well dispersed in water but they cannot form polydiacetylenes upon UV irradiation. They however can be mixed with PCDA up to 30 mol% and polymerized to form blue sols. The mixed polydiacetylene sols show blue to red thermochromic transition with two-stepped transition temperatures. The first transition temperature decreases with the increase of the glycol ester content as well as the length of their chains indicating greater fluidity of the self-assembled structure due to less collaborative hydrogen bonding among the lipid head groups. These mixed polydiacetylene sol prepared from 30 mol% of the penta(ethylene glycol) ester show linear colorimetric response selectively to Pb^{2+} in the range of 5–30 μM.

1. Introduction

Lead ion (Pb^{2+}) is one of the most toxic metal ions often found in aquatic ecosystems. Monitoring of this highly hazardous metal ion on-site is an important concern for human health and environment. The very powerful and most currently used technique for detection of Pb^{2+} is inductively coupled plasma mass spectrometry (ICPMS) but it requires expensive instruments and not suitable for on-site analyses. During the last decade, several Pb^{2+} sensing systems have been developed using detection modes such as fluorometry [1–11], colorimetry [12–16] and electrometry [17–21]. The sensors using synthetic ligands usually suffer from low aqueous solubility and cross-sensitivity toward other metal ions. While the uses of DNAzyme-based transducers showed much improved aqueous solubility, sensitivity and selectivity but their high cost, low stability as well as lengthy and intricate sample preparation have so far prevented its practical applications for on-site analyses. Low cost and stable transducers which can provide simple and selective detection of Pb^{2+} in aqueous media is thus highly desirable.

Polydiacetylenes (PDAs) has recently emerged as one of the most studied classes of colorimetric transducers. Upon aqueous dispersion, an amphiphilic diacetylene monomer such as 10,12-pentacosadiynoic acid (PCDA) can molecularly self-assemble into nano-scaled vesicles (liposomes) that is photopolymerizable into blue poly(PCDA) sol [21–31]. Due to its distinct blue to red color transition, poly(PCDA) sol has been developed into various sensing applications such as thermosensors [32–41], chemosensors [42–46], and biosensors [30,47–54]. For metal ion sensors, Kolusheva and coworkers have reported a utilization of poly(PCDA) vesicles embedded with a phospholipid and an ionophore for colorimetric detection of alkali ions [45]. Recently, poly(PCDA) attached with G-rich ssDNA has been used for selective fluorometric detection of potassium ion [55]. To the best of our knowledge, there is no report on the use of PDAs for detection of Pb^{2+} despite the fact that the surface of poly(PCDA) vesicle is packed with Pb^{2+} binding sites, carboxylic/carboxylate groups. We attribute the absence of this development to the packing within poly(PCDA) vesicles being too tight and strong to be disturbed by the ion binding.

Oligo(ethylene glycol) chains, having a crown ether-liked structure, can form ion channels [56] in lipid membrane and increase the fluidity of membrane by reducing membrane crystallinity. Such compounds have been used to prevent aggregation in many nano particulate systems [57]. They have also been installed as a pendant

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group in thermosensitive polymers to control water-solubility and thus cloud point of the polymers [58–60]. In this study, we would like to report the modification of PCDA with oligo(ethylene glycol) chains to be used incorporation with PCDA in constructing a selective colorimetric sensor for Pb^{2+} in aqueous media.

2. Materials and methods

2.1. Materials and analytical instruments

10,12-Pentacosanoic acid (PCDA) was purchased from GFS Chemical, USA and other reagents were purchased from Sigma–Aldrich and Fluka. Analytical grade solvents such as chloroform and methylene chloride were used without further purification. Column chromatography was carried out on silica gel 60 (230–400 mesh; Merck). Thin layer chromatography (TLC) was carried out using Merck 60 F254 plates with a thickness of 0.25 mm. The diacetylene monomers were purified by filtration to remove the polymerized lipid before use. The ^{1}H NMR and ^{13}C NMR spectra were collected on a 400 MHz NMR spectrometer (Murcury 400, Varian). Mass analysis was conducted with a Quattro micromass (Waters) using the electrospray ionization (ESI). The electronic absorption spectra were recorded on a temperature variable UV–vis spectrophotometer (Carry 100Bio, Varian).

