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Communications to the Editor

α-Cyclodextrin: A Molecule for Testing Colorimetric Reversibility of Polydiacetylene Supramolecules

Sumi Lee and Jong-Man Kim*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

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Polydiacetylenes (PDAs),[1−19] intriguing molecules that have the unique characteristics of self-assembly and π conjugation, are prepared by UV or γ-ray irradiation of molecularly ordered diacetylene monomers. The polymer backbone of PDAs, comprised of alternating ene−yne groups, is responsible for the intriguing stress-induced chromic (blue-to-red) transition. As such, PDAs have been extensively investigated as potential chemosensors.[20−23]

The majority of PDA-based chemosensors, reported thus far, function in an irreversible fashion. Accordingly, the blue-to-red color change that takes place when an external stimulus is applied is not reversed when the external stimulus is removed. PDA systems displaying colorimetric reversibility, especially in aqueous solution, are exceptionally rare. Although colorimetric reversibility of PDA supramolecules derived from a diacetylenic phospholipid has been described,[24] it is only reported to take place in a narrow temperature range. Recently, we proposed a new strategy for the preparation of PDAs which display a reversible colorimetric change from 25 to 100 °C that is based on the finding that strong headgroup interactions (both hydrogen bonding and aromatic interaction) are essential for complete reversibility.[25]

In the course of recent studies aimed at the development of PDA-based colorimetrically reversible chemosensors, we uncovered an interesting phenomenon. Specifically, we observed that α-cyclodextrin (α-CD) disrupts the ordered structures of PDA supramolecules derived from 10,12-pentacosadiynoic acid (PCDA) **1** by forming inclusion complexes (Figure 1).[26] In addition, α-CD induces the blue-to-red (or purple) color transition of PCDA-derived PDAs. Since the chromic transition of PDAs prepared from PCDA is irreversible, we were curious to find out if α-CD could disturb self-assembled PDA supramolecules that display reversible thermochromism. In this communication, we report a novel observation that α-CD induces blue-to-red color transition of PDAs in a selective and predictable way, depending on the structure of the diacetylene monomers. Specifically, we discovered that the α-CD induces blue-to-red color transition only on colorimetrically irreversible PDAs while it had no effect on the colorimetrically reversible PDAs, providing useful information about headgroup interactions.

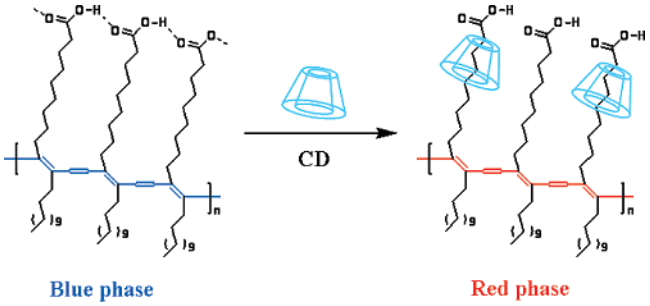

Figure 1. A schematic representation of the interaction between PDA and CD.

In Figure 2 is shown the diacetylene monomers that form PDAs that display either irreversible (IR) or reversible (R) thermochromism. Photographs of PDA solutions during thermal cycles are also presented. As explained above, irreversible color change of a PCDA **1**-derived PDA solution is demonstrated by monitoring of the chromic transition during the heating and cooling process. PDAs derived from PCDA−*m*BzA **2** show complete, thermally promoted colorimetric reversibility. In contrast, a solution of polymer vesicles prepared from PCDA−*m*CPE **3**, an ester analog of PCDA−*m*BzA **2**, does not display thermally stimulated colorimetric reversibility, indicating the significant role played by internal hydrogen-bondable amide groups in governing the reversibility of the color change.

* To whom correspondence should be addressed. E-mail: jmk@hanyang.ac.kr.

