Colorimetric and fluorometric detection of cationic surfactants based on conjugated polydiacetylene supramolecules†

Xiaoqiang Chen,[a] Jung Lee,[b] Min Jung Jou,[a] Jong-Man Kim*[b] and Juyoung Yoon*[a]

Received (in Cambridge, UK) 5th March 2009, Accepted 31st March 2009
First published as an Advance Article on the web 1st May 2009
DOI: 10.1039/b904542b

The polydiacetylenes derived from a hydroxybenzaldehyde substituted diacetylene monomer display a unique colorimetric change (blue to red) and large fluorescent enhancement in the presence of cetyl trimethylammonium salt.

Polydiacetylenes (PDAs), a family of conjugated polymers, are very intriguing materials in several ways.[1] Firstly, these polymers are generally prepared by UV irradiation of self-assembled diacetylene (DA) supramolecules. Secondly, if PDAs are prepared under optimal conditions, they, in many cases, display an intense blue color with a maximum absorption wavelength at *ca.* 640 nm. Thirdly, 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.[2] Accordingly, colorimetric detection of biologically, chemically and environmentally important target molecules such as DNAs, viruses, proteins, metal ions, organic solvents *etc.* have been reported.[2]

The development of selective optical signalling systems for ions has received considerable attention for a few decades due to their important roles in biological and environmental processes.[3] Cationic surfactants (CS) have been reported as environmental pollutants since they are heavily used as surface cleaning agents, such as soaps, shampoo, *etc.*[4] Accordingly, it is necessary to develop convenient methods for the detection of such quaternary ammonium surfactants. It is especially difficult to determine non-aromatic cationic surfactants due to their lack of chromophores. These cationic surfactants can be monitored by two-phase titration,[5] mass spectrometry,[6] high-performance liquid chromatography (HPLC),[7] or GC-MS methods by converting quaternary ammonium salts to their corresponding tertiary amines.[8] Due to the need for simple methods to detect these surfactants there have been some reports adopting either fluorescent or UV changes.[9] In this communication, we report the first example of a CS selective PDA sensor, which can display fluorescent enhancement as well as colorimetric change in the presence of CS.

It is known that the carbonyl oxygen in the aldehyde group can form a strong hydrogen bond with its adjacent phenolic hydrogen.[10] Owing to structural differences, hydroxybenzaldehyde (HBA) containing two DA monomers (**PCDA-HBA 1** and **PCDA-HBA 2**), shown in Fig. 1, are expected to adopt different headgroup interactions when they are transformed into PDA molecules (Fig. 2). Intermolecular-type hydrogen bonding between the hydroxyl groups and adjacent aldehyde carbonyl moieties could be developed in PDA supramolecules derived from **PCDA-HBA 1**. In contrast, **PCDA-HBA 2** can lead to intramolecular hydrogen bonds exclusively. Thus, it would be intriguing to investigate how the PDAs derived from two DA monomers that have structural similarity with different headgroup interactions respond to CS.

The DA monomers **PCDA-HBA 1** and **PCDA-HBA 2** were readily prepared from commercially available 10,12-pentacosadiynoic acid (PCDA) by coupling the acid with the corresponding hydroxybenzaldehydes. Experimental details and NMR spectra of the two monomers are provided in the ESI (Fig. S1–S4†).

In order to test the above hypothesis, the DA monomers **PCDA-HBA 1** and **PCDA-HBA 2** were converted to PDA supramolecules by employing a routine procedure. The detailed experimental procedure is explained in the ESI†. Polymerization was carried out at room temperature by irradiating the solution with 254 nm UV light (1 mW cm^{-2}). Fortunately, UV irradiation of the suspensions derived from both DA monomers resulted in the formation of stable, blue-colored PDA molecules.

Having prepared the PDA suspensions, we next investigated the colorimetric response of the conjugated polymers to cetyltrimethylammonium chloride (CTAC), dodecyltrimethylammonium bromide (DTAB) and other ions. Fig. 3a and b

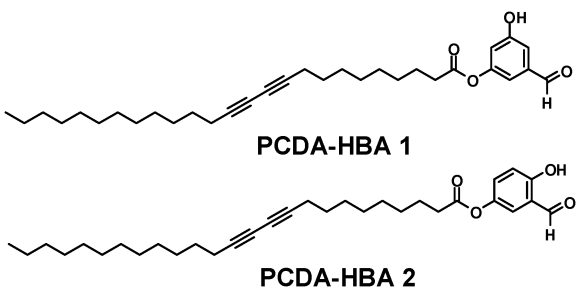

Fig. 1 Structures of diacetylene monomers investigated in the current study.

