Journal of Materials Chemistry

Cite this: *J. Mater. Chem.*, 2011, **21**, 17160

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**PAPER**



# Diverse colorimetric changes of polydiacetylenes with cationic surfactants and their mechanistic studies†

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***Received 19th June 2011, Accepted 9th August 2011***
**DOI: 10.1039/c1jm12818c**

Polydiacetylenes (PDAs), a family of conjugated polymers, are known to show stimulus-induced apparent blue-to-red transitions, which have led to the development of a variety of PDA-based chemosensors. However, in most cases, recognition sites were introduced at the terminal ends of PDAs, therefore, recognition processes on the surface of PDAs have been the primary stimulations to induce blue to red colorimetric changes. In this study, we reported that diverse colorimetric changes can be observed for PDA based sensors in which penetration of cationic surfactant into PDAs bearing benzoic acid groups can cause not only the typical blue to red change but also blue to violet, blue to yellow or blue to orange color change. We systematically demonstrated that these novel findings can be used effectively to discriminate different cationic surfactants by using three different PDAs. Furthermore, theoretical calculations and transmission electron microscope (TEM) images also confirm these unique colorimetric changes. These results suggest a new direction in which to design colorimetric sensors based on PDA polymers.

## Introduction

Fluorescent and colorimetric sensors are powerful tools to monitor biologically relevant and environmentally important species due to the simplicity of optical methods and high sensitivity of fluorescence.[1] Compared to small organic compounds, polymer based optical sensors[2] display several important advantages, such as signal amplification, enhanced binding efficiency and recognition selectivity due to multiple recognition elements and easy fabrication into devices, *etc.*

Polydiacetylenes (PDAs), a family of conjugated polymers, are very intriguing materials in several aspects.[3] These polymers are generally prepared by UV irradiation of self-assembled diacetylene (DA) supramolecules. PDAs, in many cases, display an intense blue color (*ca.* 640 nm maximum absorption wavelength) and the blue PDAs undergo a color shift to a red phase (*ca.* 550 nm maximum absorption wavelength) upon environmental stimulation. The stimulus-induced apparent blue-to-red transition of the PDAs has led to the development of a variety of PDA-based chemosensors. These unique changes have been adopted by various groups to develop temperature sensors,[4] pH sensors,[5] organic solvents,[6] *etc.* Recently, biologically, chemically and environmentally important targets have been more diverse to include $Pb^{2+}$ (ref. 7), $Zn^{2+}$ (ref. 8), $K^{+}$ (ref. 9), $Hg^{2+}$ (ref. 10), $Cu^{2+}$ (ref. 11), bacteria,[12] ATP/pyrophosphate,[13] catecholamine,[14] toxin,[15] explosives,[16] melamine,[17] *etc.* However, in most cases, recognition sites were introduced at the terminal ends of PDAs, therefore recognition processes on the surface of PDAs have been the primary stimulations to induce blue to red colorimetric changes. Recently, we reported the first example of diverse colorimetric changes in which penetration of anionic surfactant to imidazolium-PDAs can cause not only the typical blue to red change but also blue to yellow or blue to orange color change.[18]

On the other hand, due to the heavy use of cationic surfactants (CS) as surface cleaning agents such as soaps, shampoo, *etc.*,[19] it is necessary to develop a convenient method for the detection of such quaternary ammonium surfactants. In particular, it is quite challenging to detect non-aromatic cationic surfactants due to the lack of chromophores. These CS can be monitored by two-phase titration,[20] mass spectrometry,[21] high-performance liquid chromatography (HPLC),[22] or a GC-MS method by converting quaternary ammonium salt to its corresponding tertiary amines.[23] However, these methods have some limitations in their applicability, such as requiring tedious procedures, utilizing large quantity of toxic solvents, irreproducibility and signal instability.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1jm12818c

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Therefore, it is essential to develop simple methods to detect CS in water, such as chromo- or fluorogenic methods. Accordingly, there have been a few reports to adopt either fluorescent or UV changes.[24]

