hydrolysate of TB-1-Me exhibited a Cotton effect of $\Delta\epsilon$ +2.3 at 380 nm, thus showing the C-21 configuration to be *S*.

The tunichrome B-1 structure is derived from three (3,4,5-trihydroxyphenyl)alanine units; the reducing nature is due to the pyrogallol moiety which is known to reduce V(V) to V(IV) and form complexes.[26] Elucidation of the TB-1 structure will now enable one to clarify the long-standing controversy regarding the biological/biochemical function of tunichromes and vanadium and the mechanism of V(V) to V(III) reduction in ascidians, as well as to contribute to the understanding of the biochemical role of vanadium in animals.[27]

**Supplementary Material Available:** $^1H$ and $^{13}C$ NMR, mass spectra, NOEs, Cosy, and other spectroscopic data of **1** and derivatives (8 pages). Ordering information is given on any current masthead page.

(26) (a) Wenger, P.; Duckert, R.; Blancpain, C. P. *Helv. Chim. Acta* **1937**, *20*, 1427. (b) Kustin, K.; Liu, S.-T.; Nicolini, C.; Toppen, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 7410.

(27) Boyd, D. W.; Kustin, K. *Adv. Inorg. Biochem.* **1985**, *6* (9), 311.

# Electrochemical Permeability Control through a Bilayer-Immobilized Film Containing Redox Sites

Yoshio Okahata,* Gen-ichiro Enna, Kazuhiro Taguchi, and Takahiro Seki

*Department of Polymer Chemistry
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152, Japan*

We report reversible permeability control through a viologen (4,4′-bipyridinium)-containing bilayer-film deposited on a platinum minigrid sheet by electrochemical redox reactions.

Developments of various types of permeability-controllable membranes have been prompted by the need to study the transport properties of biological membranes.[1] We have reported the signal-receptive, bilayer-coated capsule membranes, in which bilayers supported on the physically strong polymer membrane act as a valve of slow releases from the capsule responding to stimuli from the outside.[2] Kunitake, Kajiyama, and co-workers recently prepared various types of the bilayer-immobilized films[3,4]

(1) (a) Maeda, M.; Kimura, M.; Hareyama, Y.; Inoue, S. *J. Am. Chem. Soc.* **1984**, *106*, 250–251. (b) Ishihara, K.; Muramoto, N.; Shinohara, I. *J. Appl. Polym. Sci.* **1984**, *29*, 211–217. (c) Kinoshita, T.; Sato, M.; Takizawa, A.; Tsujita, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 929–930. (d) Osada, Y.; Takeuchi, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 303–308. (e) Anzai, J.; Ueno, A.; Sasaki, H.; Shimokawa, K.; Osa, T. *Macromol. Chem. Rapid Commun.* **1983**, *4*, 731–734.

(2) (a) Okahata, Y.; Lim. H.-J.; Nakamura, G.; Hachiya, S. *J. Am. Chem. Soc.* **1983**, *105*, 4855–4859. (b) Okahata, Y.; Lim, H.-J.; Hachiya, S.; Nakamura, G. *J. Membr. Sci.* **1984**, *19*, 237–247. (c) Okahata, Y.; Lim. H.-J.; Hachiya, S. *J. Chem. Soc., Perkin Trans. 2* **1984**, 989–994. (d) Okahata, Y.; Lim. H.-J. *J. Am. Chem. Soc.* **1984**, *106*, 4696–4700. (e) Okahata, Y.; Seki, T. *J. Am. Chem. Soc.* **1984**, *106*, 8065–8070. (f) Okahata, Y. Hachiya, S.; Seki, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1377–1379.

(3) (a) Kunitake, T.; Tsuge, A.; Nakashima, N. *Chem. Lett.* **1984**, 1783–1786. (b) Shimomura, M.; Kunitake, T. *Polym. J.* **1984**, *16*, 187–190. (c) Nakashima, N.; Ando, R.; Kunitake, T. *Chem. Lett.* **1983**, 1577–1580.