[a] *Department of Chemistry and Nano Science and Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea. E-mail: jyoon@ewha.ac.kr; Fax: +82-2-3277-3419; Tel: +82-2-3277-2400*
[b] *Department of Chemical Engineering, Institute of Nano Science and Technology, Hanyang University, Seoul, 133-791, Korea. E-mail: jmk@hanyang.ac.kr; Fax: +82-2-2298-4101; Tel: +82-2-2220-0522*

† Electronic supplementary information (ESI) available: Experimental details, NMR spectra of two monomers **PCDA-HBA 1** and **PCDA-HBA 2**, colorimetric assays of **PCDA-HBA 1**-derived polymer with anions and alcohols, fluorescent titrations of **PCDA-HBA 1**-derived polymers (50 μM), colorimetric assays of PCDA-Acid-derived polymer with various analytes and various concentration of CTAC, colorimetric responses of PDAs derived from the mixture of **PCDA-HBA 1** and **PCDA-HBA 2**/PCDA-Acid with different ratios. See DOI: 10.1039/b904542b

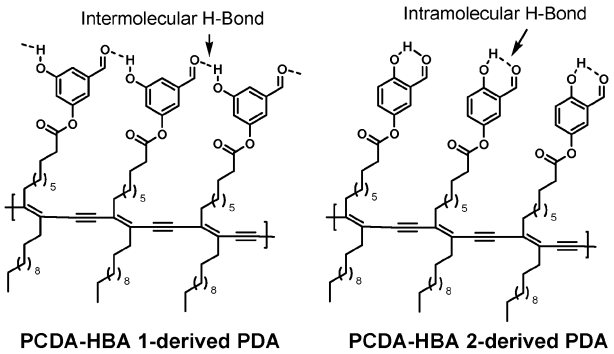

Fig. 2 Proposed structures of PDAs derived from **PCDA-HBA 1** and **PCDA-HBA 2**.

show the photographs of the PDA suspensions derived from **PCDA-HBA 1** and **PCDA-HBA 2** in the presence of various cations (100 μM), such as Li^+, Na^+, K^+, Cs^+, Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, CTAC, DTAB and SDS in HEPES (20 mM, pH 7.4)–DMSO (9 : 1, v/v). Sodium dodecyl sulfate (SDS) was also tested even though it is an anionic surfactant. Among these analytes, only CTAC and DTAB induce a clear blue-to-red transition of the PDAs prepared from **PCDA-HBA 1**. The effect of the counter ion is negligible because the addition of 100 μM NaF, NaCl, NaBr or NaI does not lead to a color change (Fig. S5†). In contrast, the suspensions containing the **PCDA-HBA 2**-derived polymers did not display any color change with these anions. Thus, it is clear from Fig. 3a and b that CTAC and DTAB promote colorimetric transition of the PDAs prepared from **PCDA-HBA 1** exclusively. Fig. 3c explains the concentration dependent colorimetric change of polymerized **PCDA-HBA 1** (1 mM) in the presence of various amounts of CTAC in HEPES (20 mM, pH 7.4)–DMSO (9 : 1, v/v). The colorimetric changes of **PCDA-HBA 1** were further examined with NH_4Cl, $NH_3(CH_3)Cl$, $NH_2(CH_3)_2Cl$, $NH(CH_3)_3Cl$, $N(CH_3)_4Br$, hexyltrimethylammonium bromide, pyridine, piperidine and piperazine in HEPES (20 mM, pH 7.4)–DMSO (9 : 1, v/v). As shown in Fig. 3d, none of these cations induced any colorimetric change. Non-ionic lipophilic molecules, such as hexanol, octanol and decanol did not induce a color change (Fig. S6†) either. Along with these observations, little colorimetric change in the presence of hexyltrimethylammonium bromide (Fig. 3d, trap 8) illustrates that long alkyl chains and ammonium groups are required for this unique sensing. DTAB displayed similar colorimetric changes to that of CTAC, which means that this system can be used for the detection of other CS with long alkyl chains in aqueous solution (Fig. 3a).

