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Polydiacetylenes Bearing Boronic Acid Groups as Colorimetric and Fluorescence Sensors for Cationic Surfactants

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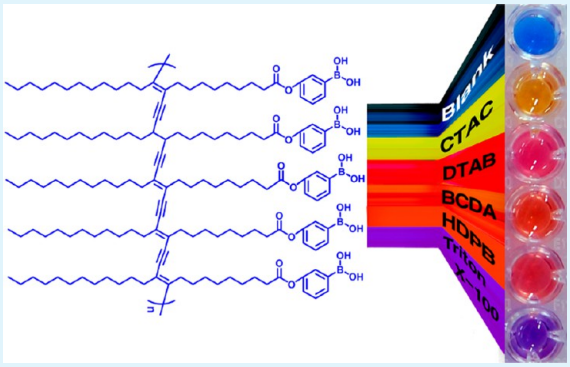
Supporting Information

ABSTRACT: A new polydiacetylene oxyphenylboronic acid (**PDA-OPBA-1**) bearing group was synthesized and showed diverse colorimetric changes, such as yellow, orange, and red, upon the addition of cationic surfactants at pH 7.4. On the other hand, anionic surfactants and simple ammonium salts did not show any color change. Specifically, color changes to yellow for cetyl trimethylammonium chloride (CTAC), red for dodecyl trimethylammonium bromide (DTAB), orange for benzylcetyldimethylammonium chloride (BCDA), and dark orange for hexadecylpyridium bromide (HDPB) are observed, respectively. Different head groups and alkyl chain lengths of cationic surfactants can be intelligently distinguished via a unique penetration process.



KEYWORDS: *polydiacetylene, PDA, colorimetric sensor, fluorescent sensor, polymer sensor, sensing cationic surfactants*

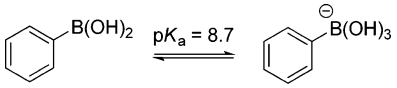
INTRODUCTION

Even though the preparation of polydiacetylene (PDA) material was reported by Wegner in 1969[1] as a new class of conjugated polymers,[2−6] the first sensing application was reported by Charych et al. in 1993.[7] During the last two decades, various PDAs have been synthesized and applied to sense diverse analytes,[8−11] which include Pb(II),[12−14] Zn(II),[15] K(I),[16] Hg(II),[17] Cu(II),[18] ATP/pyrophosphate,[19−21] toxin/bacteria,[22,23] HCl gas,[24] fake gasoline,[25] TNT,[26] and temperature,[27−29] etc.

PDAs are usually prepared by UV irradiation from self-assembled diacetylene (DA) monomers, which show a distinct blue color. These blue PDAs can undergo a color shift to a red phase upon environmental stimulation, which can be easily observed by the naked eye.[8−11] So far, most of the PDA based sensors show blue to red colorimetric changes; however, we recently reported that rather diverse color changes such as yellow, orange, or red can be observed upon the addition of surfactants.[30−32] We proposed that these diverse colorimetric changes are attributed to not only surface charge interactions but also a unique penetration process.

On the other hand, the pK_a of phenylboronic acid is known as 8.70 in water at 25 °C.[33] During the last two decades, boronic acid derivatives have been actively adopted for the development of carbohydrate selective fluorescent probes.[34−38] However, there are very few reports of PDAs bearing boronic acids.[39−41] Kim et al. reported bis PDAs bearing two boronic acid groups at each end, which was further fabricated as colored micropatterns on films, and these films showed different colorimetric changes with various organic solvents.[39]

Scheme 1. pK_a of Phenylboronic Acid



In the current study, we synthesized a new PCDA bearing boronic acid group, which was subsequently polymerized to its PDAs. **PDA-OPBA-1** (oxyphenylboronic acid (OPBA)) showed unique colorimetric changes with only cationic surfactants, while the addition of anionic surfactants did not induce any significant color change and the neutral surfactant Triton X-100 induced a violet color change. A color change to yellow for cetyl trimethylammonium chloride (CTAC), red color transition for dodecyl trimethylammonium bromide (DTAB), orange color transition for benzylcetyldimethylammonium chloride (BCDA), and dark orange change for hexadecylpyridium bromide (HDPB) are observed, respectively. Saccharides, such as glucose, lactose, maltose, sucrose, and maltotriose, did not induce any color change. In addition, **PDA-OPBA-1** preserves its blue color with simple ammonium salts. Selective colorimetric changes with cationic surfactants can be attributed to the charge interaction between ammonium