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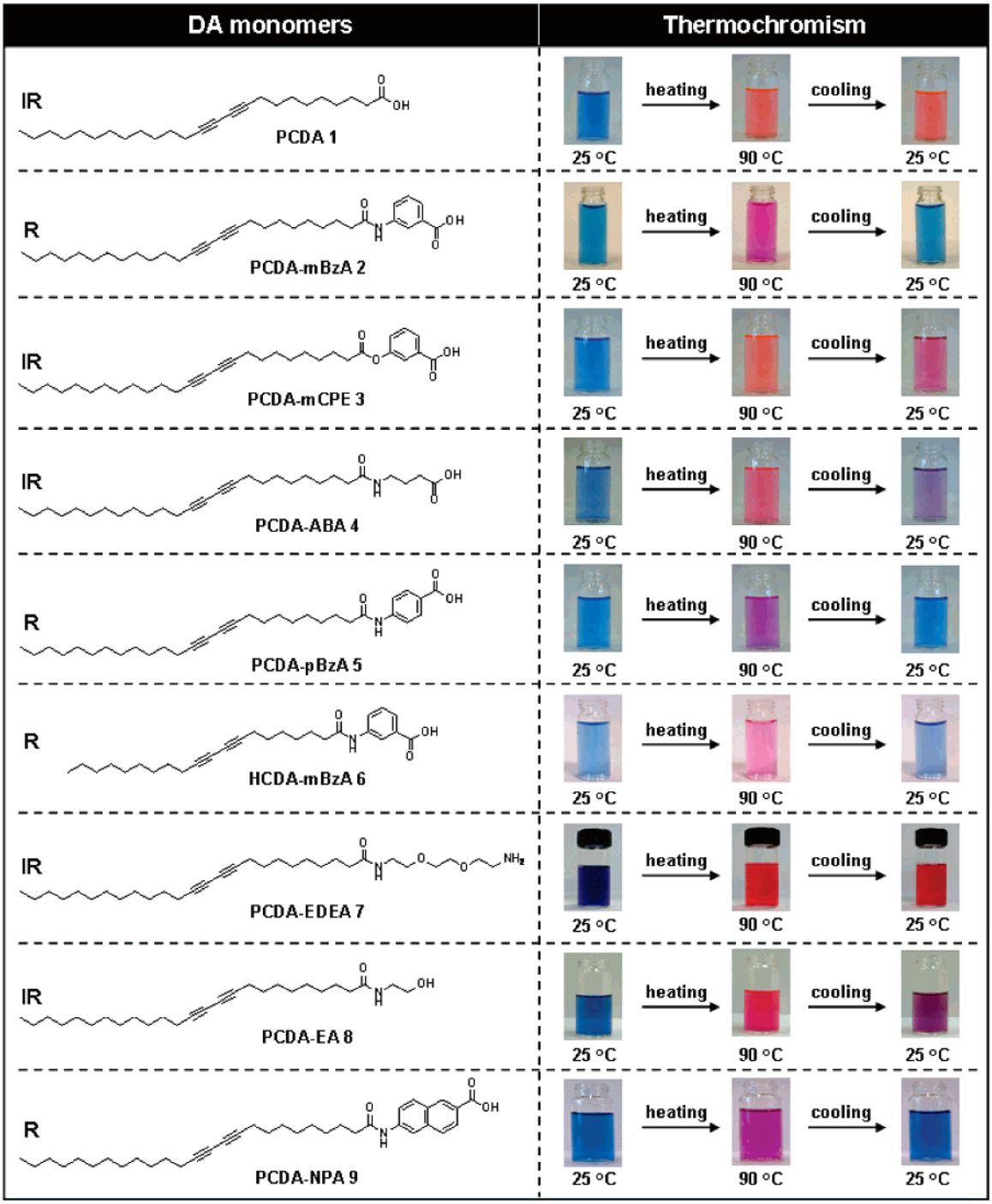

Figure 2. Diacetylene monomers and photographs of PDA solutions that display irreversible (IR) or reversible (R) thermochromism.

Another important factor in controlling the reversibility of thermochromism is aromatic interactions between the headgroups. The colorimetric irreversibility observed with PDAs made from PCDA−ABA (**4**) demonstrates this feature. The *para*-substituted diacetylene lipid PCDA−*p*BzA (**5**) generates stable, blue-colored polymer vesicles in aqueous solution that displays complete colorimetric reversibility. This observation indicates that the position of the carboxylic group does not affect the reversible thermochromism. Alkyl chain length was found to have a negligible effect on the colorimetric reversibility of the resulting polymerized vesicles, as demonstrated by the complete reversibility observed for solutions containing polymeric vesicles made from HCDA−*m*BzA **6**. The amine and hydroxy-terminated diacetylenic lipids PCDA−EDEA **(7)** and PCDA−EA (**8**), respectively, produce colorimetrically irreversible PDAs. Finally, the naphthyl group containing PDAs derived form PCDA−NPA **9** show reversible thermochromism.

In order to investigate the relationship between colorimetric reversibility and CD−PDA interactions, color changes of solutions containing 1 mM of PDAs derived from **1**−**9** containing 10 mM of CDs were monitored (Figure 3).[27−29] A blue-to-purple color transition is observed with a solution containing the PCDA **1**-derived PDAs and α-CD. Surprisingly, the CDs do not promote the color change of a PDA solution derived from PCDA−*m*BzA **2**; the original color remained unchanged even after a 24 h period. This observation demonstrates that the CDs are incapable of disturbing the ordered structure of the polymerized lipid assembly arising from PCDA−*m*BzA **2**.