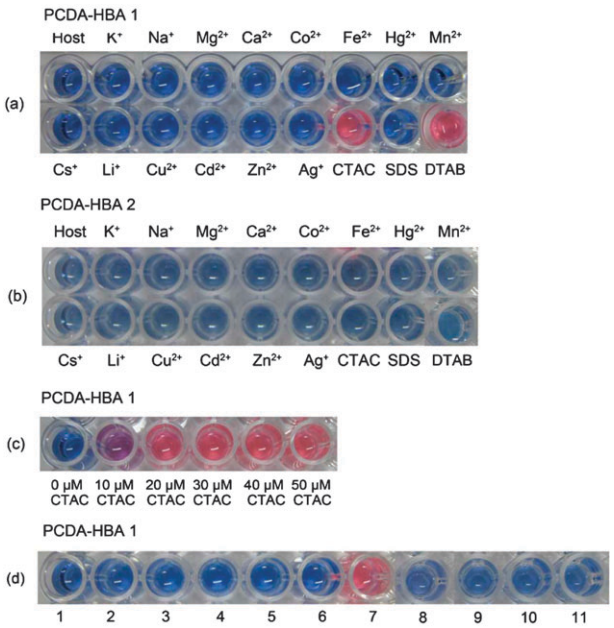

Fig. 3 Colorimetric responses of PDAs (1 mM) in the presence of analytes in HEPES–DMSO (9 : 1, v/v, 20 mM, pH 7.4). (a) PDAs derived from **PCDA-HBA 1** with various analytes (100 μM). (b) PDAs derived from **PCDA-HBA 2** with various analytes (100 μM). (c) Colorimetric titrations of **PCDA-HBA 1** with various amounts of CTAC. (d) Colorimetric changes of **PCDA-HBA 1** with various ammonium salts: 1, blank; 2, NH_4Cl; 3, $NH_3(CH_3)Cl$; 4, $NH_2(CH_3)_2Cl$; 5, $NH(CH_3)_3Cl$; 6, $N(CH_3)_4Br$; 7, CTAC; 8, hexyltrimethylammonium bromide; 9, pyridine; 10, piperidine; 11, piperazine.

The CTAC-induced phase transition of the PDAs was further monitored by visible absorption spectroscopy. As displayed in Fig. 4, addition of CTAC results in the decrease of the absorption at 620 nm with simultaneous increase of the absorption at 540 nm, a typical blue-to-red transition of the PDA sensors.

Since the blue-to-red transition of the PDAs is accompanied by the generation of fluorescence,[11] the CTAC-promoted reaction was also monitored by fluorescence spectroscopy (Fig. 5). As displayed in Fig. 5, the polymerized **PCDA-HBA 1** (1 mM) results in a large fluorescent enhancement with CTAC. The overall emission change upon the addition of CTAC was about 40-fold. Using rhodamine B as a standard, the quantum yield of the blue PDAs was calculated to be 6.3×10^{-5}, and the addition of 30 μM CTAC enhanced the quantum yield of the PDAs to 2.5×10^{-3}. The quantum yield of blue PDA, usually estimated to be $<10^{-5}$, is attributed to ultra-fast relaxation of the excited state.[12] The quantum yield of a red PDA film at room temperature is usually estimated to be <0.02.[12] The detection limit was estimated to be less than 1 μM by monitoring the emission change with different amounts of CTAC using 50 μM blue PDAs (Fig. S7†). The other ions listed in Fig. 3 were found to be inefficient in the promotion of the fluorescence

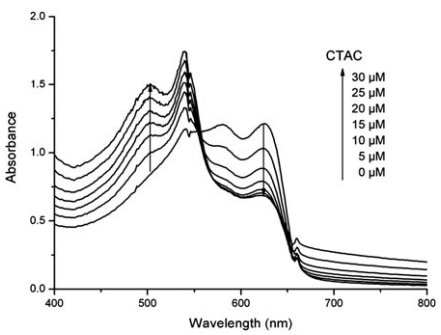

Fig. 4 Visible spectroscopic monitoring of **PCDA-HBA 1**-derived PDAs (1 mM) in the presence of various amounts of CTAC in HEPES–DMSO (9 : 1, v/v, 20 mM, pH 7.4).