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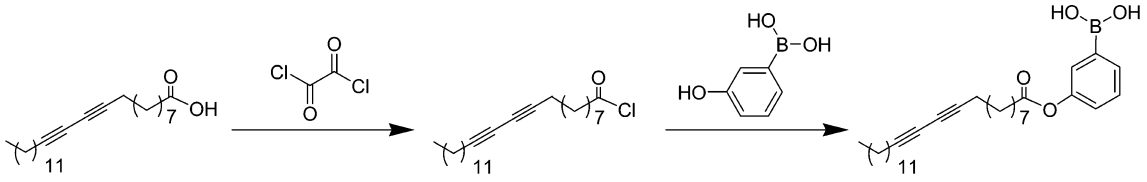
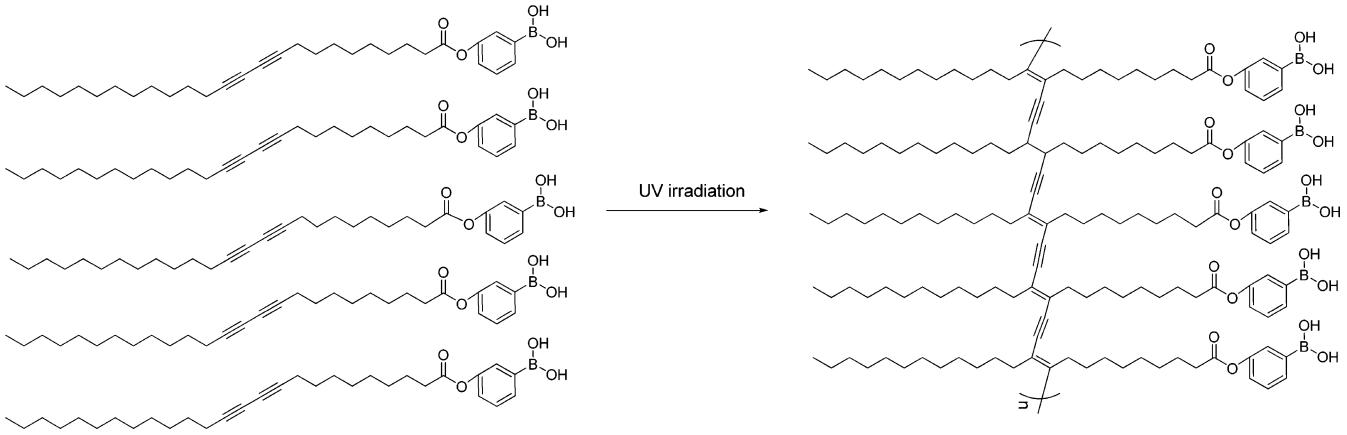
Scheme 2. Synthesis of 3-PCDA-Oxyphenylboronic Acid



Scheme 3. Preparation of PDA-OPBA-1



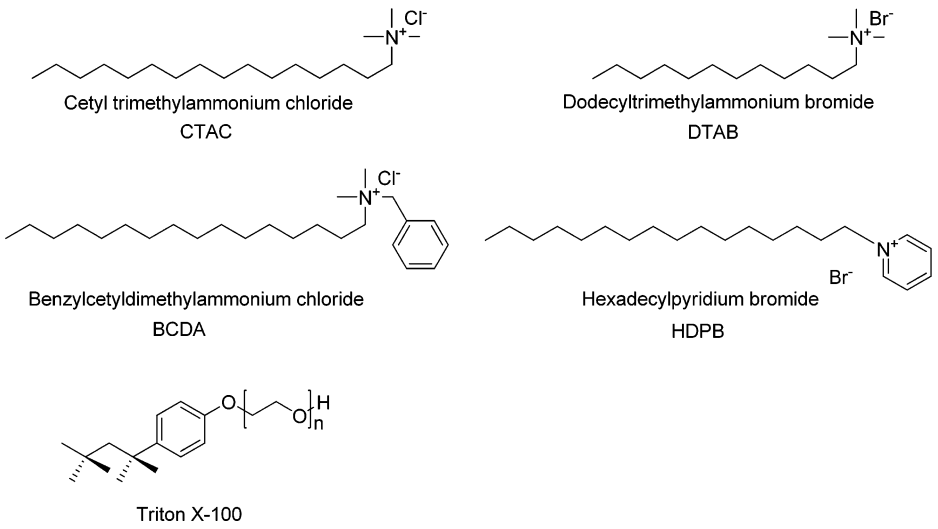


Figure 1. Structures of the surfactants.

groups in the cationic surfactants and boronate group in **PDA-OPBA-1** at pH 7.4 as well as a unique penetration process.