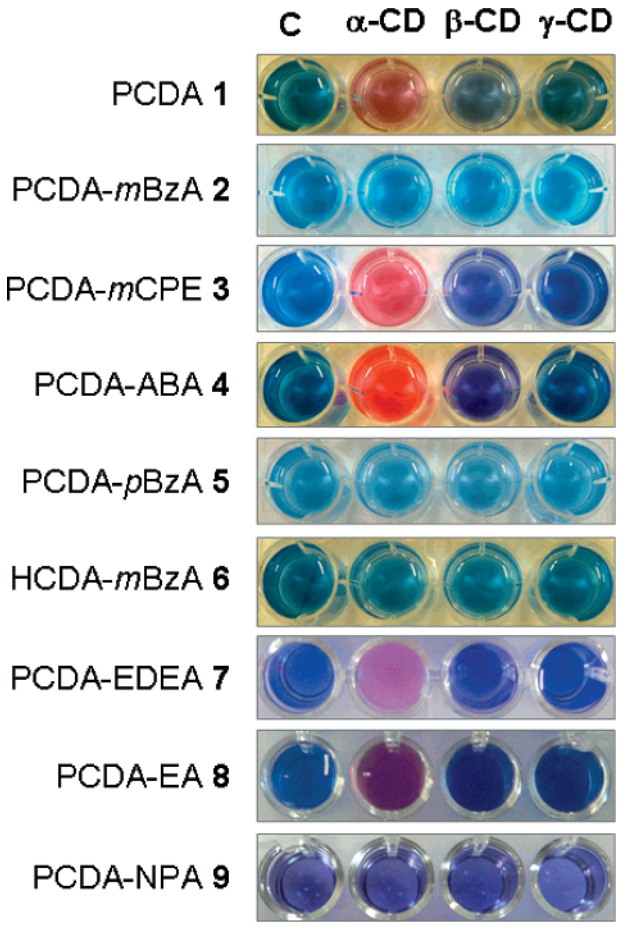

Figure 3. Photographs of PDA solutions (1 mM) in the presence of 10 mM of CDs. Photographs were taken after 10 min of incubation at 25 °C.

Interestingly, removal of the internal hydrogen-bonding amide groups has an important effect on the ability of CDs to promote the colorimetric change of PDAs. This is seen in the color transition of the PDA solution derived from PCDA−*m*CPE **3,** which changes to purple-red in the presence of α-CD. The absence of aromatic interactions is also important in governing whether or not α-CD induces a PDA color change. This is demonstrated by the PCDA−ABA **4**-derived PDA which undergoes the blue-to-red color transition. Moreover, the color of PDA solutions derived from PCDA−*p*BzA **5** and HCDA−*m*BzA **6** that display reversible thermochromism are not affected by α-CD. As expected, α-CD is found to efficiently promote color transition of colorimetrically irreversible PDAs arising from PCDA−EDEA **7** and PCDA-EA **8**. The PDA solution derived from naphthyl group containing diacetylene PCDA-NPA **9** does not undergo a color transition upon incubation with CDs.

Further information about the relationship between colorimetric reversibility and CD−PDA interactions was obtained by monitoring the visible absorption spectral changes of PDA solutions in the presence of CD. As displayed in Figure 4A, α-CD (10 mM) promotes superior visible absorption spectral change of PCDA **1**-derived PDAs compared to β- or γ-CD. Thus, a dramatic decrease in the intensity of the PDA band at 640 nm and a simultaneous increase in the intensity of the band at 550 nm are observed with α-CD. β- or γ-CD alters the PDA visible spectra to a much lesser extent than the α-CD. The CD-induced spectral change was not observed with the colorimetrically reversible PDAs derived from PCDA−*m*BzA **2** (Figure 4B). The colorimetric stability of PCDA−*m*BzA **2**-derived PDA was demonstrated further by exposure of the polymer solution

