Some lipophilic pyridylpyridinium tetrakis [3, 5-bis (trifluoromethyl) phenyl] borates as catalytic electron mediators

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Some lipophilic pyridylpyridinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borates as catalytic electron mediators

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1-Butyl-4-(4-pyridyl)pyridinium bromide, 1, 3-bis [4-(4-pyridyl)pyridinio]-propane dibromide, and 1, 8-bis[4-(4-pyridyl)pyridiniomethyl]naphthalene dibromide were prepared. Their redox potentials measured by cyclic voltammetry depended remarkably upon pH of the solution media, and their protonated species were capable to work as electron carriers as efficiently as methylviologen. Ionpair extraction of the pyridylpyridinium ions with tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate ion indicated that their ion pairs had the compositions of 1 : 1-, 1 : 2-, and 3 : 4 molar ratios and quantitatively partitioned into hydrophobic organic phase.

Introduction

Viologen, *N*,*N*′-dialkyl-4,4′-bipyridinium ion, is known to be an effective electron mediator in the photoinduced electron-transfer reactions and its redox behaviors have been extensively investigated in various systems.[1] This compound is, however, highly hydrophilic and hardly soluble in hydrophobic organic solvents because of its doubly charged ionic structure. The redox reactions with viologen are, therefore, usually performed in homogeneous aqueous or polar solvent systems. On the other hand, several attempts have been made to incorporate viologen into hydrophobic organic media on the purpose of its applications to the electron-transfer process across an organic liquid membrane and reduction reactions in nonpolar organic media.[2,3]

The cation radical form of viologen becomes more lipophilic with extended lengths of alkyl chains on the pyridinium nitrogens, and partitions increasingly into an organic phase in a two-phase system.[3] However, the modification of alkyl groups on the pyridinium nitrogens

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affects the redox potential of the viologen ; usually elongated *N*-alkyl chains cause decreased reduction efficiency.

In the previous report, we described the formation of the hydrophobic ion pair from methylviologen (MV^{2+}) and lipophilic fluorinated organic anion of tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate ion (TFPB), [4] and a successful performance of the ion pair as a catalytic electron mediator which transmitted electron from a donor in an aqueous phase to an acceptor in a separate aqueous one across an organic liquid membrane separating in between the two aqueous phases (Fig. 1).[5]

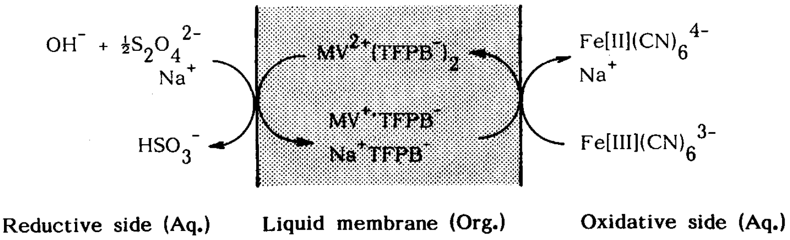

Fig.1 Electron transfer across a hydrophobic organic membrane containing the ion pair of MV^{2+} $(TFPB^-)_2$; Fe (III) → Fe (II) reduction with dithionite in a separate aqueous phase.

It should be noted that in the three-phase system shown in Fig. 1, the metal cation transport process was coupled with the electron transfer in the same direction. If an appropriate proton transporter can be combined with the electron carrier in the liquid membrane, one can construct a catalytic process which transports electron and proton in parallel ; formally an equivalent of hydrogen radical.

On the purpose of constructing such an electron-transmission process coupled with proton transport, the following three kinds of pyridylpyridinium derivatives were designed.