2.2. Synthetic procedures

EG–PCDA: In a 50 mL round bottom flask with a magnetic stirrer, PCDA (332.1 mg, 0.89 mmol) was dissolved in toluene (10 mL) and ethylene glycol (0.6 mL, 10.77 mmol) and sulfuric acid (1 drop) was added. The mixture was then refluxed for 5 h at 100 °C, allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The residue was dissolved with CH_2Cl_2 (50 mL) and washed with saturated Na_2CO_3 solution (2× 50 mL). The organic phase was collected and dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The product was further purified by column chromatography (hexane/ethyl acetate gradient from 0:100 to 20:80) to afford the desired product as a white solid (317.7 mg, 86% yield). ^{1}H NMR ($CDCl_3$): δ 4.22 (t, 2H, $CH_2OC{=}O$, J = 4.6 Hz), 3.83 (m, 2H, CH_2O), 2.35 (t, 2H, $CH_2C{=}O$, J = 7.5 Hz), 2.24 (t, 4H, $CH_2C{\equiv}C{-}C{\equiv}CCH_2$, J = 6.9 Hz), 1.63 (m, 2H, CH_2), 1.51 (m, 4H, CH_2), 1.31 (m, 26H, CH_2), 0.88 (t, 3H, CH_3, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$): δ 174.20 (C=O), 77.33 (C≡C), 76.70 (C≡C), 65.94 (CH_2O), 65.31 (C≡C), 65.21 (C≡C), 61.39 (CH_2O), 34.16 (CH_2), 31.92 (CH_2), 29.65 (CH_2), 29.63 (CH_2), 29.61 (CH_2), 29.48 (CH_2), 29.35 (CH_2), 29.07 (2C, CH_2), 29.05 (CH_2), 28.88 (CH_2), 28.87 (CH_2), 28.74 (CH_2), 28.36 (CH_2), 28.29 (CH_2), 24.88 (CH_2), 22.68 (CH_2), 19.21 (CH_2), 19.19 (CH_2), 14.12 (CH_3); MS (ESI$^+$): $[M]^+$ found 418.63 (calcd. for $C_{27}H_{46}O_3$ 418.34).

3EG–PCDA: According to the above synthetic procedure and column chromatographic purification (hexane/ethyl acetate gradient from 0:100 to 40:60), 3EG–PCDA (348 mg, 73% yield) was obtained as a colorless viscous liquid from PCDA (348.4 mg, 0.93 mmol) and triethylene glycol (1.5 mL, 11.24 mmol). ^{1}H NMR ($CDCl_3$): δ 4.25 (t, 2H, $CH_2OC{=}O$, J = 4.8 Hz), 3.70 (m, 10H, CH_2O), 2.35 (t, 2H, $CH_2C{=}O$, J = 7.6 Hz) 2.25 (t, 4H, $CH_2C{\equiv}C{-}C{\equiv}CCH_2$, J = 7.0 Hz), 1.63 (m, 2H, CH_2), 1.52 (m, 4H, CH_2), 1.32 (m, 26H, CH_2), 0.89 (t, 3H, CH_3, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 173.82 (C=O), 77.32 (C≡C), 76.68 (C≡C), 72.47 (CH_2O), 70.58 (CH_2O), 70.38 (CH_2O), 69.23 (CH_2O), 65.30 (C≡C), 65.22 (C≡C), 63.21 (CH_2O), 61.78 (CH_2O), 34.15 (CH_2), 31.91 (CH_2), 29.64 (CH_2), 29.62 (CH_2), 29.60 (CH_2), 29.47 (CH_2), 29.34 (CH_2), 29.09 (2C, CH_2), 29.05 (CH_2), 28.90 (CH_2), 28.86 (CH_2), 28.76 (CH_2), 28.35 (CH_2), 28.31 (CH_2), 24.85 (CH_2), 22.68 (CH_2), 19.21 (CH_2), 19.19 (CH_2), 14.10 (CH_3); MS (ESI$^+$): $[M+Na]^+$ found 528.71 (calcd. for $C_{31}H_{54}O_5{\cdot}Na$529.39).

5EG–PCDA: According to the above synthetic procedure and column chromatographic purification (hexane/ethyl acetate gradient from 0:100 to 60:40), 5EG–PCDA (309.3 mg, 62% yield) was obtained as a colorless viscous liquid from PCDA (312.8 mg, 0.85 mmol) and pentaethylene glycol (2 mL, 9.46 mmol). ^{1}H NMR ($CDCl_3$): δ 4.22 (t, 2H, $CH_2OC{=}O$, J = 4.8 Hz), 3.67 (m, 18H, CH_2O), 2.32 (t, 2H, $CH_2C{=}O$, J = 7.6 Hz) 2.23 (t, 4H, $CH_2C{\equiv}C{-}C{\equiv}CCH_2$, J = 7.0 Hz), 1.61 (m, 2H, CH_2), 1.50 (m, 4H, CH_2), 1.30 (m, 26H, CH_2), 0.87 (t, 3H, CH_3, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 173.80 (C=O), 77.32 (C≡C), 76.68 (C≡C), 72.55 (CH_2O), 70.63 (CH_2O), 70.60 (CH_2O), 70.58 (CH_2O), 70.33 (CH_2O), 70.11 (CH_2O), 69.23 (CH_2O), 65.30 (C≡C), 65.21 (C≡C), 63.21 (CH_2O), 61.73 (CH_2O), 34.16 (CH_2), 31.90 (CH_2), 29.63 (CH_2), 29.61 (CH_2), 29.59 (CH_2), 29.46 (CH_2), 29.33 (CH_2), 29.08 (2C, CH_2), 29.06 (CH_2), 28.90 (CH_2), 28.85 (CH_2), 28.76 (CH_2), 28.35 (CH_2), 28.31 (CH_2), 24.85 (CH_2), 22.67 (CH_2), 19.20 (CH_2), 19.18 (CH_2), 14.10 (CH_3); MS (ESI$^+$): $[M+Na]^+$ found 617.98 (calcd. for $C_{35}H_{62}O_7Na$ 617.44).