EXPERIMENTAL SECTION

Synthesis of 3-PCDA-Oxyphenylboronic Acid. Oxalyl chloride (0.4 mL, 4.8 mM) was added dropwise to the methylene chloride solution containing 0.502 g (1.34 mmol) of 10,12-pentacosadiynoic acid. After 1 h of stirring, one drop of dimethylformamide (DMF) was added to the solution and the resulting mixture was stirred for another 4 h. After the solvent was evaporated, to a solution containing 0.53 g (3.84 mmol) of 3-hydroxyphenyl boronic acid and 1.93 mL (13.8 mM) of triethylamine in 20 mL of THF was added to PCDA-Cl in an ice bath. The resulting solution was stirred overnight at room temperature under N_2. After the solvent was evaporated, the crude residue was dissolved in a small amount of methanol and added dropwise to water. The precipitates formed were collected and subjected to column chromatography on a silica gel with 10:1 methylene chloride:methanol as an eluent to give the desired product (yield = 63%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.83−0.88 (t, J = 7.5 Hz, 3H), 1.36−1.67 (m, 32H), 2.14−2.31 (m, 8H), 7.11−7.14 (d, J = 9 Hz, 1H), 7.34−7.39 (t, J = 7.8 Hz, 1H), 7.45 (s, 1H), 7.64−7.67 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 175.17, 150.71, 132.08, 129.27, 127.62, 124. 10, 78.68, 78.65, 73.03, 70.48, 66.04, 60.90, 34.18, 31.99, 29.69, 29.63, 29.55, 29.39, 29.29, 29.24, 29.19, 29.07, 29.05, 29.00, 28.97, 28.86, 28.84, 28.40, 28.37, 25.16, 25.08, 22.79, 18.96, 14.64. ESI MS m/z = 495.2 [M + H]$^+$, calc. For $C_{56}H_{97}N_2O_4^+$ = 495.3.

Prepation of Diacetylene Assembly and Photopolymerization (PDA-OPBA-1). A mixture containing 3-PCDA-oxyphenylboronic acid was dissolved in 20 mL of CH_2Cl_2 in a 2-neck round-bottom flask. The solvent was completely evaporated under nitrogen gas and a buffered aqueous solution (HEPES, 10 mM pH 7.4) was added to give a 1 mM lipid solution. The solution was sonicated at 80 °C for 40 min, passed through a syringe filter to remove the lipid aggregates, and was cooled and stored at 0 °C for overnight. The diacetylene monomer was polymerized by irradiation with 254 nm UV light (1 mW cm^{-2}) for 30 s.

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RESULTS AND DISCUSSION

For the synthesis of **PDA-OPBA-1**, oxalyl chloride was treated with 10,12-pentacosadiynoic acid to make its acid chloride derivative, which was then reacted with 3-hydroxyphenyl boronic acid to give 3-PCDA-oxyphenylboronic acid in 63% yield after the column chromatography with methylene chloride:methanol (10:1) (Scheme 2). This monomer (3-PCDA-oxyphenylboronic acid) was polymerized to **PDA-OPBA-1** by irradiating the solution with 254 nm UV light (1 mW/cm^2) for 30 s (Scheme 3). The detailed procedures are explained in the Experimental Section, and the ^{1}H and ^{13}C NMR spectra are explained in the Supporting Information.

The colorimetric changes, UV absorption, and fluorescence emission changes of **PDA-OPBA-1** (250 μM) were examined with cationic surfactants, anionic surfactants, neutral surfactant (Triton X-100), other ammonium salts, and saccharides in HEPES (10 mM, pH 7.4). The analytes (200 μM) examined are cetyltrimethylammonium chloride (CTAC), dodecyltrimethylammonium bromide (DTAB), benzylcetyldimethylammonium chloride (BCDA), hexadecylpyridium bromide (HDPB), sodium dodecyl sulfate (SDS), sodium dodecyl phosphate (SDP), sodium dodecylbenzenesulfonic acid (SDBS), NH_4Cl, $NH_3(CH_3)Cl$, $NH_2(CH_3)_2Cl$, $NH(CH_3)_3Cl$, $N(CH_3)_4Br$, glucose, lactose, maltose, sucrose, and maltotriose. Figure 1 explains the structures of cationic surfactants and Triton X-100. Among these various analytes, only the cationic surfactants (CTAC, DTAB, BCDA, and HDPB) induced diverse and distinct color changes from blue to yellow, orange, and red even though the neutral surfactant, Triton X-100, induced a violet color change as shown in Figure 2. No change was observed