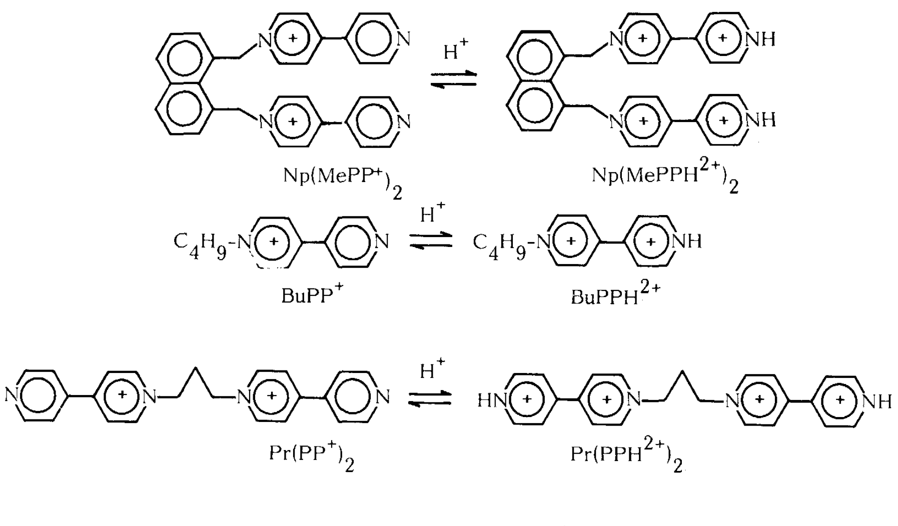

Fig.2 The pyridylpyridinium derivatives as electron-proton carriers.

Their structures are shown in Fig. 2. On the basis of the fundamental structure of viologen, one of the two *N*-alkyl groups was replaced with an available proton so that the doubly charged ionic structure same as that of MV^{2+} was retained. Thus, in 1-butyl-4-(4-pyridinio)-pyridinium dibromide [$BuPPH^{2+}2Br^-$], the *N*-alkyl group was chosen to be a butyl one owing to easy handling of the precursor, butylbromide, in the preparation. 1, 3-Bis [4-(4-pyridinio)pyridinio]propane tetrabromide [$Pr(PPH^{2+})_2 4Br^-$] and 1,8-bis[4-(4-pyridinio)-pyridiniomethyl]naphthalene tetrabromide [$Np(MePPH^{2+})_2 4Br^-$] were designed to be favorable to a two electrons-two protons simultaneous transfer process. In the latter bipyridinium compound, steric restriction was contrived so that the two protons were kept closely. Deduced from the redox behavior of methylviologen, these compounds were expected to transfer electrons reversibly with large enough negative potential, besides bearing available proton(s) on the ring nitrogen(s).

This paper is to describe the syntheses and the redox behaviors of the pyridylpyridinium derivatives, and their ion-pair extraction with TFPB.

Experimental

Redox potentials were measured on a Yanagimoto Polarographic Analyzer P-1100. NMR spectra were recorded on a JEOL FT-NMR spectrometer FX-100 and a Hitachi NMR R-24B.

Preparation of the pyridylpyridinium salts:

1-Butyl-4-(4-pyridyl)pyridinium bromide [$BuPP^+Br^-$] : A solution of butyl bromide (13.7g, 10.0mmol) and 4,4′-bipyridine (31.2g, 20.0mmol) in acetonitrile (60cm^3) was heated under reflux overnight. Resulting yellow solid was filtered and recrystallized from ethanol-acetone, to give pale yellow crystals (2.13g, 73% yield of the theoretical (*lit.*[6] 80% yield), mp 202-204°C (decomp.) (*lit.*[6] 199-201°C (decomp.)). Found: C, 57.37; H, 5.81; N, 9.40%; Calcd for $C_{14}H_{17}N_2Br$: C, 57.55; H, 5.52; N, 9.59%. ^{1}H-NMR (in D_2O against H_2O internal standard): -3.3---2.2 (7H, m, $C_3H_7CH_2$-N^+); -0.1 (2H, m, $-\mathbf{CH_2}$-N^+); 3.1$-$4.3 (8H, m, pyridylpyridinium ring **H**).