NEG–PCDA: In a 50 mL round bottom flask with a magnetic stirrer, a solution of PCDA (302.6 mg, 0.81 mmol) in methanol (25 mL) was added sulfuric acid (cat.) and refluxed for 3 h at 65 °C. The resulting mixture was evaporated under reduced pressure, redissolved with CH_2Cl_2 (50 mL) and washed with saturated Na_2CO_3 solution (2× 50 mL). The organic phase was collected, dried over anhydrous $MgSO_4$ and the solvent was removed under vaccou. The residue was dissolved with tetrahydrofuran (25 mL) and ethanolamine (0.5 mL, 8.2 mmol) was added at room temperature. After refluxing the mixture overnight, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/ethyl acetate gradient from 0:100 to 60: 40) to yield a white solid as the desired product (232.8 mg, 69% yield).

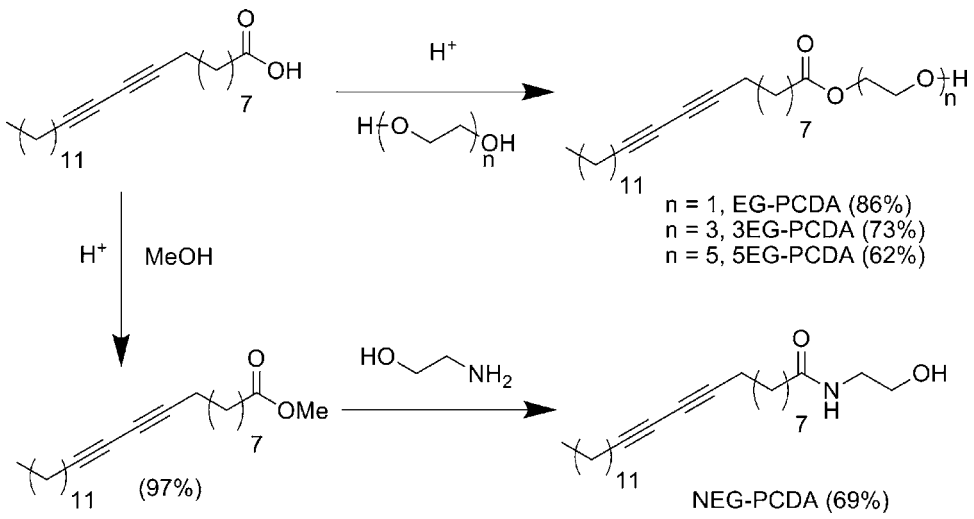
^{1}H NMR ($CDCl_3$): δ 5.88 (s, 1H, NH), 3.74 (m, 2H, CH_2N), 3.45 (m, 2H, CH_2O,), 2.23 (m, 6H, $CH_2C{\equiv}C{-}C{\equiv}C$ CH_2 and $CH_2C{=}O$), 1.64 (m, 2H, CH_2), 1.52 (m, 4H, CH_2), 1.32 (m, 26H, CH_2), 0.89 (t, 3H, CH_3, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 173.80 (C=O), 77.32 (C≡C), 76.68 (C≡C), 65.29 (C≡C), 65.20 (C≡C), 62.54 (CH_2O), 42.45 (CH_2N), 36.61 (CH_2), 31.89 (CH_2), 29.62 (CH_2), 29.60 (CH_2), 29.58 (CH_2), 29.45 (CH_2), 29.32 (CH_2), 29.15 (CH_2), 29.11 (CH_2), 29.07 (CH_2), 28.87 (CH_2), 28.84 (CH_2), 28.72 (CH_2), 28.34 (CH_2), 28.26 (CH_2), 25.63 (CH_2), 22.66 (CH_2), 19.18 (CH_2), 19.16 (CH_2), 14.09 (CH_3); MS (ESI$^+$): $[M]^+$ found 417.69 (calcd. for $C_{27}H_{46}NO_2$ 417.36).

2.3. Preparation of mixed lipid PDA sols

Preparation of an aqueous sol of mixed lipid PDA vesicles was accomplished by the following method. In brief, solution of PCDA (10 mM) and a diacetylene monomer (10 mM) in dichloromethane were mixed in test tube in various ratio and solvent was removed by flowing nitrogen gas to dryness. After removing organic solvent, MiliQ water was added to yield a total concentration of the mixed monomers of 0.1 mM. The lipid suspension was sonicated at 75–80 °C for 30 min to obtain a clear suspension. After that, the suspension product was kept in a refrigerator for 24 h and the polymerization was carried out by UV irradiation (254 nm, 1 mW/cm^2) for 1 min at 25 °C.