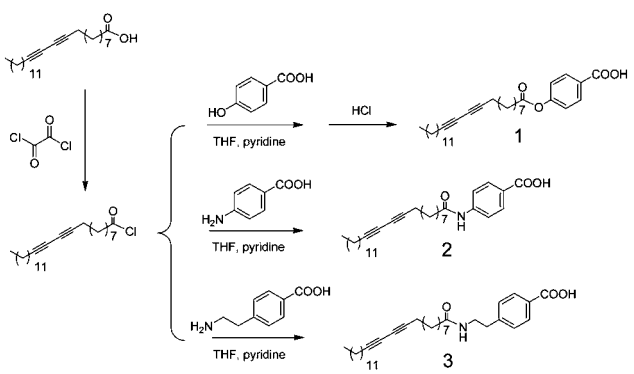
In this report, we synthesized three different representative PDAs which contain benzoic acid groups with various linkers. Unlike other PDA based sensors, these polymers showed diverse colorimetric changes *via* penetration processes. These PDAs displayed very unique colorimetric changes with different cationic surfactants: penetration of cationic surfactant into PDAs bearing benzoic acid groups can cause not only typical blue to red change but also blue to violet, blue to yellow or blue to orange color change. On the other hand, other ammonium salts containing short chains and anionic surfactants did not display any significant colorimetric changes. We systematically demonstrated that these novel findings can be used effectively to discriminate different cationic surfactants by using three different PDAs. Furthermore, theoretical calculations and transmission electron microscope (TEM) images also confirm these unique colorimetric changes. Most importantly, we believe our results can provide a new direction to design penetration induced multi-color sensors based on PDA polymers.

## Results and discussion

### Synthesis

For the synthesis of monomers, commercially available 10,12-pentacosadiynoic acid (PCDA) was reacted with oxalyl chloride to give corresponding acyl chloride, which was then reacted with 4-hydroxybenzoic acid, 4-aminobenzoic acid and 4-(2-aminoethyl)benzoic acid, respectively, to afford monomers **1**, **2** and **3** in 60, 88, 67% yields, respectively (Scheme 1). Monomer 2 was synthesized by modifying the reported procedure.[25] The detailed experimental procedures and characterization data can be found in the Experimental section and the NMR spectra of these monomers are provided in the ESI†.

Polymerization was carried out at room temperature by irradiating the solution with 254 nm UV light (1 mW $cm^{-2}$). UV irradiation of the suspensions derived from DA monomers resulted in the formation of stable and blue-colored PDA molecules, **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** (Fig. 1).




**Scheme 1** Synthesis of benzoic acid series.

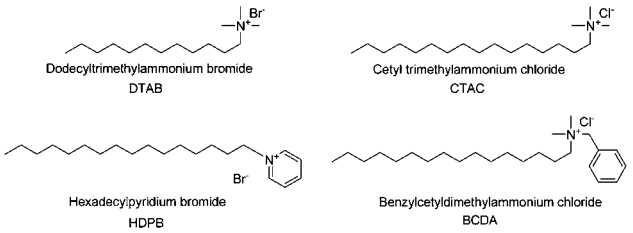



**Fig. 1** Structures of cationic surfactants used.

### The naked eye detection of cationic surfactants

As shown in Fig. 2, we investigated the colorimetric responses of **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** (250 μM) with cationic surfactants, other ammonium salts and anionic surfactants, such as cetyltrimethylammonium chloride (CTAC), dodecyltrimethylammonium bromide (DTAB), hexadecylpyridinium bromide (HDPB), benzylcetyldimethylammonium chloride (BCDA), sodium dodecyl sulfate (SDS), sodium dodecyl phosphate (SDP), sodium dodecylbenzenesulfonic acid (SDBS), $NH_4Cl$, $NH_3(CH_3)Cl$, $NH_2(CH_3)_2Cl$, $NH(CH_3)_3Cl$ and $N(CH_3)_4Br$ in HEPES (10 mM, pH 7.4). Among these various analytes, only the cationic surfactants (CTAC, DTAB, HDPB and BCDA) induced diverse color changes. No changes were observed with anionic surfactants (SDS, SDP and SDBS) or other ammonium salts. Interestingly, the four cationic surfactants (CTAC, DTAB, HDPB and BCDA) (500 mM) showed different color switches and furthermore, three different PDAs used in the current study displayed diverse colorimetric outputs. In Fig. 2, for **PCDA-HBA**, CTAC induced a blue-to-light yellow transition, DTAB induced a blue-to-red transition, HDPB

