A Chiral Switch Based on Dye-Intercalated Layer-by-layer Assembled DNA Film

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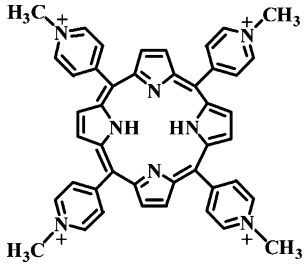
Molecular switches have attracted persistent interest due to their potential applications in data storage[1,2] and sensor systems.[3,4] So far, various switching systems have been proposed based on photochromism,[5−7] fluorescence,[8] intersystem crossing,[9,10] electrochemically and photochemically induced changes in liquid crystals,[11,12] and photoinduced electron transfer and energy transfer.[13−15] Chiral switches, which endow the reversible change in chirality with the other reversible properties, are particularly attractive. Many chiraloptical switches[16] and chiral memory systems[17] have been proposed. In this communication, we propose a dye−DNA film system which exhibits a reversible change in chirality. DNA (deoxyribonucleic acid) is one of the most fascinating polymers found in nature and shows many unique structural and functional properties such as double-helix, chirality, and intercalation with certain dye molecules. Some achiral dye molecules can exhibit induced chirality when intercalated into DNA.[18] Previously, we have found that cationic dye TMPyP (tetrakis (*N*-methylpyridinium-4-yl) porphine, Scheme 1) could be incorporated into a layer-by-layer (LbL) assembled DNA/PAH (poly (allylamine hydrochloride)) film, and

Scheme 1. Chemical Structure of Free Base TMPyP



induced circular dichroism (ICD) of TMPyP could be observed due to the intercalation of TMPyP into DNA.[19] In this work, we further found that the induced chirality of TMPyP−DNA/PAH film could be wiped off by exposing the film to HCl gas. Interestingly, the ICD could be recovered by subsequently exposing the film to NH_3 gas and water vapor. This process could be repeated many times and the film could be used as a chiral switch.

An LbL assembled DNA/PAH film was formed by the alternating deposition of a quartz plate in DNA (Wako Pure Chemical Industries, pH 6.8, 1 mM) and PAH aqueous solutions (average mol. wt. 8500−11000, Nippon Boseki, pH 2.4, 1 mg/mL). Loading of TMPyP into the DNA/PAH film was performed by immersing the DNA/PAH film into a TMPyP aqueous solution (pH 9.0, 1 mM) for 10 min. In investigating chiral switching, the film was subjected to HCl gas, NH_3 gas, and water vapor for 30 s, respectively, and then the UV−vis and CD spectra were recorded immediately after exposure. Water vapor was obtained by heating the water at about 70 °C. To get correct CD spectra, the film was placed perpendicular to the light path and rotated within the film plane to avoid the polarization-dependent reflections and eliminate the possible angle dependence of the CD signals.[20,21]

Figure 1B shows the UV−Vis spectral changes of the TMPyP-incorporated DNA/PAH film in various conditions. The as-prepared film shows two distinct absorption bands at 439 and 262 nm, which can be attributed to the Soret band of free base TMPyP and the characteristic absorption of DNA, respectively. When the film was exposed to HCl gas, its color changed from yellow to green in a few seconds and the maximum absorption band of TMPyP was red-shifted to 455 nm. This band can be ascribed to the protonation of the TMPyP in the inner nitrogen atom.[22] Further verification of the protonation of TMPyP can be from the fact that four peaks