2.4. Colorimetric measurement

A quantitative evaluation of the blue-to-red color transition is given by the colorimetric response (%CR) which is defined as the equation; $\%CR = (FB_0 - FB)/FB_0 \times 100$. FB is a fraction of blue phase determined from $A_{blue}/(A_{blue}+A_{red})$, where A_{blue} and A_{red} are the absorbance of the blue and the red phase at 640 and 540 nm, respectively. FB_0 is the initial fraction blue phase of the vesicle solution and film before being subjected to a stimulant. The electronic absorption measurements in the metal ion sensing



Scheme 1. Synthesis of EG–PCDA, 3EG–PCDA, 5EG–PCDA and NEG–PCDA.

experiment were carried out at 25 °C. Each %CR was determined as an average ± standard deviation of 9 data points obtained from 3 samples × 3 measurements.

3. Results and discussion

3.1. Synthesis

Three ethylene glycol esters and one ethanolamido derivatives of PCDA were synthesized and studied as modulators for poly(PCDA) sensors. Ethylene glycol (EG–PCDA), triethylene glycol (3EG–PCDA) and pentaethylene glycol esters (5EG–PCDA) were synthesized by simple acid catalyzed esterification of PCDA with ethylene glycol and the corresponding oligo(ethylene glycol) [61]. The preparation of the amido derivative, NEG–PCDA, was performed via a condensation between the methyl ester of PCDA and ethanolalmine [62–64]. The desired products were all obtained in good yields after silica gel column chromatographic purification (Scheme 1).

3.2. PDA sol formation and thermochromic property

The oligo(ethylene glycol) ester derivatives i.e. 3EG–PCDA and 5EG–PCDA were liquids at room temperature which can be frozen and photopolymerized to form deep blue PDAs by UV irradiation. These lipids dispersed well in milli-Q water by ultrasonication (340 W) for 30 min at 75 °C but the resulting sols remained colorless after UV irradiation at 0–5 °C. The results suggest that molecular self assemblies of these lipids in aqueous media do not meet the topological requirements for diacetylene polymerization [65–68] that is in contrast to the parent PCDA which can be polymerized into a blue polydiacetylene in both solid and aqueous sol states. However, the EG–PCDA and NEG–PCDA sols prepared under similar condition were polymerizable to form a red and blue PDA, respectively. It is interesting to note that the carboxylic and amide but not the ester group can provide the necessary hydrogen bonding for the formation of blue PDA [69].

To investigate the effect of oligo(ethylene glycol) chains on the molecular assembly of PCDA and its sensing properties, mixed lipid PDA sols of EG–PCDA/PCDA, 3EG–PCDA/PCDA, 5EG–PCDA/PCDA and NEG–PCDA/PCDA were prepared at various mixing ratios. Upon UV irradiation, blue PDA sols were obtained from the mixed lipid containing up to 50 mol% of the esters while the mixed lipids containing 80 mol% of the esters remained colorless after the irradiation. The blue color of polymerized mixed lipid containing 50 mol% of 3EG–PCDA and 5-EG–PCDA is however considerably paler than those from the mixed lipid containing 30 mol% of the PCDA esters.

The mixed lipid sols were gradually heated from 20 °C to 80 °C and the thermochromic transitions were monitored by observing the absorbance of the red phase of the PDAs at 540 nm to evaluate their colorimetric sensitivity. The electronic absorbance (A) of the sols increased with the temperature (T) in correspondence to the blue to red color change (Fig. 1). As clearly seen in the first derivative (dA/dT) plot, the mixed lipid sols of the EG–PCDA, 3EG–PCDA and 5EGP–CDA showed two steps of color transition while the NEG–PCDA mixed lipid sols exhibited continuous one-stepped color transition. In the two-stepped color transition, the second step observed around 65 °C is the same as the color transition temperature of poly(PCDA) [32] while the first step appeared at the temperature between 40 and 50 °C and decreased with the increase of the oligo(ethylene glycol) chain length. The absorbance change in the first transition step also clearly increased with the content of the PCDA ester up to at least 30 mol% in the mixed lipid.

Since pure PCDA ester does not form blue PDA vesicles, the first color transition step is likely to be derived from a copolymer between the PCDA ester and PCDA within the mixed lipid vesicles. The amount of the copolymer increases with the PCDA ester with an expense of PCDA homopolymer. From the results of EG–PCDA/PCDA, the absorbance change of the first step mixed lipid sols increased up to 50 mol% of EG–PCDA where the second color transition corresponding to poly(PCDA) was totally disappeared. However, for 3EG–PCDA/PCDA and 5-EG–PCDA/PCDA sols, the absorbance change of the first transition step increased only up to 30 mol% the PCDA esters. The results may be attributed to the poor vesicle formation of the mixed lipid at higher content of 3EG–PCDA and 5EG–PCDA as evidenced by the pale color of the sols prepared at 50 mol% content of these PCDA esters. The difference between the highest content of the PCDA esters being incorporated into the mixed lipid sols implies that the copolymer formed between PCDA and its esters are of different ratios.