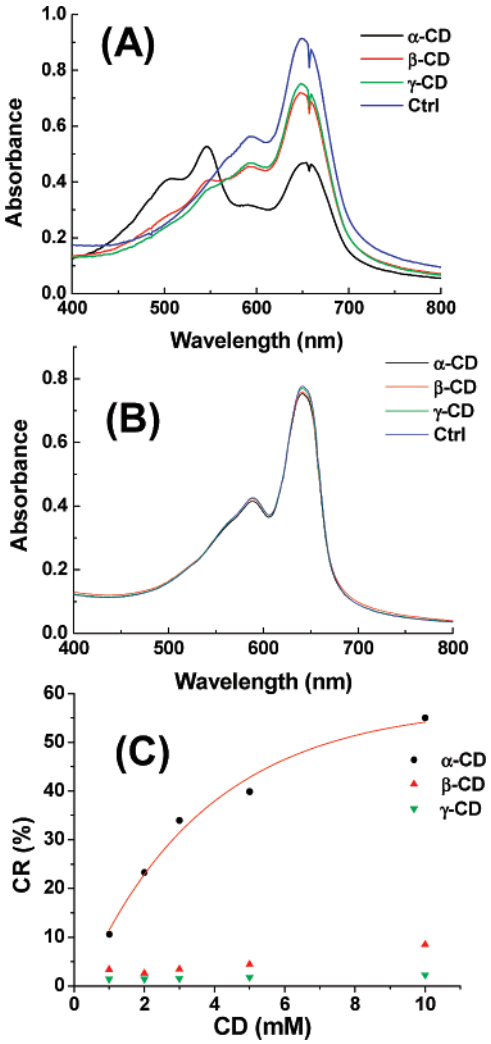

Figure 4. Visible absorption spectroscopic monitoring of PDA solutions derived from PCDA **1** (A) and PCDA-ABA **2** (B) in the presence of 10 mM of CD. Plots of colorimetric response (CR) of PCDA **1**-derived PDAs as a function of CD concentration (C). The data were obtained after 30 min of incubation.

to a high concentration of α-CD. No spectral change was monitored even in the presence of 50 mM of α-CD (data not shown). Figure 4C displays colorimetric response (CR) of PCDA **1**-derived PDA solutions plotted against the concentration of the CDs. The CR values are calculated from the well-defined equation, $CR = (PB_0 - PB_f)/PB_0 \times 100\%$, where PB_0 and PB_f are the percent blue before and after the color transition, respectively, and $PB = A_{640nm}/(A_{640nm} + A_{550nm})$. The plots show that α-CD has a much higher CR values than β- or γ-CD in all tested CD concentrations. This indicates that α-CD perturbs the effective conjugation length of the PDAs to a much greater extent than either β- or γ-CD.

A significant observation made in this effort is that, without exception, the color change of PDAs promoted by α-CD is irreversible. In addition, PDAs capable of strong headgroup interactions (e.g., PDAs derived from PCDA−*m*BzA **2**, PCDA−*p*BzA **5**, HCDA−*m*BzA **6,** and PCDA−NPA **9**) do not respond to the CDs. We previously described the results of in situ FTIR studies which showed that the headgroup hydrogen-bonding interactions in colorimetrically reversible PDAs are maintained during thermal cycles.[25] The current findings show that strong headgroup interactions present in PDAs that display reversible thermochromism are not disrupted by CDs.

In order to gain more information about the effect of CDs on the colorimetric reversibility of PDA supramolecules, a solution containing PDA vesicles derived from PCDA−*m*BzA **2** and α-CD (10 mM) was subjected to a thermal cycle (25−95−25 °C). If α-CD is capable of disturbing the highly ordered lipid assembly by forming inclusion complexes at higher temperature, the PDAs should no longer exhibit reversible thermochromism. In fact, the colorimetric reversibility of PCDA−*m*BzA **2**-derived PDAs was not affected by α-CD. Thus, it appears that even at higer temperatures α-CD does not perturb the ordered structures of PDAs that have strong headgroup interactions and, as a result, are colorimetrically reversible.

In conclusion, this study has led to the discovery of a receptor molecule that can be used to distinguish between two types of PDA supramolecules that undergo colorimetric changes. α-CD was found to promote a blue-to-purple or blue-to-red color transition of only those PDAs that are colorimetrically irreversible. In contrast, α-CD was unable to induce a color change of PDAs that display reversible thermochromism behavior. The results of this effort, which provide useful information about headgroup interactions in PDA supramolecules, have resulted in an important diagnostic methodology. *Specifically, if α-CD causes color transition, the PDA is not colorimetrically irreversible.*

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(27) 10,12-Pentacosadiynoic acid (PCDA) **1** and its derivatives **2**−**6** and **9** (ref 25), PCDA−EDEA **7** (ref 19), and PCDA-EA **8** (ref 10) were previously reported.
(28) Preparation of PDA vesicles in aqueous solution was achieved by employing the general method described in ref 5. Briefly, a diacetylene monomer was dissolved in a small amount of DMF, and the organic solution was injected into deionized water to yield a total monomer concentration of 1 mM. The sample was then heated at 80 °C for 15 min and probe-sonicated for 15 min. The resulting solution was filtered through a 0.8 μm filter and the filtrate was cooled at 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solution with 254 nm UV light (1 mW/cm^2).
(29) The effect of CD on color transition of PDAs was investigated by adding α-, β-, or γ-CD (10 mM final concentration) to PDA solutions and the color changes were monitored by both visible absorption spectroscopy and the naked eyes.

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