1, 3-Bis[4-(4-pyridyl)pyridinio]propane dibromide [$Pr(PP^+)_2 2Br^-$]: A solution of 1, 3-dibromopropane (1.15g, 5.70mmol) and 4, 4′-bipyridine (4.00g, 25.6mmol) in acetonitrile (100cm^3) was treated in a similar manner as described above. The resulting yellowish green solid was filtered, washed with water thoroughly, and recrystallized from ethanol-acetone, to give pale yellow crystals (996mg, 48.8% yield) (*lit.*[7] 55% yield), mp 226-228°C (decomp.). Found: C, 50.96; H, 4.48; N, 10.39%. Calcd for $C_{23}H_{22}N_4Br_2 1.5H_2O$: C, 51.03; H. 4.66; N, 10.35%. ^{1}H-NMR (in D_2O against H_2O internal standard): -2.1---1.7 (2H, m, central $\mathbf{CH_2}$); 0.0-0.2 (4H, m, $-\mathbf{CH_2}$-N^+); 3.0-4.3 (16H, m, pyridylpyridinium ring **H**).

1, 8-Bis[4-(4-pyridyl)pyridiniomethyl]naphthalene dibromide [$Np(MePP^+)_2 2Br^-$]: A solution of 1, 8-bis(bromomethyl)naphthalene[8] (1.0g, 3.2mmol) and 4, 4′-bipyridine (1.5g, 9.6mmol) in acetonitrile (100cm^3) was treated in a similar manner as described above. The resulting yellow solid was recrystallized from methanol-acetone to give yellowish green crystals (3.43g, 81.7% yield), mp 202-204°C. Found: C, 55.82; H, 4.16; N, 7.92%. Calcd for $C_{32}H_{26}N_4Br_2$ $3.2H_2O$: C, 56.19; H, 4.77; N, 8.19%. ^{1}H-NMR (in CD_3OD against TMS internal standard): 6.8 (4H, m, $\mathbf{CH_2}$); 7.8-8.2 (6H, m, Ar**H**); 8.0-9.2 (16H,m, bipyridinium ring **H**).

Cyclic voltammetric measurements:

Cyclic voltammetry was carried out in aqueous solutions containing 0.1mol dm^{-3} tetrabutylammonium bromide as the supporting electrolyte. The aqueous solutions were adjusted to pH1-3, 3-6, 6-9, and 9-10 ranges, by use of hydrochloric acid-sodium acetate, acetic acid-sodium acetate, potassium dihydrogen phosphate-disodium hydrogen phosphate, and boric acid-sodium carbonate buffers, respectively. A three-electrode cell was used for measurements, in which the working electrode is glassy carbon, the auxiliary electrode a platinum coil, and reference electrode a saturated calomel electrode. Scanning rate was set at 100mV sec^{-1}.

Partition of the ion pair with TFPB in a dichloromethane-water two-phase system:

An aqueous 5-cm^3 solution of the pyridylpyridinium derivative was equilibrated by vigorous shaking with an equal volume of dichloromethane solution of sodium TFPB. The initial concentration of the aqueous pyridinium salt was maintained constant throughout a series of extraction experiments on the same pyridinium salt. $MV^{2+}2Br^-$, $BuPP^+Br^-$, $Pr(PP^+)_2 2Br^-$, and $Np(MePP^+)_2 2Br^-$ were 1.0×10^{-4}, 1.0×10^{-4}, 5.0×10^{-5}, and 1.0×10^{-5}mol dm^{-3}, respectively. The concentration of TFPB was varied so that the molar ratio to the cation was from null to 2.0-2.5 times more. After equilibration, the pyridylpyridinium remained in the aqueous phase was determined by spectrophotometry at each UV-absorption maximum, 257, 260, 261, and 259nm, respectively.

Results and Discussion

pH-Dependence of the redox potentials of the pyridylpyridinium salts.

The pyridylpyridinium ion in an aqueous solution in equilibrium with its protonated species, whose fraction depends on the pH of the solution. Cyclic voltammograms of $BuPP^+$ and $Pr(PP^+)_2$ at various pH's are shown in Figs. 3 and 4, respectively. $Np(MePP^+)_2$ was not soluble in aqueous buffer so enough for the cyclic voltammetric measurements. The voltammograms show that the first wave shifts remarkably toward the negative potential with the increased pH's, while the shift of the second wave with pH is relatively small, thus the peak separation narrows with the pH-increase, that of $BuPP^+$ merging into a single wave at a higher pH region.