The observation of one-stepped color transition of NEG–PCDA/PCDA sol suggested that only one type of PDA is formed, most likely a copolymer between NEG–PCDA and PCDA. The NEG–PCDA/PCDA sols also exhibited transition temperature lower than the sols of pure NEG–PCDA (~63 °C) and pure PCDA (~65 °C) [32], and decreased with the increase of NEG–PCDA

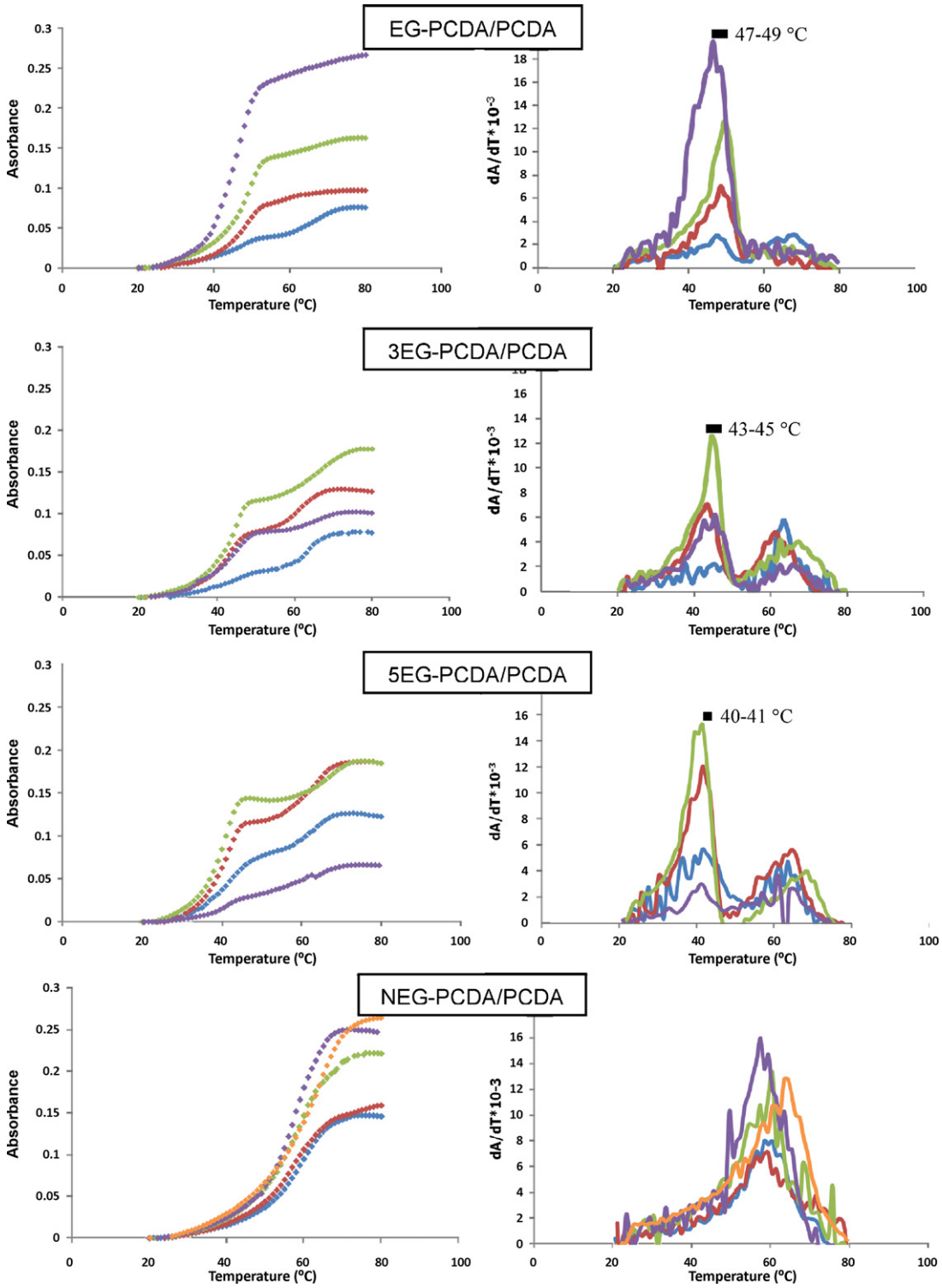


Fig. 1. Temperature dependence of the absorpbance (A) at 540 nm of the mixed lipid sols (left) and their first derivative, dA/dT (right). The absorbance of each sol was set to zero at 20 °C. The black bars indicate transition temperature ranges obtained from the maxima in the derivative plots; 10% ( ); 20% ( ); 30% ( ); 50% ( ); 100% ( ).

content in the range of 10–50 mol%. The hydrogen bond forming secondary amide group in NEG–PCDA is probably a main contributor to this thermochromic behavior which is very different from those of the mixed lipid sols containing PCDA esters.