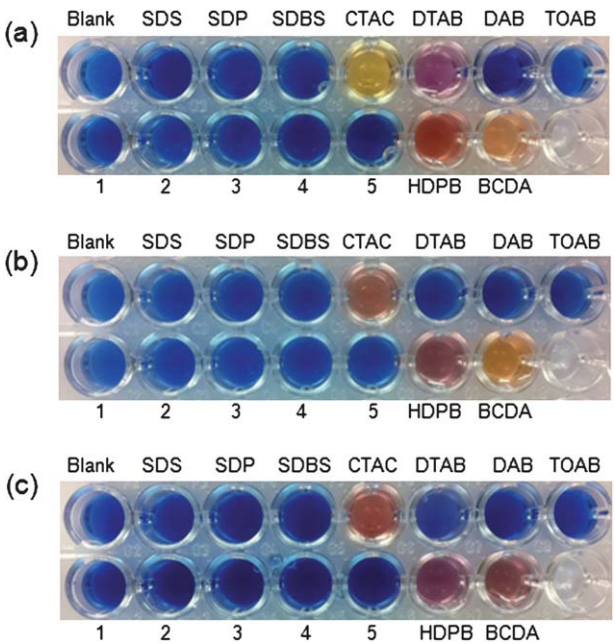



**Fig. 2** Colorimetric responses of **PCDA-HBA** (a), **PCDA-ABA** (b) and **PCDA-EBA** (c) (250 μM) in the presence of various surfactants (500 μM), such as SDS, SDP, SDBS, CTAC, DTAB, DAB, TOAB, 1; $NH_4Cl$, 2; $NH_3(CH_3)Cl$, 3; $NH_2(CH_3)_2Cl$, 4; $NH(CH_3)_3Cl$, 5; $N(CH_3)_4Br$, HDPB, BCDA in HEPES (10 mM, pH 7.4).

induced a blue-to-dark orange transition, and BCDA produced a blue-to-light yellow transition. On the other hand, for **PCDA-ABA**, CTAC induced a blue-to-orange transition, DTAB induced no color change, HDPB induced blue-to-Indian red transition, and BCDA produced a blue-to-yellow transition. **PCDA-EBA** displayed a blue-to-red transition with CTAC, no color change with DTAB, a blue-to-dark red transition with HDPB and a blue-to-violet red transition with BCDA.

### UV, fluorescent spectra and CR value

The spectroscopic behaviors of PDA solutions were investigated upon addition of cationic surfactants such as CTAC, DTAB, HDPB and BCDA. Using PCDA solutions diluted to a concentration of 100 μM, UV-Vis and fluorescence responses were monitored. Fig. 3 demonstrates the difference in the UV-Vis absorption spectra of **PCDA-HBA** with CTAC and DTAB. Before the addition of CTAC and DTAB, the **PCDA-HBA** spectra showed the typical blue color corresponding to an absorption maximum at 640 nm. The absorbance in the presence of CTAC was changed to a maximum at 520 nm, which is comparable to that of DTAB at 530 nm. Fig. 3 demonstrated the addition of CTAC induced blue to yellow color changes, whereas DTAB induced blue to purple to red color transitions. Furthermore, colorimetric change with CTAC occurred at a lower concentration compared to DTAB. These differences can be attributed to different degrees of perturbations by alkyl chain lengths of CTAC and DTAB, respectively.

The titration data of UV absorptions are explained in the ESI†. For example, addition of CTAC led to ratiometric changes in the UV/Vis spectra (Fig S8†). By increasing the concentration of CTAC (1–15 μM), the absorption intensities at 630 nm for **PCDA-HBA** decreased, while the absorption intensities at 517 nm increased.

The presence of cationic surfactants could also be examined by the changes in fluorescence because this colorimetric transition of the PDAs is accompanied by the generation of fluorescence (Fig. S8†). This is consistent with previous observation that the blue PDAs are non-fluorescent, while red PDAs are fluorescent.[25] Although the mechanistic origin for this fluorescence behavior has not been fully understood, it was proposed that the lowest excited state with $A_g$ symmetry of blue PDAs has the dipole forbidden emission, hence non-fluorescent.[26] Another reason for the fluorescence quenching of blue PDAs should be the excitation wavelength. In this study, 510 nm was used for excitation, which can be strongly absorbed by red PDAs, while little by blue

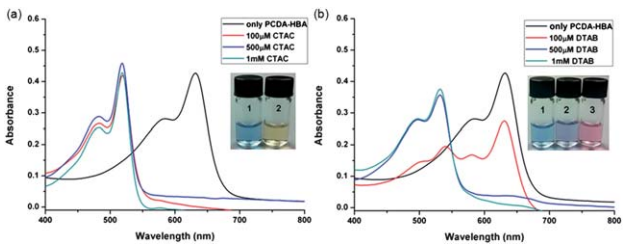



**Fig. 3** UV-Vis spectra of **PCDA-HBA** liposome in HEPES (10 mM, pH 7.4) with different concentrations of CTAC and DTAC: (a) color change of **PCDA-HBA** with CTAC; 1, blank; 2, 500 μM; (b) color change of **PCDA-HBA** with DTAB; 1, blank; 2, 500 μM; 3. 1 mM.