Figs.5 and 6 show the relationships of the pH and the redox potentials calculated from

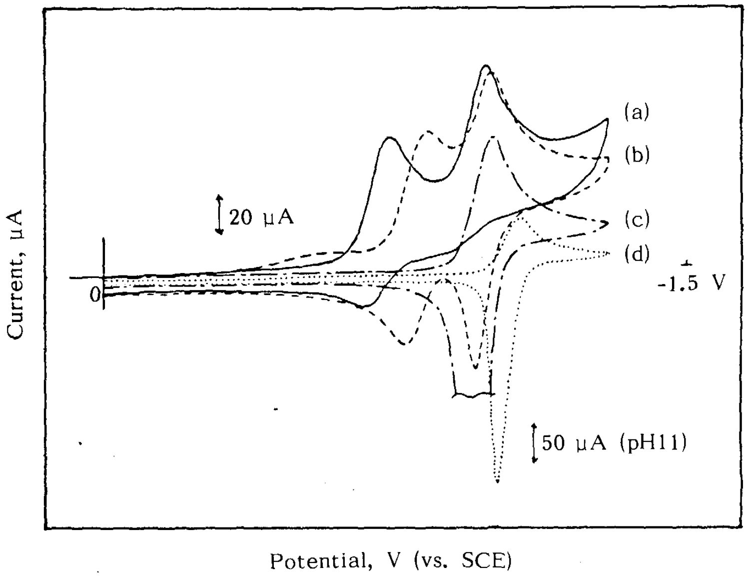

Fig.3 Cyclic voltammograms of BuPP$^+$ at (a) pH2, (b) pH5, (c) pH8, and (d) pH11.

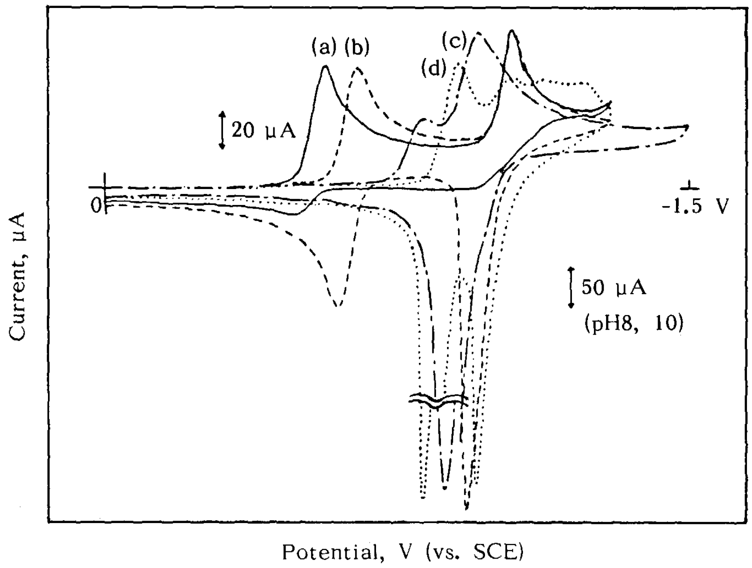

Fig.4 Cyclic voltammograms of Pr(PP$^+$)$_2$ at (a) pH2, (b) pH5, (c) pH8, and (d) pH10.

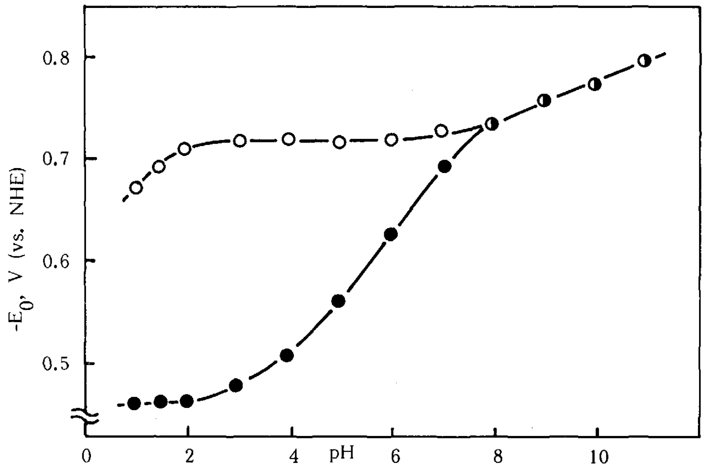

Fig.5 The pH-dependence of redox potential ($-E_0$) of $BuPP^+$.