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(1) Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1686.
(2) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658.
(3) Cao, Y.; Zheng, Q.; Chen, C.; Huang, Z. *Tetrahedron Lett.* **2003**, *44*, 4751.
(4) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968.
(5) Tamai, N.; Saika, T.; Shimidzu, T.; Irie, M. *J. Phys. Chem.* **1996**, *100*, 4689.
(6) De Jong, J. J. D.; Lucas, L. N.; Kellogg, R. M.; van Esch, J. H.; Feringa, B. L. *Science* **2004**, *304*, 278.
(7) Tsivgoulis, G. M.; Lehn, J. M. *Adv. Mater.* **1997**, *9*, 39.
(8) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E.; *Chem. Rev.* **1997**, *97*, 1515.
(9) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H.; *J. Am. Chem. Soc.* **1999**, *121*, 7726.
(10) Kuciauskas, D.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1998**, *120*, 10880.
(11) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N.; *J. Am. Chem. Soc.* **1997**, *119*, 7791.
(12) Kurihara, S.; Sakamoto, A.; Nonaka, T. *Macromolecules* **1998**, *31*, 4648.
(13) Van Patten, P. G.; Shreve, A. P.; Lindsey, J. S.; Donohoe, R. J. *J. Phys. Chem. B.* **1998**, *102*, 4209.
(14) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578.
(15) Kijima, H.; Takeuchi, M.; Robertson, A.; Shinkai, S.; Cooper, C.; James, T. D. *Chem. Commun.* **1999**, 2011.
(16) (a) Feringa, B. L.; Huck, N. P. M.; Schoevaars, A. M. *Adv. Mater.* **1996**, *8*, 681. (b) Feringa, B. L.; Huck, N. P. M.; van Doren, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 9929.
(17) Lauceri, R.; Raudino, A.; Scolaro, L. M.; Micali, N.; Purrello, R. *J. Am. Chem. Soc.* **2002**, *124*, 894.
(18) Pasternack, R. F.; Gibbs, E. J. In *Metal−DNA Chemistry*; Tullius, T., Ed.; ACS Symposium Series 402; American Chemical Society: Washington, DC, 1989; pp 59−73. (b) Pasternack, R. F.; Gibbs, E. J.; Collings, P. J.; dePaula, J. C.; Turzo, L. C.; Terracina, A. *J. Am. Chem. Soc.* **1998**, *120*, 5873. (c) Pasternack, R. F.; Giannetto, A.; Pagano, P.; Gibbs, E. J. *J. Am. Chem. Soc.* **1991**, *113*, 7799. (d) Pasternack, R. F.; Gibbs, E. J.; Bruzewicz, D.; Stewart, D.; Engstrom, K. S. *J. Am. Chem. Soc.* **2002**, *124*, 3533. (e) Pasternack, R. F.; Bustamante, C.; Collings, P. J.; Giannetto, A.; Gibbs, E. J. *J. Am. Chem. Soc.* **1993**, *115*, 5393.
(19) Lang, J.; Liu, M. *J. Phys. Chem. B* **1999**, *103*, 11393.
(20) Spitz, C.; Dahne, S.; Ouart, A.; Abraham, H. W. *J. Phys. Chem. B* **2000**, *104*, 8664.
(21) Yuan, J.; Liu, M. *J. Am. Chem. Soc.* **2003**, *125*, 5051.
(22) Chernia, Z.; Gill, D. *Langmuir* **1999**, *15*, 1625.

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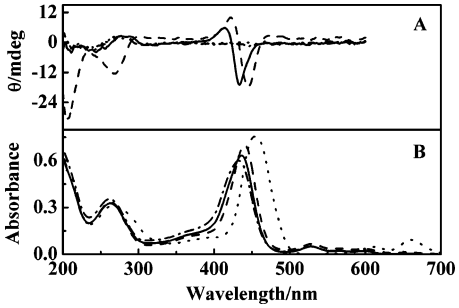


Figure 1. CD (A) and UV−Vis (B) spectral changes of the TMPyP-incorporated DNA/PAH multilayer film in various conditions: dashed line, as-prepared; dotted line, exposed to HCl gas; dashed-dotted line, exposed to NH_3 gas; and solid line, exposed to water vapor.

of the Q-band diminished into two after exposure to HCl gas. The absorption band of the DNA base pair is also slightly red-shifted and its bandwidth increased, indicating the protonation of base pairs. This protonated TMPyP/DNA/PAH film was stable and would not change in the air for a long time. However, if this film was exposed to NH_3 gas, its color recovered immediately and the Soret band appeared at 432 nm. This band is slightly blue shifted about 7 nm as compared with the as-prepared TMPyP-incorporated DNA/PAH film. This suggests that reorganization may occur for the dye molecules in the film during the vapor-exposing process. The peak position and bandwidth of the DNA base pair are also recovered precisely. When such film was further alternately exposed to HCl and NH_3 gases, the spectral changes went on in a manner similar to the above, indicating that the process was reversible. In addition, when the NH_3-exposed TMPyP/DNA/PAH film was further exposed to a water vapor, the Soret band of TMPyP appeared at 434 nm without changing the positions of the other absorptions.