3.3. Colorimetric sensing to metal ions

To apply the mixed lipid sols for colorimetric detection of heavy metal ions, an aqueous solution of metal salts such as $CdCl_2$, $Co(OAc)_2$, $Cu(OAc)_2$, $FeCl_2$, $HgCl_2$, $Ni(OAc)_2$, $Pb(NO_3)_2$, and $Zn(OAc)_2$ was added to the mixed lipid sols containing 30 mol% of PCDA esters. At 100 μM, only Pb^{2+} caused a distinct color change of the sol from blue to red for only 5EG–PCDA/PCDA sol (Fig. 2). The colorimetric response (%CR) of the sols to the metal ions recorded at 30 min after mixing showed the highest %CR of 55% for 5EG–PCDA/PCDA sol in the presence of Pb^{2+} (Fig. 2). Significantly lower %CRs of 20% and 10% were observed for 3EG–PCDA/PCDA and EG–PCDA/PCDA sols, respectively. To our delight, 5EG–PCDA/PCDA

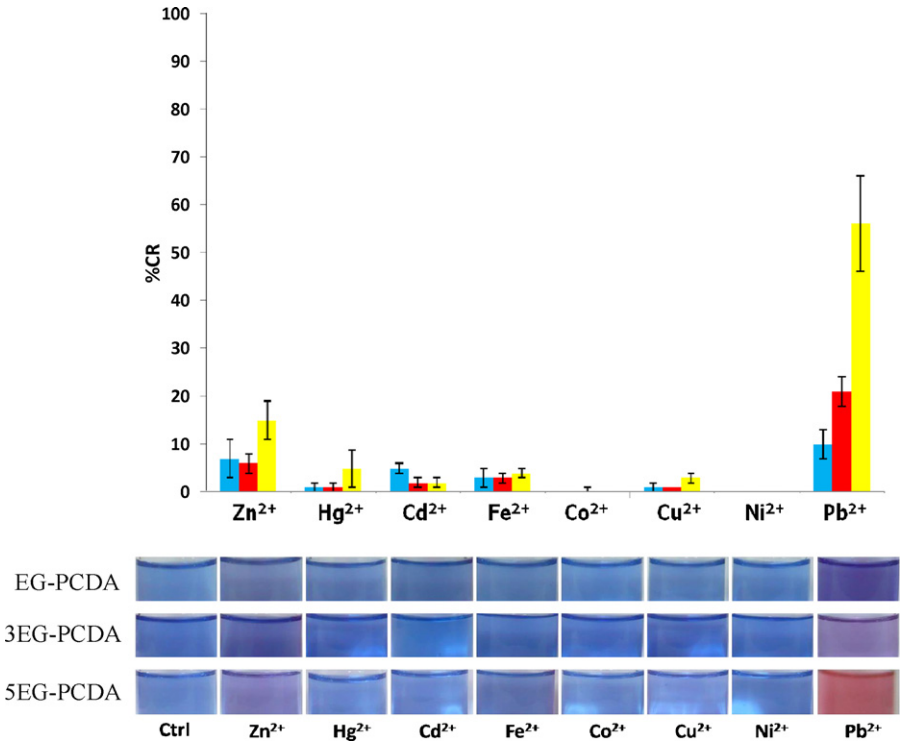


Fig. 2. Colorimetric responses (%CR) of the mixed lipid PDA sols containing 30 mol% of EG–PCDA ( ), 3EG–PCDA ( ) and 5EG–PCDA ( ) upon addition of metal ions (100 μM). The photograph underneath the histogram is the visual appearance of the corresponding sols.

sol also showed excellent selectivity toward Pb^{2+} with Zn^{2+} gave significantly lower %CR of 15%.

Oligo(ethylene glycol) chains and crown ethers are well known ionophores for alkali ions and has been known to form ion channel in lipid membrane [56]. There is also a literature report proposed that the crown ether is responsible for lead ion recognition in lipid membrane [8]. According to the thermochromic sensitivity results of the mixed lipid sols, we however suspected that the oligo(ethylene glycol) chains act as a sensitivity enhancer while the carboxylic/carboxylate groups of PCDA are responsible for the Pb^{2+} selectivity. To substantiate this proposition two pure lipid and three mixed lipid PDA sols viz. PCDA, NEG–PCDA, 5EG–PCDA/NEG–PCDA (30/70 mol%), 5EG–PCDA/PCDA (30/70 mol%) and 5EG–PCDA/PCDA/NEG–PCDA (30/35/35 mol%) were prepared and studied. There is no colorimetric response (%CR ~ 0) observed upon the addition of 100 μM of Pb^{2+} to the sols having no carboxylic head group (Fig. 3) denoted that the carboxylic/carboxylate groups are responsible for the ion binding. As for the sols containing carboxylic head group, the %CR increased with the incorporation of 30 mol% of 5EG–PCDA probably attributed to the membrane fluidity enhancement by lowering the collaborative hydrogen bonding on the vesicle surface. These results agree well with the thermochromic behavior of the mixed lipid sols described earlier. It is also interesting to note that replacing half of PCDA (35 mol%) with NEG–PCDA resulted in lower colorimetric response in correspondence to the lower numbers of carboxylic/carboxylate groups available for Pb^{2+} binding.

The Pb^{2+} induced color change of the PDA sols was also investigated by dynamic light scattering (DLS) technique and atomic force microscopy (AFM). Although 5EG–PCDA/PCDA vesicles were relatively fragile, many spherical particles with diameters less than 100 nm remained observable in the AFM image of a dry sample of 5EG–PCDA/PCDA sol on mica surface (Fig. 4a). The AFM images of the dry sol containing 100 μM Pb^{2+} clearly showed large aggregation and fusion of the PDA vesicles (Fig. 4b). The DLS revealed that the average hydrodynamic particle size increased from 67.3 nm (solid line) to 134.0 nm (dash line) upon the addition of 100 μM Pb^{2+} (Fig. 4c). These results suggested that the color transition involved vesicle aggregation and deformation probably induced by coordination between the vesicle spheres and Pb^{2+} ions (Fig. 4d).