(4) (a) Kajiyama, T.; Kumano, A.; Takayanagi, M.; Okahata, Y.; Kunitake, T. *Chem. Lett.* **1979**, 645–648. (b) Kumano, A.; Kajiyama, T.; Takayanagi, M.; Kunitake, T.; Okahata, Y. *Ber. Bunsengs. Phys. Chem.* **1984**, *88*, 1216–1222. (c) Kumano, A.; Kajiyama, T.; Takayanagi, M.; Kunitake, T. *Chem. Lett.* **1984**, 915–918. (d) Kunitake, T.; Higashi, N.; Kajiyama, T. *Chem. Lett.* **1984**, 717–720.
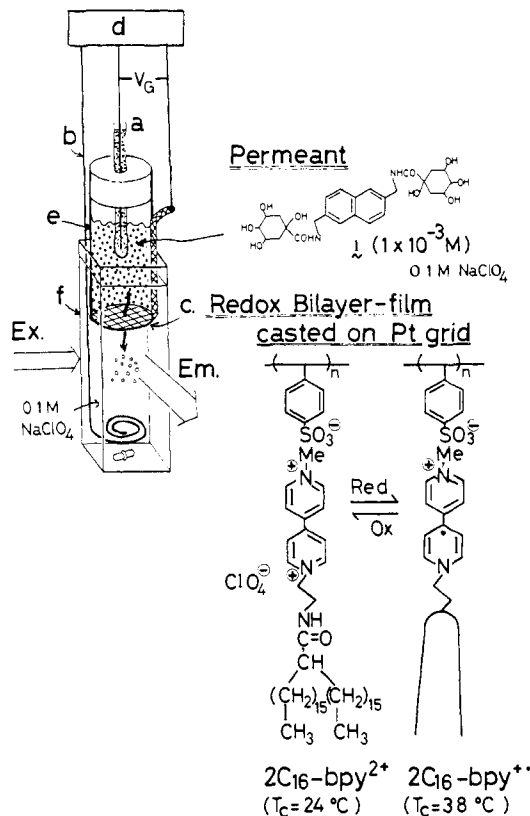


**Figure 1.** Experimental setup for the permeation of fluorescent probe **1** controlled by electrochemical redox reactions. (a) Reference electrode, Ag/AgCl in saturated KCl (–0.05 V vs. SCE); (b) Pt wire for counter electrode; (c) Pt minigrid sheet (100 mesh, 28 mm²) embedded in $2C_{16}$-bpy$^{2+}$-PSS⁻ bilayer films; (d) potentiostat; (e) Polyethylene tube (diameter, 7 mm); (f) 1-cm quartz cell.
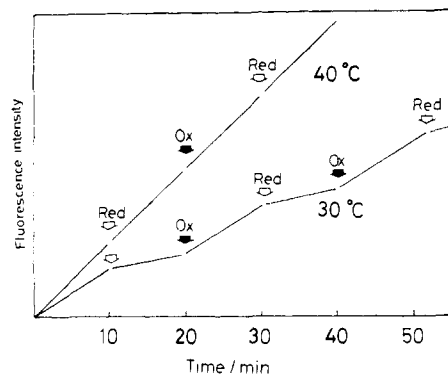


**Figure 2.** Permeation controls of the probe **1** across the viologen-containing film on a Pt grid by electrochemical redox reactions. The potential of –0.5 and 0 V vs. SCE was applied to Pt grid/film at Red and Ox, respectively.

and reported that the permeability across the bilayer- or liquid-crystal-immobilized film could be changed by phase transition phenomena[4] and photoirradiation.[5] We also observed the permeability of the bilayer film could be regulated by the electric transmembrane potential.[6] Burgmayer and Murray first reported that the permeability of anions through a polypyrrole film deposited on a Au grid could be changed by positive charge formation on the film by electrochemical redox reactions.[7]

(5) Kumano, A.; Niwa, O.; Kajiyama, T.; Takayanagi, M.; Kunitake, T. *Polym. J.* **1984**, *16*, 461–469. (b) Kumano, A.; Niwa, O.; Kajiyama, T.; Takayanagi, M.; Kano, K.; Shinkai, S. *Chem. Lett.* **1983**, 1327–1330.

(6) Okahata, Y.; Taguchi, K.; Seki, T. *J. Chem. Soc., Chem. Commun.*, in press.

(7) Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6139–6140. (b) *J. Phys. Chem.* **1984**, *88*, 2515–2521.

In this paper, we prepared viologen-containing, bilayer-immobilized films by the polyion complex method[3a] and controlled the permeability across a film cast on a platinum minigrid sheet by electrochemical redox reactions. A schematic illustration of the apparatus is shown in Figure 1.