PDAs as seen in Fig. 3. Emission spectra of the three PDAs in HEPES (10 mM, pH 7.4) were accompanied by the fluorescence enhancements in response to various cationic surfactants. The fluorescence responses of **PCDA-HBA** with CTAC in HEPES solutions are presented in Fig. S8† with the maximum wavelength of 569 nm. As shown, the polymerized **PCDA-HBA** (100 μM) displayed large fluorescent enhancements with DTAB and BCDA. The detection limit of the PDAs (100 μM) was evaluated to be with a signal-to-noise ratio of 3 as shown in Fig. S7–S9†. Under optimum conditions, the extent of fluorescence increase of **PCDA-HBA** is linearly proportional to the concentration of CTAC from $2.0 \times 10^{-7}$ to $5.0 \times 10^{-6}$ M with a detection limit 0.4 ppm. Similarly, detection limits for **PCDA-ABA** and **PCDA-EBA** were calculated as 9.3 ppm and 2.1 ppm, respectively. The overall emission change upon the addition of DTAB was about 400-fold and the detection limit was estimated to be less than 1 μM by monitoring the emission change with different amounts of DTAB using 100 μM blue PDAs. The UV/Vis spectra and fluorescence spectra of **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** with CTAC, DTAB, HDPB and BCDA are explained in the ESI† (Fig. S8–S10).

**PCDA-HBA** was further treated with commercial detergents, such as shampoo, hair rinse and hair treatment. 100 μg of each commercial detergent was diluted with 1 mL of water, which was then added to the **PCDA-HBA** solution. The color changes of these solutions are explained in Fig. S11†. Hair rinse caused blue to red transition and hair treatment induced blue to violet color change.

As mentioned previously, PCDA vesicle solutions showed colorimetric changes between blue-to-red, blue-to-orange or blue-to-yellow when their conjugated backbone is perturbed from ordered to disordered states. To quantify the extent of the blue-to-red or blue-to-yellow color transitions within the polymer, the colorimetric response value (CR %) was calculated using the following equation:

$$CR = [(PB_0 - PB_1)/PB_0] \times 100$$

where $PB = A_{blue}/(A_{blue} + A_{red(yellow)})$, $A$ is the absorbance at either the blue component or the red (yellow) component in the UV-vis spectrum. Fig. S11† shows the representative CR%, calculated for CTAC, DTAB, HDPB and BCDA from the visible spectra recorded for these cationic surfactants. When the concentration of cationic surfactants increased from 10 μM to 1 mM, the solution displayed obvious color changes and the CR (%) of the resulted PCDA solutions increased upon the PDA binding with cationic surfactants as expected. The CR (%) value of the **PCDA-ABA** from DTAB was lower than those from other surfactants with the same concentration, presumably because its shorter chain length diminished the interactive stress caused by the **PDA-ABA** binding. Based on these results, **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** are considered to be sensitive to cationic surfactants and they are suitable for colorimetric sensors to detect cationic surfactants.

### Theoretical calculations

To get an insight on the color changes of **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** upon the addition of CTAC and DTAB,