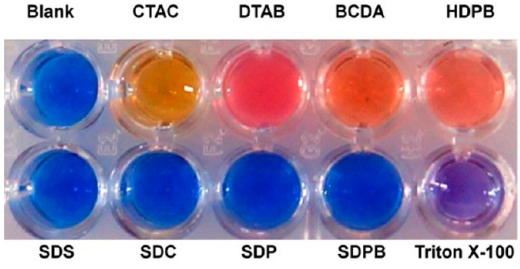

Figure 2. Colorimetric responses of PDA-oxyphenylboronic acid (250 μM) in the presence of various analytes (200 μM) in HEPES buffer (10 mM, pH 7.4).

with anionic surfactants (SDS, SDP, and SDBS), other ammonium salts (NH_4Cl, $NH_3(CH_3)Cl$, $NH_2(CH_3)_2Cl$, $NH(CH_3)_3Cl$, $N(CH_3)_4Br$), and saccharides (glucose, lactose, maltose, sucrose, and maltotriose) (Figures 2 and 3). The colorimetric changes upon the addition of 200 μM of cationic surfactants are as follows (Figure 2); a color change to yellow for cetyl trimethylammonium chloride (CTAC), red for dodecyl trimethylammonium bromide (DTAB), orange for benzylcetyldimethylammonium chloride (BCDA), and dark orange for hexadecylpyridium bromide (HDPB).

PDA-OPBA-1 can intelligently distinguish the different head groups of cationic surfactants and the different alkyl chain lengths. Tetramethylammonium bromide did not induce any color change and CTAC and DTAB clearly displayed different color changes, which bear the same headgroup but different alkyl chain length. As we previously explained,[30,31] these different colorimetric changes can be attributed to different degrees of perturbations by alkyl chain lengths of CTAC and

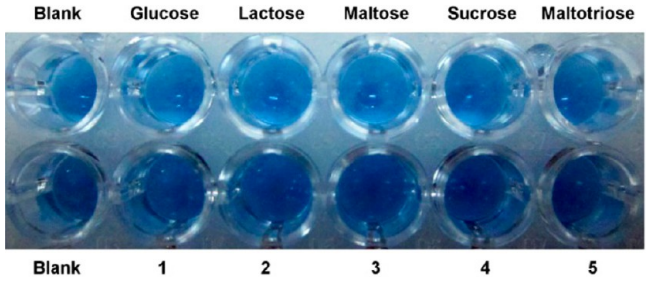

Figure 3. Colorimetric responses of **PDA-OPBA-1** (250 μM) in the presence of various analytes such as glucose, lactose, maltose, sucrose, maltotriose, (1) NH_4Cl, (2) $NH_3(CH_3)Cl$, (3) $NH_2(CH_3)_2Cl$, (4) $NH(CH_3)_3Cl$, and (5) $N(CH_3)_4Br$ in HEPES (10 mM, pH 7.4).

DTAB, respectively. Selective colorimetric changes with cationic surfactants can be attributed to the charge interaction between ammonium groups in the cationic surfactants and boronate group in **PDA-OPBA-1** at pH 7.4. Similar colorimetric changes were observed with surfactants at pH 7.0 and 8.0 as shown in Figure S3 (Supporting Information). Unfortunately, aggregation of **PDA-OPBA-1** was observed at acidic and basic pHs using different buffer solutions.

Even though it is known that boronic acid can bind with carbohydrates, **PDA-OPBA-1** did not show any significant change with the examination of saccharides (Figure 3). Either surface interaction between saccharides with boronic acid cannot provide enough perturbation on the backbone of PDA or these interactions may not occur efficiently due to the steric problem of the head groups. Figure 4 explains the colorimetric titrations with CTAC, DTAB, BCDA, and HDPB.

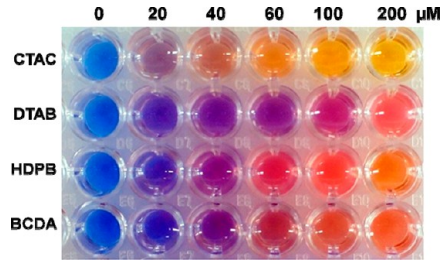

Figure 4. Colorimetric titrations of **PDA-OPBA-1** (250 μM) with various amounts of CTAC, DTAB, HDPB, and BCDA in HEPES buffer (10 mM, pH 7.4): 0, 20, 40, 60, 100, 200 μM.