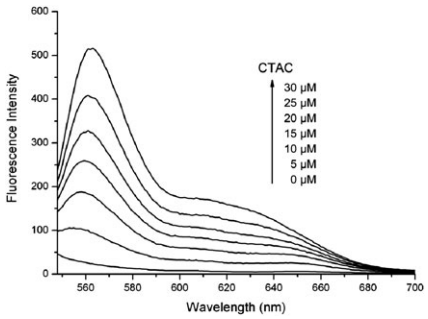

Fig. 5 Fluorescence titrations of **PCDA-HBA 1**-derived polymers (1 mM) with CTAC in HEPES–DMSO (9 : 1, v/v, 20 mM, pH 7.4; excitation at 535 nm, slit: 5 nm/5 nm).

enhancement of the polymer. The colorimetric and fluorescent changed images are also povided in Fig. S8†.

The selectivity of **PCDA-HBA 1**-derived PDAs for CTAC could be attributed to the unique head group interactions in aqueous solution as shown in Fig. 6. The addition of CTAC can disturb the regularly arrayed hydrogen bonding between head groups by ionic interactions between the phenolate of the head group and the ammonium group. The disruption of the hydrogen bonding could allow the release of the strain energy imposed on the alkyl side chains generated during polymerization.[13] The release of the side chain strain can cause partial distortion of the arrayed p-orbitals, leading to a decrease in the effective conjugation length of the polymer. On the other hand, the salicylaldehyde group of the polymerized **PCDA-HBA 2** is involved in intramolecular hydrogen bonding and the addition of CTAC has a negligible effect on the colorimetric transition of the PDA supramolecules.

Also, the behaviour of PCDA-Acid (10,12-pentacosadiynoic acid)-derived PDAs was examined towards various cations including CTAC. PCDA-Acid displayed a similar selectivity, however, the colorimetric change was much smaller than that of **PCDA-HBA 1**-derived PDAs (Fig. S9†), which can be due to the extensive headgroup hydrogen bonding in the PCDA-Acid derived PDAs.

Finally, the mixtures of **PCDA-HBA 1**, **PCDA-HBA 2** and PCDA-Acid were examined to find out the required fraction of **PCDA-HBA 1** for the detection of CS. In the presence of 100 μM CTAC, we checked the colorimetric responses of the PDAs derived from the mixtures with different ratios of **PCDA-HBA 1** and **PCDA-HBA 2** or PCDA-Acid. More than 60% **PCDA-HBA 1** was necessary to make a color change for the mixed vesicles of **PCDA-HBA 1** and **PCDA-HBA 2** (Fig. S10†). This result also provides the key proof for the importance of intermolecular hydrogen bonding. For the mixed vesicles of **PCDA-HBA 1** and PCDA-Acid, only 40% **PCDA-HBA 1** is necessary (Fig. S11†), which might be attributed to the possible intermolecular hydrogen bonding between **PCDA-HBA 1** and PCDA-Acid.

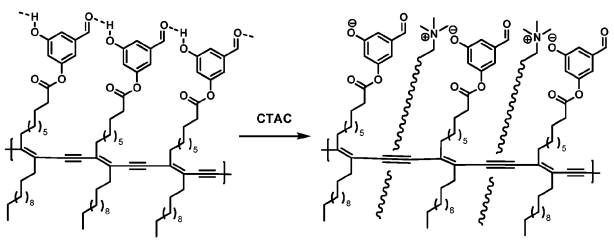

Fig. 6 Proposed headgroup structures of the PDAs derived from **PCDA-HBA 1** in the presence of CTAC.

In summary, we have developed a conceptually new PDA-based chemosensor system for the detection of CS in aqueous solution. The colorimetrically and fluorometrically responses of the conjugated polymers can be attributed to the disruption of the headgroup hydrogen bonding, for which both ammonium groups and long alkyl chains are required. Since this is, to the best of our knowledge, the first example of a PDA-based CS sensor, the results described above should be an important addition to PDA sensor systems.