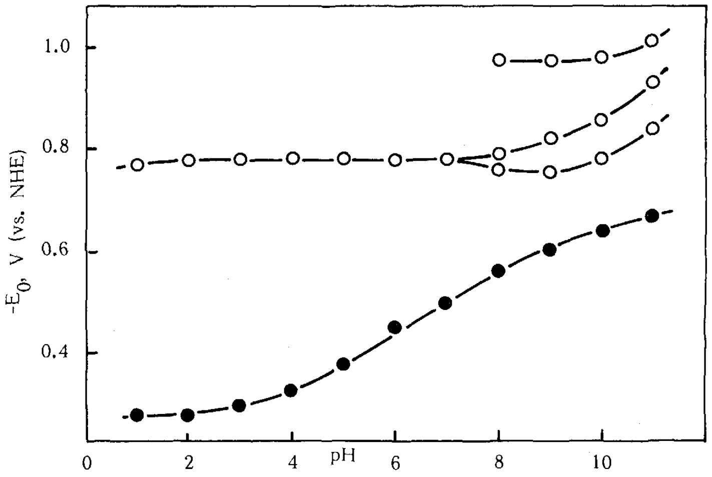

Fig.6 The pH-dependence of redox potential ($-E_0$) of $Pr(PP^+)_2$.

midpoints between the forward and reverse peaks. The pH-dependence of the redox potential of $\mathrm{BuPP^+}$ can be interpreted in accordance with the proton dissociation process of the conjugate acid, $\mathrm{BuPPH^{2+}}$, and its radical cation form, $\mathrm{BuPPH^{+\bullet}}$.

$$\mathrm{BuPPH^{2+}} \xrightarrow{K_{a1}} \mathrm{BuPP^+} + \mathrm{H^+} \qquad (1)$$

$$\mathrm{BuPPH^{+\bullet}} \xrightarrow{K_{a2}} \mathrm{BuPP^\bullet} + \mathrm{H^+} \qquad (2)$$

The value of $\mathrm{p}K_{a1}$ can be estimated as approximately 3, based on that of the first deprotonation process of the conjugate acid of 4,4′-bipyridine,[9] and K_{a2} is reasonably assumed to be much smaller than K_{a1}.

Thus, the five kinds of cationic and radical species could be involved in the electron-transfer process, depending upon pH as summarized in Fig.7. In the region of pH $<$ $\mathrm{p}K_{a1}$, the pyridylpyridinium ion is present in the form of $\mathrm{BuPPH^{2+}}$ in the aqueous phase, and the two successive electron-transfer processes proceed *via* the paths (a) and (b) stepwise.

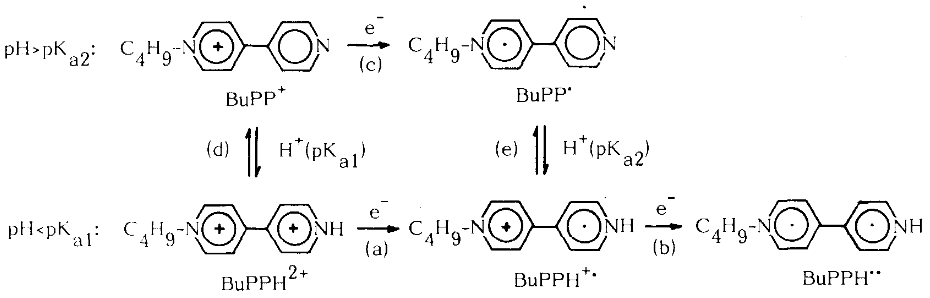

Fig.7 Scheme of the electron-transfer paths of $\mathrm{BuPP^+}$ under varied pH conditions.

In the region of $\mathrm{p}K_{a2}$ $<$ pH, the pyridylpyridinium ion, $\mathrm{BuPP^+}$, is present as it is not protonated, and is reduced by one-electron transfer *via* the path (c) to $\mathrm{BuPP^\bullet}$, which can be no longer protonated in this pH region.