The dynamic range of 5EG–PCDA/PCDA (30/70 mol%) sol for Pb^{2+} detection was determined by varying the solution of $Pb(NO_3)_2$ concentration from 5 to 100 μM. Linear colorimetric response was obtained with Pb^{2+} concentration in the range of 5–30 μM (Fig. 5). Noticeable color change with %CR of 20% was observed with the concentration of Pb^{2+} as low as 10 μM (~2 ppm). As the second most sensitive ion, Zn^{2+} showed low %CR of less than 20% up to 100 μM. Importantly, no color change was observed in the presence of alkaline and alkaline earth metal ions such as Li^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} at 100 μM concentration (Fig. 6) indicating that there is

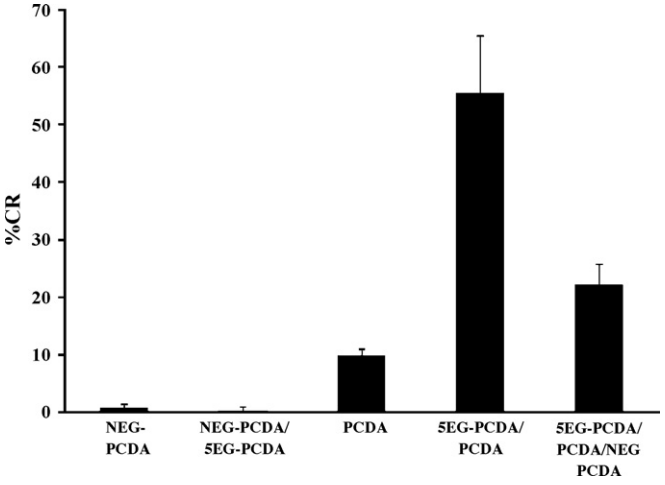


Fig. 3. Colorimetric responses (%CR) to Pb^{2+} (100 μM) of PDA sols prepared from NEG–PCDA, 5EG–PCDA/NEG–PCDA (30/70 mol%), PCDA, 5EG–PCDA/PCDA (30/70 mol%), and 5EG–PCDA/PCDA/NEG–PCDA (30/35/35 mol%).