Figure 1A shows the CD spectral changes of the TMPyP-incorporated DNA/PAH film with the corresponding UV−Vis spectral changes. In the CD spectrum of as-prepared TMPyP-incorporated DNA/PAH film, two CD bands are observed. One is ascribed to TMPyP where positive and negative Cotton effects are observed at 423 and 445 nm, respectively, with a crossover at 432 nm. The other is the negative Cotton effect at 268 nm. The positive and negative Cotton effects at 423 and 445 nm can be ascribed to the electrostatically attached and intercalated TMPyP, respectively.[23] The negative Cotton effect appearing at 268 nm can be assigned to DNA. The Cotton effect for DNA is obviously different from the spectrum measured in solution. This is because DNA formed the so-called polymer-salt induced (PSI) aggregate during the assembly with PAH in the film.[24,25] Upon exposing the film to HCl gas, however, the ICD of TMPyP disappeared completely. When we exposed the film to NH_3 gas, although the UV−Vis spectrum was recovered, as shown in Figure 1B, the ICD signal did not recover. Surprisingly, we found that the ICD could

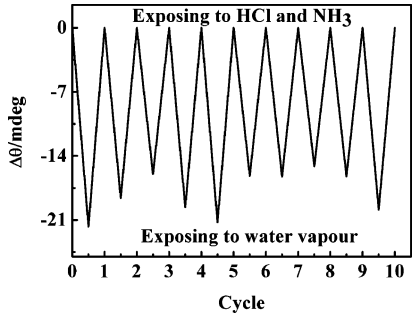


Figure 2. ICD magnitude ($\Delta\theta = \theta_{434\ nm} - \theta_{414\ nm}$) of TMPyP as a function of exposing cycles.

be recovered by subsequently exposing the film to the water vapor. After the film was treated by the water vapor, positive and negative Cotton effects were observed at 414 and 434 nm, respectively, as shown in Figure 1A. Such process can be repeated. That is, when the film was further exposed to HCl gas, the ICD disappeared and it could be recovered by exposing the film to NH_3 and subsequent water vapor. The magnitude of the negative ICD of TMPyP was plotted as a function of exposing cycles and is shown in Figure 2. It was clear that the ICD of TMPyP become near zero when the film was exposed to HCl, whereas it recovered nearly to its original intensity when the film was exposed to water vapor. Such process can be repeated more than 10 cycles. After 10 cycles, a reduction of the ICD intensity was observed.

It is well-known that TMPyP can interact strongly with DNA through intercalation, which results in the ICD of TMPyP.[18] Upon exposing the film to HCl gas, TMPyP and DNA base pairs were protonated. Such protonation could cause strong electrostatic repulsion between the protonated TMPyP and DNA base, which resulted in the change of DNA conformation and the deintercalation of TMPyP. Therefore, no ICD was observed when the film was exposed to HCl gas. When the film was exposed to NH_3 gas, although TMPyP and DNA recovered to its original charge, the deintercalated TMPyP could not interact with DNA yet. When the film was further exposed to water vapor, DNA could return to its natural B-form conformation and the water molecules help TMPyP interact with the base pairs of DNA, which resulted in the appearance of ICD of TMPyP. This can be verified from the CD spectra of the TMPyP/DNA in the UV region. The film after treatment with water vapor shows negative and splitting positive Cotton effecs at 250, 276 and 288 nm, respectively, with a crossover at 262 nm, which is similar to that of TMPyP intercalated DNA in solution.[26] We could get the reproducible results in many experiments.