UV−vis and fluorescence data of **PDA-OPBA-1** (100 μM) at pH 7.4 are explained in Figure 5. The addition of CTAC induced nice ratiometric changes in its UV absorption spectra (Figure 5a). In the absence of cationic surfactants, a typical blue color is observed with an absorption maximum of 640 nm. Upon the addition of CTAC, the absorption maximum was changed to 520 nm. Much lesser changes were observed with DTAB. On the other hand, HDPB and BCDA induced the new absorption maximum of 540 nm.

Large fluorescence enhancements with the maximum wavelength of 560 nm were accompanied upon the addition of these cationic surfactants as shown in Figure 5. In addition, cationic surfactants also induced significant fluorescence enhancements. It is known that the blue phase is non-fluorescent and the red phase is fluorescent. The reason for this fluorescence enhancement is not clear yet; however, it is proposed that the blue PDAs have A_g symmetry and they are nonfluorescent due to the dipole-forbidden transition during

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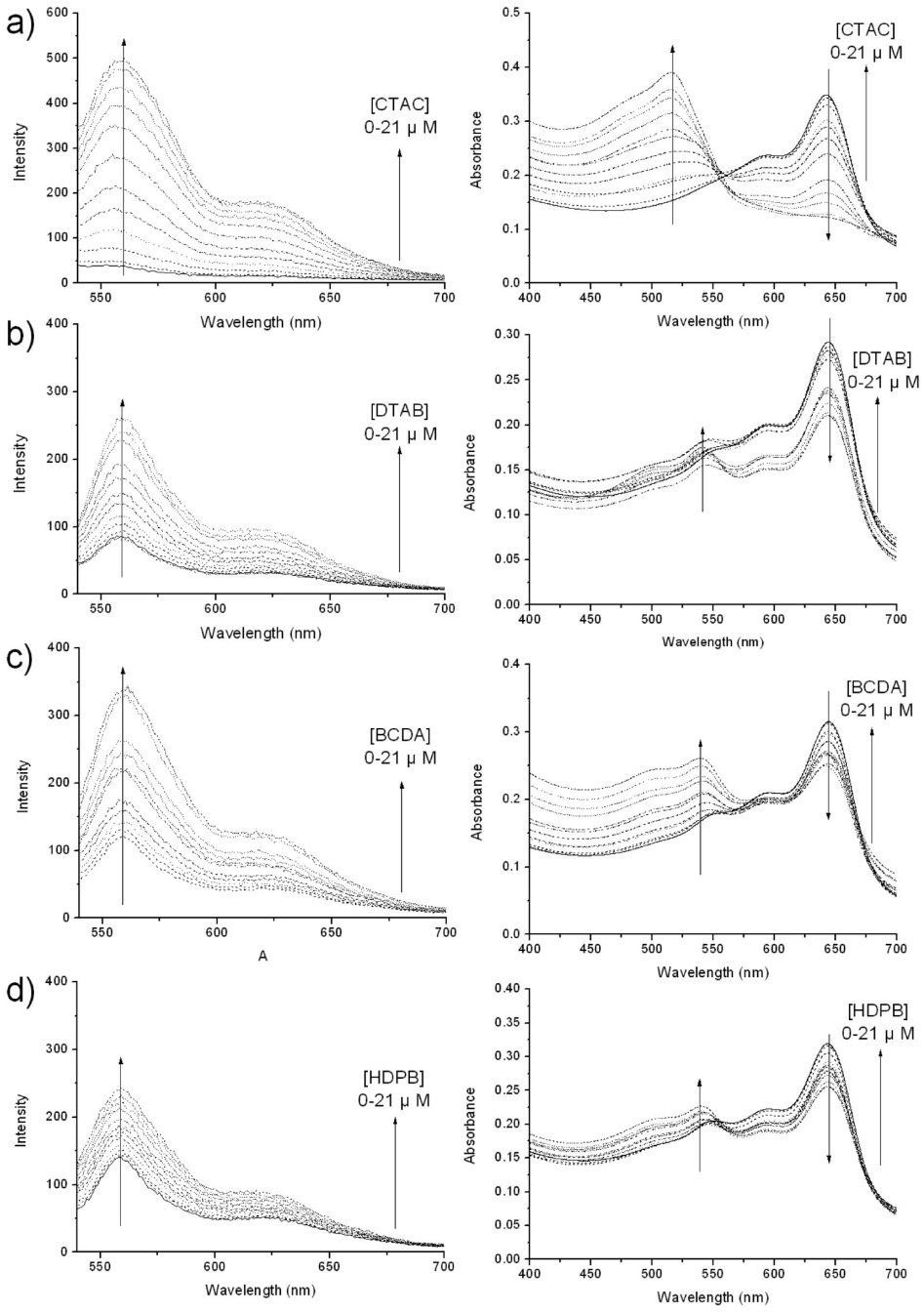