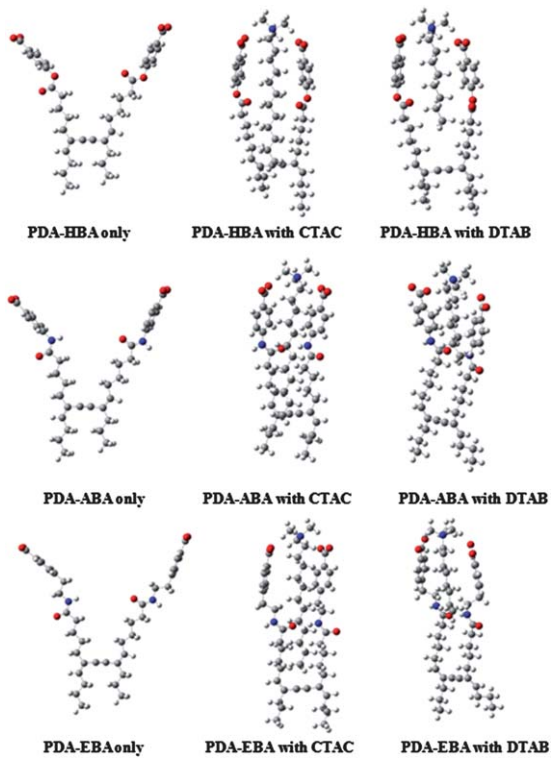



**Fig. 4** Calculated structures representing binding modes between HBA, ABA, EBA and CTAC, DTAB.

we investigated the absorption wavelength using time-dependent density functional theory (TDDFT) calculations. All the calculations were performed with 6-31G* basis sets and the Becke three-parameterized Lee–Yang–Parr (B3LYP) exchange functional using a suite of Gaussian 09 programs.[27] The binding modes between **PCDA-HBA/PCDA-ABA/PCDA-EBA** and CTAC/DTAB obtained by DFT calculations are shown in Fig. 4. As noted, both CTAC and DTAB have strong electrostatic interactions between the deprotonated –COO– group of the polymer, the positively charged ammonium group of CTAC/DTAB, and the van der Waals interactions between the aliphatic chains. The noticeable difference between CTAC and DTAB is the chain length. CTAC has a long chain to cause the partial distortion of the arrayed p orbitals of the backbone (ethylene) of the polymer, and hence induces color change more severely than DTAB does. This is in agreement with the experimental observations that CTAC induces color changes to all the polymers **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA**, however, DTAB induces a color change to only **PCDA-HBA**. **PCDA-ABA** and **PCDA-EBA** have H-bonding, while **PCDA-HBA** does not. DTAB has a short chain and does not seem to cause the distortion of the arrayed p orbitals of the backbone in H-bonded **PCDA-ABA** and **PCDA-EBA**, while it can cause some distortion of the p orbitals of the backbone in non-H-bonded **PCDA-HBA**. The simulated absorption spectra of **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** obtained by TDDFT calculations were shown in the ESI†. The maximum wavelengths of **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** were calculated at approximately 296 nm (Fig. 5). In binding with CTAC/DTAB, the wavelengths were blue-shifted at 278.4/278.7, 279.8/297.4, and 278.8/300.8 nm,

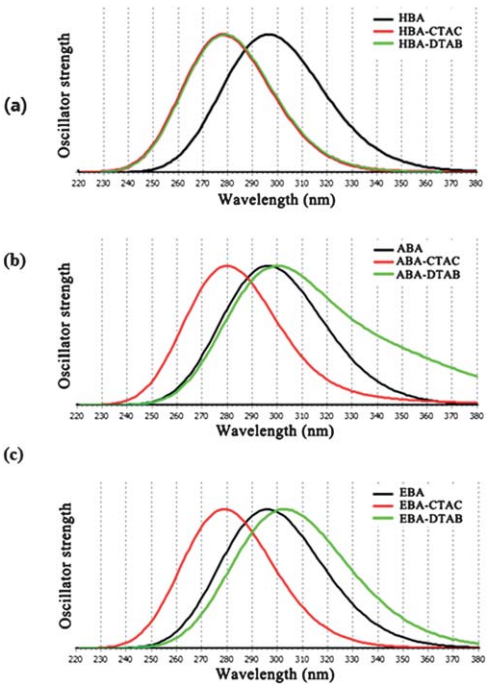



**Fig. 5** Simulated UV-Visible absorption spectra of (a) HBA, (b) ABA, and (c) EBA along with their complexes with CTAC and DTAB.

respectively. This tendency is qualitatively consistent with the color change of the PDAs from blue to yellow/red when they interact with CTAC and DTAB. Fig. 4 shows the calculated structures representing binding modes between **PDA-HBA/HBA/EBA** and CTAC/DTAB.