The bilayer-immobilized, polyion-complex film was prepared as follows, according to the Kunitake's method.[3a] Equivalent amounts of an aqueous dispersion of bilayer-forming $2C_{16}$-bpy$^{2+}$2ClO$_4^-$ amphiphiles[8] and an aqueous of sodium poly(styrene sulfonate) PSS$^-$ (MW > 2 × 10$^6$) were mixed. The precipitates, pale yellow powders (recovery: 90%), were dissolved in chloroform and cast on a Pt minigrid (100 mesh) supported on a polyethylene tube (see Figure 1). The polyion-complex film ($2C_{16}$-bpy$^{2+}$-PSS$^-$ClO$_4^-$) was transparent, water-insoluble, and estimated to be 100 $\mu$m thick from SEM observations. X-ray diffraction analyses[9] showed that $2C_{16}$-bpy$^{2+}$ amphiphiles form extended lamellae parallel to the film plane in polyion complexes with PSS$^-$, as well as other bilayer-immobilized films.[3] The $2C_{16}$-bpy$^{2+}$-PSS$^-$ and the reduced $2C_{16}$-bpy$^{+\cdot}$-PSS$^-$ films showed phase transition temperatures ($T_c$) at 24 and 38 °C from DSC measurements, respectively, as well as other bilayer films.[3]

Permeation of the freely water-soluble, nonionic fluorescent probe 1[10] across the bilayer film cast on a Pt-grid was followed fluorometrically at 340 nm (excited at 280 nm) in 0.1 M NaClO$_4$ aqueous solution according to the apparatus of the thermostated quartz cell in Figure 1. Typical time courses of permeation of probe 1 under an intermittent potential applied to the electrode/film in a nitrogen atmosphere are shown in Figure 2. The bilayer film showed a relatively high resistance to the permeation of probe 1 [$P = (2.28–2.63) \times 10^{-7}$ cm$^2$ s$^{-1}$], as well as other polymer membranes.[1,4,6]

A cyclic voltammetry study of viologen films cast on a Pt electrode in 0.1 M NaClO$_4$ aqueous solution showed two well-known peaks at −0.55 V vs. SCE in cathodic region ($2C_{16}$-bpy$^{2+}$/$2C_{16}$-bpy$^{+\cdot}$) and at −0.35 V vs. SCE in anodic region ($2C_{16}$-bpy$^{+\cdot}$/$2C_{16}$-bpy$^{2+}$). The peak currents were largely dependent on the fluidity of bilayer films: the reduction of $2C_{16}$-bpy$^{2+}$ to $2C_{16}$-bpy$^{+\cdot}$ films occurred only in the fluid-liquid-crystalline state of $2C_{16}$-bpy$^{2+}$ bilayer films above the $T_c$ = 24 °C, but not in the solid state below the $T_c$.

Upon applying the potential of −0.50 V vs. SCE to the Pt grid/film, the film turned from pale yellow to violet within 30 s which shows the reduction of the dicationic $2C_{16}$-bpy$^{2+}$ to the radical cationic $2C_{16}$-bpy$^{+\cdot}$ bilayers, and then the permeability was decreased by a factor of 3.3 (P = 7.72 × 10$^{-8}$ cm$^2$ s$^{-1}$) at 30 °C. Upon switching off the Pt grid/film potential to 0 V even after a long duration (5–10 min) at 30 °C, the violet $2C_{16}$-bpy$^{+\cdot}$ bilayers were oxidized again to the yellow $2C_{16}$-bpy$^{2+}$ bilayer film in 30 s and the permeability reverted to the original fast rate. These permeability changes due to the redox of $2C_{16}$-bpy$^{2+}$/$2C_{16}$-bpy$^{+\cdot}$ bilayer films on a Pt grid could be reproduced repeatedly in the range 25–35 °C. In contrast, the permeation of probe 1 was hardly affected by the −0.5-V potential on Pt grid/film at 40 °C in contrast to 25 °C, although the redox reaction of viologen films was confirmed to occur on Pt grid at 40 °C.

Redox-sensitive permeations at 30 °C but not at 40 °C of Figure 2 may be explained by the transition of the $T_c$ between the oxidized $2C_{16}$-bpy$^{2+}$ bilayers (24 °C) and the reduced $2C_{16}$-bpy$^{+\cdot}$ bilayers (38 °C). At a temperature of 30 °C, the oxidized $2C_{16}$-bpy$^{2+}$ bilayers are in the liquid crystalline state above $T_c$ = 24 °C and

probe 1 can permeate smoothly through the fluid and disordered bilayers, while the reduced $2C_{16}$-bpy$^{+\cdot}$ bilayers are in the solid state below $T_c$ = 38 °C and have a high resistance to the permeation. In contrast, at 40 °C, both $2C_{16}$-bpy$^{2+}$ and $2C_{16}$-bpy$^{+\cdot}$ bilayers are in the fluid state above their $T_c$ values and showed a similar high permeability independent of their redox forms. Thus, the permeability changes may be attributed to the fluidity change of the bilayer film on a Pt grid because of the $T_c$ transitions of bilayers by redox reactions. The change of membrane charges by redox reactions should be unimportant for the permeation of nonionic probes.