This research was supported by the Korea Science and Engineering Foundation (KOSEF) grant (NRL) (R04-2007-000-2007-0, R04-2008-000-20047-0), the SRC program of KOSEF/MEST (R11-2005-008-02003-0) and WCU program (R31-2008-000-10010-0). J.L. and M.J.J. ackknowledge the BK21 fellowship.

Notes and references

1 (*a*) D. J. Ahn and J.-M. Kim, *Acc. Chem. Res.*, 2008, **41**, 805; (*b*) G. Wegner, *Makromol. Chem.*, 1972, **154**, 35; (*c*) Y. Okawa and M. Aono, *Nature*, 2001, **409**, 683; (*d*) A. Sun, J. W. Lauher and N. S. Goroff, *Science*, 2006, **312**, 1030; (*e*) Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt and C. J. Brinker, *Nature*, 2001, **410**, 913; (*f*) S. H. Kang, B. M. Jung and J. Y. Chang, *Adv. Mater.*, 2007, **19**, 2780.
2 (*a*) D. H. Charych, J. O. Nagy, W. Spevak and M. D. Bednarski, *Science*, 1993, **261**, 585; (*b*) J. Yoon, S. K. Chae and J.-M. Kim, *J. Am. Chem. Soc.*, 2007, **129**, 3038; (*c*) S. Kolusheva, O. Molt, M. Herm, T. Schrader and R. Jelinek, *J. Am. Chem. Soc.*, 2005, **127**, 10000; (*d*) G. Ma, A. M. Müller, C. J. bardeen and Q. Cheng, *Adv. Mater.*, 2006, **18**, 55; (*e*) C. Wang and Z. Ma, *Anal. Bioanal. Chem.*, 2005, **382**, 1708; (*f*) J. Lee, H.-J. Kim and J. Kim, *J. Am. Chem. Soc.*, 2008, **130**, 5010.
3 (*a*) C.-H. Lee, H. Miyaji, D.-W. Yoon and J. L. Sessler, *Chem. Commun.*, 2008, 24; (*b*) J. Yoon, S. K. Kim, N. J. Singh and K. S. Kim, *Chem. Soc. Rev.*, 2006, **35**, 355; (*c*) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094; (*d*) P. A. Gale, *Acc. Chem. Res.*, 2006, **39**, 465; (*e*) H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim and J. Yoon, *Chem. Soc. Rev.*, 2008, **37**, 1465; (*f*) S. K. Kim, D. H. Lee, J.-I. Hong and J. Yoon, *Acc. Chem. Res.*, 2009, **42**, 23.
4 H. P. Drobeck, *Surfactant Sci. Ser.*, 1994, **53**, 61.
5 R. A. Llenado and T. A. Neubecker, *Anal. Chem.*, 1983, **55**, 93.
6 A. P. Morrow, O. Kassim and F. O. Ayorinde, *Rapid Commun. Mass Spectrom.*, 2000, **15**, 767.
7 V. T. Wee and J. M. Kennedy, *Anal. Chem.*, 1982, **54**, 1631.
8 W. H. Ding and P. C. Tsai, *Anal. Chem.*, 2003, **75**, 1792.
9 (*a*) S. Motomizu, M. Oshima, Y. Gao, S. Ishihara and K. Uemura, *Analyst*, 1992, **117**, 1775; (*b*) X.-L. Diao, Y.-S. Xia, T.-L. Zhang, Y. Li and C.-Q. Zhu, *Anal. Bioanal. Chem.*, 2007, **388**, 1191; (*c*) H.-Y. Liu and W.-H. Ding, *J. Chromatogr. A*, 2004, **1025**, 303.
10 (*a*) K.-S. Lee, H.-J. Kim, G.-H. Kim, I. Shin and J.-I. Hong, *Org. Lett.*, 2008, **10**, 49; (*b*) S. K. Kwon, S. Kou, H. N. Kim, X. Chen, H. Hwang, S.-W. Nam, S. H. Kim, K. M. K. Swamy, S. Park and J. Yoon, *Tetrahedron Lett.*, 2008, **49**, 4102.
11 R. R. Chance, *Macromolecules*, 1980, **13**, 396.
12 M. A. Reppy and B. A. Pindzola, *Chem. Commun.*, 2007, 4317.
13 D.-C. Lee, S. K. Sahoo, A. L. Cholli and D. J. Sandman, *Macromolecules*, 2002, **35**, 4347.