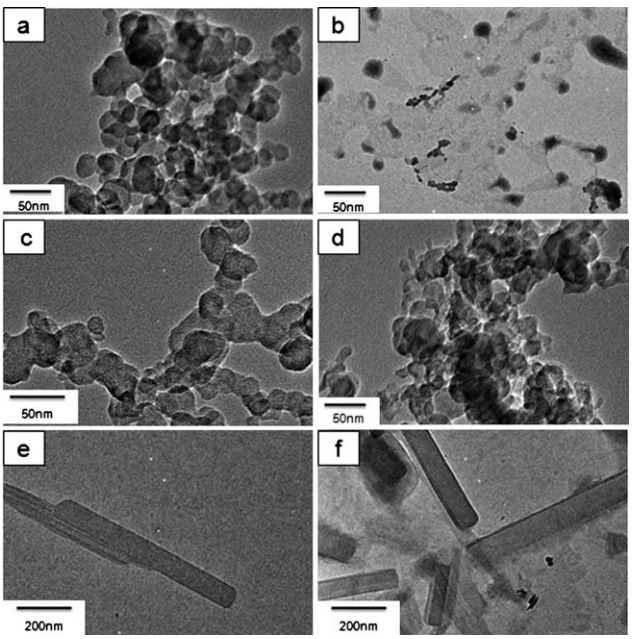



**Fig. 6** TEM images of (a) **PCDA-HBA** after 254 nm UV irradiation, (b) **PCDA-HBA** with 50 μM of CTAC, (c) **PCDA-ABA** after 254 nm UV irradiation, (d) **PCDA-ABA** with 50 μM of CTAC, (e) **PCDA-EBA** after 254 nm UV irradiation, and (f) **PCDA-EBA** with 50 μM of CTAC.

**Table 1** Results of DLS particle size measurements for **PCDA-HBA** and **PCDA-ABA**

| | Before irradiation/nm | After irradiation/nm | Standard deviation |
|---|---|---|---|
| **PCDA-HBA** | 131.8 | 113.1 | 1.2 |
| **PCDA-ABA** | 161.6 | 126.2 | 1.9 |

### TEM images and DLS data

Furthermore, the aggregation and morphology of the **PCDA-HBA**, **PCDA-ABA** and **PCDA-EBA** before and after the addition of cationic surfactants have been characterized with dynamic light scattering (DLS) and transmission electron microscopy (TEM). The apparent sizes of PDA solution aggregates in HEPES (10 mM, pH 7.4) were studied by a dynamic light scattering instrument at 25 °C. PDA solutions were diluted 5-fold and at least three measurements were performed for each solution.

**PCDA-HBA** liposomes after 254 nm UV irradiation were somewhat aggregated as shown in Fig. 6a. The addition of CTAC (50 μM) induced structureless images presented in Fig. 6b, which can be attributed to the penetration of CTAC into the liposomes. On the other hand, **PCDA-ABA** was able to maintain similar structures even after CTAC was added. Interestingly, **PCDA-EBA** displayed rod-like structures observed in Fig. 6e. **PCDA-EBA** still maintained its rod-like structures, however, the surface lines of few rods began to disappear upon the addition of CTAC. The structures of **PCDA-ABA** and **PCDA-EBA** after the addition of CTAC can be again attributed to the intramolecular hydrogen bonding between amide groups, which is absent in the case of **PCDA-HBA** (Table 1).

## Conclusions

In this report, we synthesized three different representative PDAs that contained benzoic acid groups with different linkers. By changing these linkers, we were able to modify the intramolecular hydrogen bonding abilities. Unlike other PDA based sensors reported so far, these polymers showed diverse colorimetric changes upon the addition of cationic surfactants. These PDAs displayed very unique colorimetric changes with different cationic surfactants, while other ammonium salts containing short chains and anionic surfactants did not display any significant colorimetric changes. Penetration processes of cationic surfactants into PDAs bearing benzoic acid groups can cause not only typical blue to red change but also blue to violet, blue to yellow or blue to orange color change. We systematically demonstrated that these novel findings can be used effectively to discriminate different cationic surfactants by using these three different PDAs. Furthermore, theoretical calculations also confirm these unique colorimetric changes. Most importantly, we believe that these results can be a new direction to design penetration induced multi-color sensors based on PDA polymers.

## Experimental section

### Materials and methods

10,12-Pentacosadiynoic acid (PCDA), 4-hydroxybenzoic acid, 4-aminobenzoic acid, 4-(2-aminoethyl)benzoic acid were purchased from Aldrich, South Korea. All organic solvents for synthesis were obtained from Aldrich and were used without further purification. $^{1}$H NMR and $^{13}$C NMR spectra were recorded using Brucker 250 or Varian 500 spectrometers. Mass spectra were obtained using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL). UV absorption spectra were obtained on UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).