The permeability of chloride anions through polypyrrole films deposited on a Au grid has been reported to be changed by the positive charge formation on the film by electrochemical redox reactions.[7] This ion gate film of polypyrrole, however, showed slow responses, taking 15–30 min for the permeability change, and the poor reproducibility because of the morphological damages of the polymer film by redox reactions.[7b] In contrast, our viologen-containing bilayer films showed high fluid stability and the quick response for a permeability change, because the electrochemical redox reaction was converted to the fluidity change of bilayer films. A fluid, bilayer-immobilized film which is electrically switchable by redox reactions would provide a new idea for studying signal-receptive permeability-controllable membranes.

## Phosphine Oxides and LiAlH₄–NaBH₄–CeCl₃: Synthesis and Reactions of Phosphine–Boranes

Tsuneo Imamoto,* Tetsuo Kusumoto, Nobuyo Suzuki, and Kazuhiko Sato

*Department of Chemistry, Faculty of Science Chiba University, Yayoi-cho, Chiba 260, Japan*

*Received April 23, 1985*

Phosphine–boranes (R$_3$PBH$_3$) have attracted little attention of chemists.[1] We wish to report a novel synthesis and some characteristic reactions of this class of compounds.

Our one-pot synthesis of phosphine–boranes from phosphine oxides employs a new reagent system, LiAlH₄–NaBH₄–CeCl₃. Various phosphine oxides reacted smoothly with this reagent in THF at room temperature under N$_2$ to afford the corresponding phosphine–boranes (1a–i) in good yields (Table I).[2] It is note-
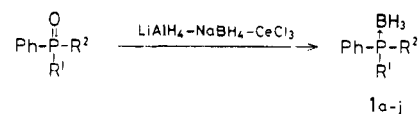
(1) Preparation and reaction of phosphine–boranes have only been described in a few scattered papers. (a) Frisch, M. A.; Heal, H. G.; Mackle, H.; Madden, I. O. *J. Chem. Soc.* **1965**, 899. (b) Nainan, K. C.; Ryschkewitsch, *Inorg. Chem.* **1969**, *8*, 2671. (c) Mathur, M. A.; Myers, W. H.; Sisler, H. H.; Ryschkewitsch, G. E. *Inorg. Synth.* **1974**, *15*, 128. (d) Schmidbaur, H.; Weiss, E.; Zimmer-Gasser, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 782. (e) Rosser, R.; Mills, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1041. (f) Kuznetsov, N. T. *Zh. Neorgan. Khim.* **1964**, *9*, 1817.

(2) General procedure for the preparation of phosphine–boranes: Cerium chloride (CeCl₃·7H₂O) (3.3 g, 9 mmol) was quickly powdered in a mortar and was placed in a 50-mL two-necked flask. The flask was heated with stirring in vacuo to 140 °C during 1 h, maintained at this temperature for 2 h, and cooled to room temperature. Dry THF (20 mL) was then added with stirring under N₂. After 0.5 h, NaBH₄ (0.34 g, 9 mmol) was added and stirring was continued for 1 h. The flask was immersed in an ice bath and phosphine oxide (3 mmol) was added, and finally LiAlH₄ (0.14 g, 3.6 mmol) was added by portions. The ice bath was removed and the mixture was stirred at room temperature for 2–15 h. The reaction mixture was diluted with benzene (ca. 15 mL) and poured slowly to ice–water containing 12 N HCl (4 mL). The mixture was filtered through Celite and the organic layer was separated. The aqueous layer was extracted twice with benzene. The combined extracts were dried (Na₂SO₄) and evaporated. The residue was subjected to chromatography on a short column of silica gel to give phosphine–borane. When the product was crystalline solid, it was recrystallized from hexane–benzene.

(8) The new compound $2C_{16}$-bpy$^{2+}$ was synthesized by monoquarternization of excess 4,4'-bipyridine with *N*-(2-bromoethyl)-α,α-dihexadecylacetamide (mp 94–95 °C), followed by methylation with methyl bromide: mp 190 → 228 °C (liquid crystalline behavior), $R_f$ 0.4 (CHCl₃/CH₃OH/CH₃COOH/H₂O = 60:30:5:5). The counteranions of $2C_{16}$-bpy$^{2+}$ were changed from 2Br$^-$ to 2ClO$_4^-$ in excess aqueous NaClO$_4$ before preparing polyion complexes.

(9) When the incident X-ray beam was parallel to the film plane which was held vertically, highly oriented diffractions with 3.8-nm spacings corresponding to the bilayer thickness were observed.

(10) Preparation and permeation of the fluorescent probe 1 across the capsule membrane are reported elsewhere: Okahata, Y.; Iizuka, N.; Nakamura, G.; Seki, T. *J. Chem. Soc., Perkin Trans. 2*, in press.