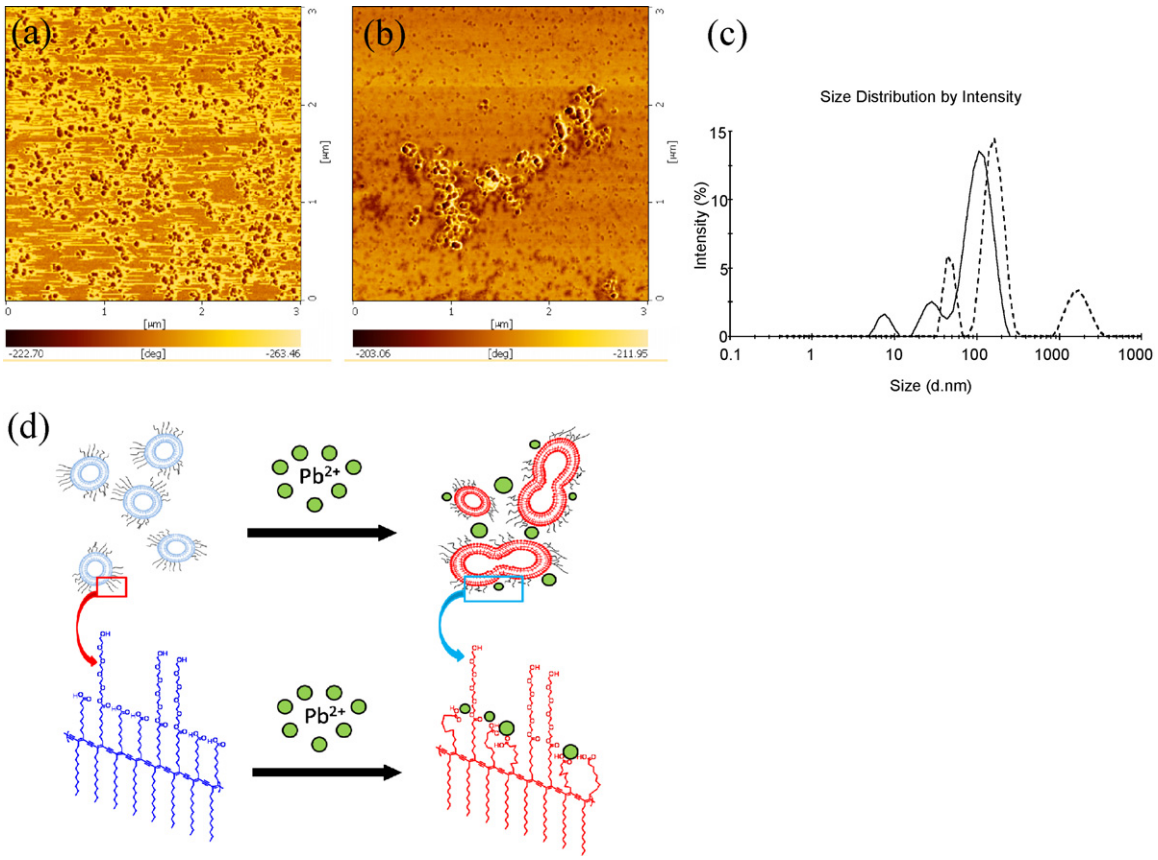


Fig. 4. AFM images of PDA vesicles obtained from air dry samples of 5EG–PCDA/PCDA (30/70 mol%) mixed lipid sols on mica surface before (a) and after (b) an addition of 100 μM Pb^{2+}. DLS particle size distribution before (solid line) and after an addition of 100 μM Pb^{2+} (dash line) (c). Proposed mechanism for the Pb^{2+} induced color transition (d).

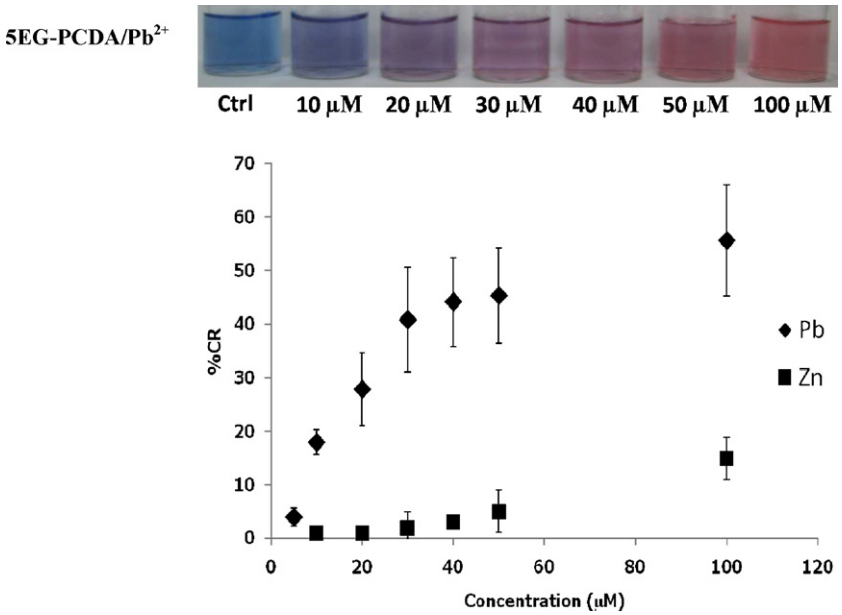


Fig. 5. Colorimetric responses (%CR) to various concentration Pb^{2+} and Zn^{2+} of the PDA sol (0.1 mM) prepared from PCDA mixed with 30 mol% of 5EG–PCDA. The picture at the top shows visual appearance of the sols upon the addition of Pb^{2+} ion at the corresponding concentrations.

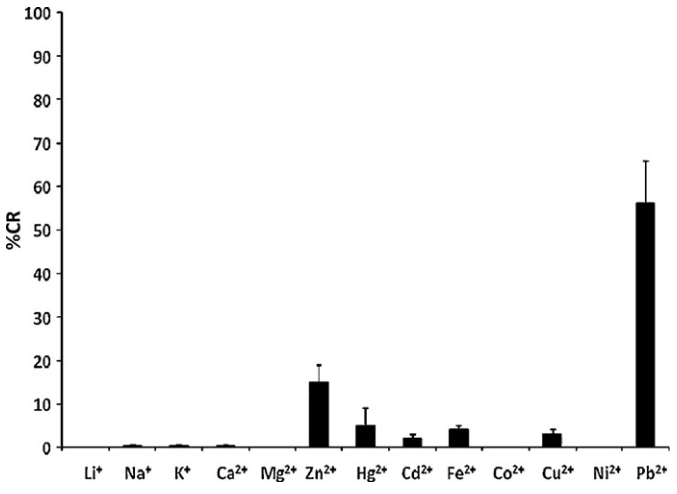


Fig. 6. Colorimetric responses (%CR) to various metal ions (100 μM) of the mixed lipid PDA sols of 5EG–PCDA/PCDA (30/70 mol%).

no interference from such metal ions to this PDA sensor system.

4. Conclusion

The polydiacetylene sols prepared from 10,12-pentacosadiynoic acid (PCDA) and its oligo(ethylene glycol) ester showed blue to red colorimetric response selectively to Pb^{2+} offered a method for naked eye detection of Pb^{2+} at part per million levels. The color transition is induced by the selective binding between Pb^{2+} and carboxylate groups of PCDA causing vesicle aggregation and fusion. The incorporation of the ethylene glycol chain increased the fluidity of the self-assembled structure by lessening the collaborative hydrogen bonding among the lipid head groups as evidenced by the decreases in the first color transition temperature in the thermochromic behavior.

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