### Synthesis of 4-(pentacosa-10,12-diynoyloxy)benzoic acid (1)

To a solution containing 1.01 g (2.69 mmol) of 10,12-pentacosadiynoic acid in 20 mL of methylene chloride, 1 mL (11.82 mmol, 4.4 eq) of oxalyl chloride was added dropwise at room temperature. The resulting solution was stirred at room temperature under $N_2$. After 1 hour, a catalytic amount of DMF was added to the solution and then stirred for an additional 6 hours. After evaporating the solvent *in vacuo*, the residue was redissolved in 10 mL of tetrahydrofuran (THF). The resulting solution was added dropwise to the solution containing 0.42 g (3.04 mmol, 1.1 eq) of 4-hydroxybenzoic acid dissolved in 15 mL THF and 5 mL pyridine in an ice bath. The mixture was stirred overnight at room temperature under $N_2$. Then the mixture was acidified with 1 M of HCl, and the white solid formed was filtered and purified by silica gel column chromatography ($CH_2Cl_2$ : $CH_3OH$ = 100 : 1) to give 0.80 g (59.98%) of the desired monomer. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta$ (ppm): 0.83–0.87 (t, $J$ = 6.3 Hz, 3H), 1.24–1.46 (m, 29H), 1.62–1.67 (m, 2H), 2.25–2.31 (m, 5H), 2.54–2.62 (t, $J$ =1.8 Hz, 2H) 7.20–7.23 (d, $J$ = 8.4 Hz, 2H), 7.96–7.99 (d, $J$ = 8.7 Hz, 2H). $^{13}$C NMR (500 MHz, $CDCl_3$) $\delta$ (ppm) 171.85, 170.80, 155.33, 132.07, 126.74, 122.01, 77.89, 77.67, 77.63, 77.49, 77.24, 76.99, 76.81, 65.58, 65.44, 34.61, 32.15, 29.88, 29.86, 29.84, 29.72, 29.58, 29.33, 29.30, 29.24, 29.12, 29.10, 28.97, 28.59, 28.51, 25.02, 22.92, 19.45, 19.43, 14.35. FAB HRMS $m/z$ = 517.3294 $[M + Na]^+$, calc. for $C_{32}H_{46}O_4Na$ = 517.3296.

### Synthesis of 4-pentacosa-10,12-diynamidobenzoic acid (2)

The diacetylene monomer was prepared from commercially available 10,12-pentacosadiynoic acid by amide formation. To a solution containing 0.51 g (1.3 mmol) of 10,12-pentacosadiynoic acid in 20 mL of methylene chloride, 0.35 mL (4.1 mmol, 3 eq) of oxalyl chloride was added dropwise at room temperature. The resulting solution was stirred at room temperature under $N_2$. After 1 hour, a catalytic amount of DMF was added to the solution, and the resulting solution was stirred for an additional 3–4 hours. After evaporating the solvent *in vacuo*, the residue was redissolved in 10 mL of THF. The resulting solution was added dropwise to the solution containing 0.27 g (2.0 mmol) of 4-aminobenzoic acid dissolved in 5 mL THF and 5 mL pyridine in an ice bath. This mixture was allowed to stir overnight at room temperature under $N_2$. The solvent was dropped to distilled water (DW) to give 0.59 g (89.9%) of the desired monomer. $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta$ (ppm): 0.78–0.83 (t, $J$ = 6.3 Hz, 3H), 1.22–1.58 (m, 32H), 1.93 (s, 1H), 2.12–2.19 (m, 6H), 7.68–7.71 (d, $J$ = 8.7 Hz, 2H), 7.85–7.88 (d, $J$ = 8.7 Hz, 2H), 10.19 (s, 1H), 12.69 (s, 1H). $^{13}$C NMR (500 MHz, DMSO-

$d_6$) $\delta$ (ppm) 172.48, 167.61, 144.06, 131.02, 125.49, 118.89, 78.65, 78.64, 66.04, 37.17, 31.99, 29.70, 29.64, 29.55, 29.40, 29.34, 29.28, 29.08, 29.01, 28.88, 28.85, 28.40, 28.38, 25.63, 22.79, 18.97, 14.64. FAB HRMS $m/z$ = 494.3634 $[M + H]^+$, calc. for $C_{32}H_{48}O_3N$ = 494.3636.