Figure 5. UV−vis and fluorescence spectra of **PDA-OPBA-1** (100 μM) with various amounts of CTAC, DTAB, BCDA, HDPB (0−21 μM) in HEPES buffer (10 mM, pH 7.4).

the emission from a singlet excited state. On the other hand, the red PDAs are fluorescent due to the lowest excited B_u state.[8−12,42]

The fluorescence increase of **PDA-OPBA-1** was linearly proportional to the concentration of CTAC from 1.0×10^{-6} to 2.1×10^{-5} M with a detection limit of 1.93×10^{-6} M.

Transmission electron microscopy (TEM) data are explained in Figure 6. **PDA-OPBA-1** displayed a thin-film-like structure (Figure 6a). On the other hand, the addition of CTAC induced significant changes in the TEM images (Figure 6b). Thick needle type images are observed, but structureless images are also observed. Ribonlike somewhat aggregated structures are observed with DTAB (Figure 6c) and HDPB (Figure 6e). With BCDA, larger thin films and their aggregates are observed. Scanning electron microscopy (SEM) data are also explained in Figure S4 (Supporting Information). **PDA-OPBA-1** showed platelike structures and similar thick needle type structures were observed upon the addition of CTAC as observed in TEM images.

CONCLUSIONS

In the current study, we synthesized new **PDA-OPBA-1** bearing boronic acid groups, which showed unique and diverse colorimetric changes only with cationic surfactants. Unique color changes to yellow for cetyl trimethylammonium chloride (CTAC), red for dodecyl trimethylammonium bromide (DTAB), orange for benzylcetyldimethylammonium chloride

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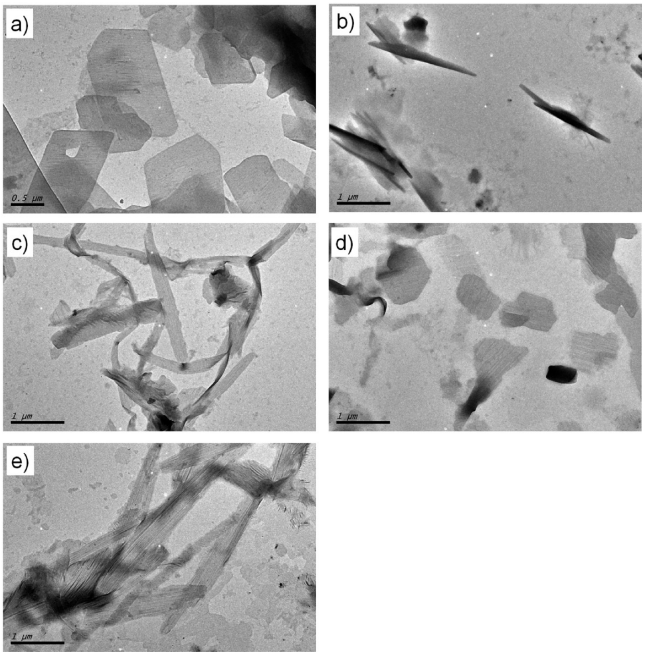

Figure 6. TEM images of (a) **PCDA-OPBA-1** after 254 nm UV irradiation, (b) **PCDA-OPBA-1** with 50 mM of CTAC, (c) **PCDA-OPBA-1** with 50 mM of DTAB, (d) **PCDA-OPBA-1** with 50 mM of BCDA, (e) **PCDA-OPBA-1** with 50 mM of HDPB.

(BCDA), and dark orange for hexadecylpyridium bromide (HDPB) are observed, respectively. On the other hand, anionic surfactants and simple ammonium salts did not show any color change. These changes were attributed to the partial negative charges on the boronate groups. In addition, different head groups and alkyl chains are also recognized especially via the penetration process. Lastly, we believe the current results can envision a new direction to design penetration induced multicolor sensors based on PDA polymers via introducing various head groups to PDAs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of monomer and SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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