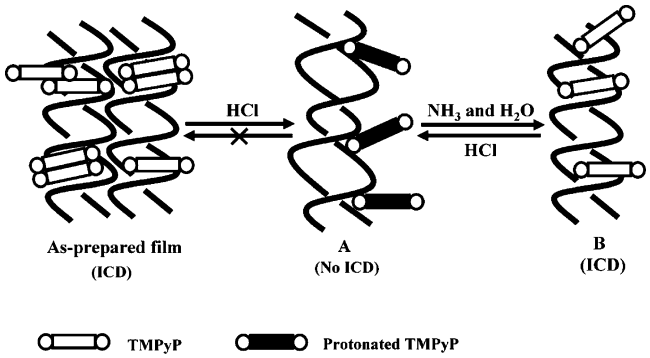
It is noted that both the CD signal of DNA and the ICD signal of TMPyP appeared in a different manner between the as-prepared film and the film exposed to water vapor. The latter CD spectra can be repeated many times upon alternate exposure to HCl−NH_3 and water vapor. This is because, at the beginning, the DNA/PAH film forms a PSI film containing aggregate of DNA.[25] When the film was immersed into the aqueous TMPyP solution, TMPyP could incorporate into the film

(23) (a) Pasternack, R. F.; Garrity, P.; Ehrlich, B.; Davis, C. B.; Gibbs, E. J.; Orloff, G.; Giartosio, A.; Turano, C. *Nucl. Acids Res.* **1986**, *14*, 5919. (b) Pasternack, R. F.; Gibbs, E. J.; Villafranca, J. J. *Biochemistry* **1983**, *2*, 2406.
(24) Pasternack, R. F. *Chirality* **2003**, *15*, 329.
(25) Phillips, C. L.; Mickols, W. E.; Maestre, M. F.; Tinoco, I., Jr. *Biochemistry* **1986**, *25*, 7803.
(26) Fiel, R. J.; Howard, J. C.; Nark, E. H.; Datta Gupta, N. *Nucl. Acids Res.* **1979**, *6*, 3093.

through intercalation and electrostatic interactions. In this process, TMPyP itself could also aggregate and showed red shift in the UV−Vis spectra. Therefore, we observed the position of ICD peak at a longer wavelength for the as-prepared film. When the film was exposed to HCl both the aggregation between DNA and TMPyP were destroyed. After the film was recovered by NH_3, although a typical UV−Vis absorption band of free base of TMPyP was obtained, the interaction between DNA and TMPyP was not recovered. When the film was exposed to water vapor, the water molecules helped TMPyP to electrostatically attach and intercalate with DNA. This resulted in the recovery of the ICD band in the film. Here, water vapor played an important role in getting back the ICD of the TMPyP in the film. To further verify the function of the water vapor, we immersed the NH_3-exposed film into deionized water and ICD was really found to be recovered. However, it was unavoidable that TMPyP dissolved from the film into the solution. The vapor adsorption proved to be a more effective way in realizing the recovery of the chirality. Such process is illustrated by Scheme 2. The as-prepared film contains the aggregate of both DNA and TMPyP. When the film is exposed to HCl gas, the aggregation is destroyed. In addition, both the DNA and TMPyP can be protonated by exposure to excess HCl to form state A, where deintercalation of TMPyP from DNA occurs and ICD disappears. When the film in state A is further exposed to NH_3 and water vapor consecutively, the film can change into state B, where the ICD of TMPyP appears. The reversible changes between state A and B can be realized by subsequently exposing the film to HCl, NH_3, and water. This process can be repeated many times and a chiral switch between these two states is realized.

In summary, we have successfully realized a chiral switch based on the TMPyP-incorporated LbL assembled DNA/PAH film. The TMPyP-incorporated DNA/PAH film showed induced chirality in the Soret band of TMPyP. The ICD could be wiped off by exposing the film to HCl gas and recovered by subsequently exposing the film to NH_3 and water vapor. In realizing the recovery of the ICD, the water vapor played an important role. DNA/PAH film was very stable in a larger pH range, therefore, the results provide an important clue to realize a chiral switch using a supramolecular film system based on biological compounds.

Scheme 2. Illustration of Reversible Change of Color and Chirality in the TMPyP-Incorporated DNA/PAH Multilayer Film



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