### Synthesis of 4-(2-pentacosa-10,12-diynamidoethyl)benzoic acid (3)

The diacetylene monomer was prepared from commercially available 10,12-pentacosadiynoic acid by amide formation. To a solution containing 0.50 g (1.34 mmol) of 10,12-pentacosadiynoic acid in 20 mL of methylene chloride, 0.35 mL (4.14 mmol, 3.1eq) of oxalyl chloride was added dropwise at room temperature. The resulting solution was stirred at room temperature under $N_2$. After 1 hour, a catalytic amount of DMF was added to the solution. The resulting solution was stirred for an additional 3–4 hours. After evaporation of the solvent *in vacuo*, the residue was redissolved in 10 mL of THF. The resulting solution was added dropwise to the solution containing 0.40 g (1.99 mmol) of 4-(2-aminoethyl)benzoic acid dissolved in 5 mL THF and 5 mL pyridine in an ice bath. The resulting mixture was stirred overnight at room temperature under $N_2$. The solvent was dropped to DW to give 0.47 g (67.22%) of the desired monomer. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ (ppm): 0.78–0.83 (t, $J$ = 6.3 Hz, 3H), 1.24–1.48 (m, 32H), 1.98–2.03 (t, $J$ = 7.5 Hz, 2H), 1.26–2.21 (t, $J$ = 7.5 Hz, 2H), 2.25–2.29 (t, $J$ = 6.9 Hz, 4H), 2.44–2.92 (t, $J$ = 7.2 Hz, 2H), 7.30–7.33 (d, $J$ = 8.4 Hz, 2H), 7.84–7.87 (d, $J$ = 8.4 Hz, 2H), 12.05 (s, 1H). $^{13}$C NMR (500 MHz, $CDCl_3$) $\delta$ (ppm) 173.48, 171.19, 145.58, 130.77, 129.17, 127.87, 76.99, 65.54, 65.45, 40.44, 36.99, 14.06, 32.15, 29.88, 29.86, 29.84, 29.71, 29.58, 29.33, 29.29, 29.22, 29.10, 28.98, 28.52, 24.88, 22.92, 19.44, 19.42, 14.35. FAB HRMS $m/z$ = 522.3947 $[M + H]^+$, calc. for $C_{34}H_{52}O_3N$ = 522.3949.

### Preparation of diacetylene assembly and photopolymerization

Preparation of lipid solution in aqueous solution was achieved by the following method. A monomer was dissolved in 1 mL of DMSO. While shaking 19 mL of HEPES buffer (10 mM, pH 7.4), the dissolved monomer was slowly added dropwise to yield a total monomer concentration of 1 mM. The solution was sonicated at 80 °C for 40 min and then was passed through a syringe filter to remove the lipid aggregates, and was cooled and stored at 0 °C overnight. The diacetylene monomer was polymerized by irradiation with 254 nm of UV light (1 mW cm$^{-2}$). Liposome containing 4-hydroxybenzoic acid was named **PCDA-HBA**, liposome containing 4-aminobenzoic acid was named **PCDA-ABA**, and liposome containing 4-aminoethyl benzoic acid was named **PCDA-EBA**.

### UV titrations

In a typical experiment, 100 μM of stock solution was prepared by placing 100 μL of the PDAs (1 mM) into a test tube, diluting the solution to 900 μL with 10 mM HEPES (pH 7.4). UV titration was performed using 100 μM solution of PDA-DPA in HEPES (10 mM, pH 7.4).

### Fluorescence titrations

Stock solutions of PDAs (100 μM) were prepared by mixing 100 μL PDAs (1 mM) and 900 μL of HEPES buffer (10 mM, pH 7.4). Both the excitation and emission slit widths were 5 nm per 5 nm.

### Dynamic light scattering (DLS) and transmission electron microscopy (TEM)

The apparent sizes of PDA solutions in HEPES (10 mM, pH 7.4) were observed by a dynamic light scattering instrument (ALV 5000-60X0) at 25 °C. Transmission electron microscopy (TEM) images were acquired on a JEM-2100F TEM operating at an acceleration voltage of 200 kV. TEM samples were prepared by depositing several drops of diluted solution onto standard carbon-coated copper grid, followed by drying under ambient conditions overnight.

## Acknowledgements

This work was supported by the National Research Foundation (NRF) grants (2011-0020450, 20110001334) and WCU (R31-2008-000-10010-0) Seoul R&BD Program (10816). The work at SKKU was supported by the NRF grant (no. 20110001211).

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