In the region inbetween, the pyridylpyridinim species, $\mathrm{BuPP^+}$, is present in the equilibrium of Eq. 1 (the path (d)) and is reduced by one-electron transfer to $\mathrm{BuPP^\bullet}$. The last radical species is protonated (the path (e) and Eq. 2) to form $\mathrm{BuPP^{+\bullet}}$, which is additionally reduced to $\mathrm{BuPPH^{\bullet\bullet}}$ *via* the path (b), showing the second reduction wave. All the electron-transfer paths in this scheme seems to be reversible.

The change of voltammograms of $\mathrm{Pr(PP^+)_2}$ depending on the pH of the solution were rather complicated; the first wave was not merged with the second one in the pH range so far as examined, meanwhile the additional waves were observed in the higher pH region. The voltammometric behaviors could not be explained only by the protonation equilibrium of the cationic and radical species, but some other factors responsible to these complexities, which are remained to be elucidated at this stage.

BuPP$^+$ and Pr(PP$^+$)$_2$ show the lowest redox potentials, -0.48 and -0.35V (*vs.* NHE), respectively, in the region of pH < 3. These values are comparable to those of viologens, suggesting that the protonated forms of those pyridylpyridiniums would be capable to work as an electron mediator as efficiently as viologens.

Partition of the ion pair of pyridylpyridinium TFPB in a two-phase system.

The retention of an electron-carrying agent in an organic liquid membrane is one of the important requirements to be fulfilled for the usefulness of an electron-transmitting liquid membrane. In our previous study, we have successfully applied a new concept of ion-pair extraction to the incorporation of hydrophilic methylviologen into a hydrophobic organic phase, by use of a highly lipophilic stable TFPB as a counter anion. In the present work, we also designed to use TFPB anion in the ion-pair extraction of the pyribylpyridinium ions.

The compositions of the ion pairs were determined by a mole-ratio method. The extraction behaviors summarized in Fig.8. BuPP$^+$ and Pr(PP$^+$)$_2$ were extracted in the form of 1 : 1-and 1 : 2 ion pairs, respectively, corresponding to the equivalent ratios proportional to their ionic charge numbers, while Np(MePP$^+$)$_2$ formed a 3 : 4-ion pair despite the charge number ratio of 1 : 2. This seems ascribable to the hydrophobicity of Np(MePP$^+$)$_2$ itself. These pyridylpyridinium ions were quantitatively extracted in a dichloromethane phase in the presence of an excess amount of TFPB.

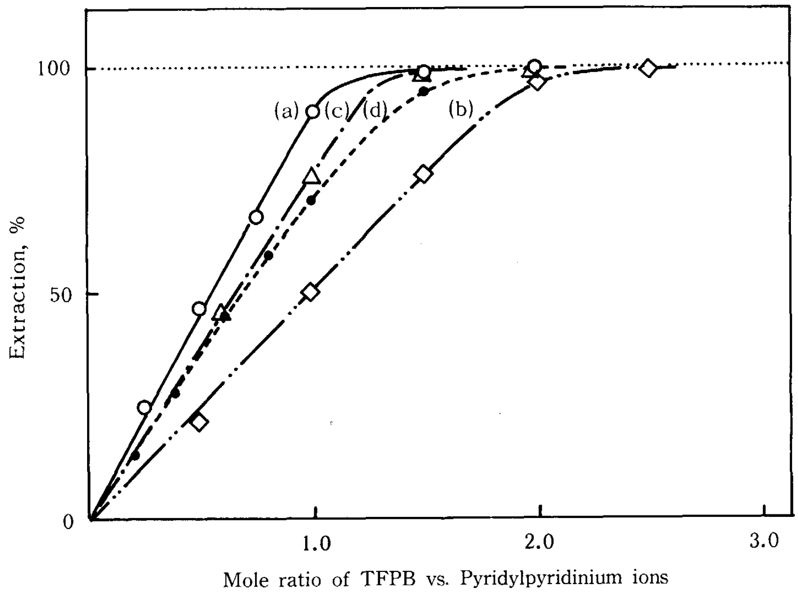

Fig.8 Ion-pair extractions of the aqueous pyridylpyridinium ions with varied molar amounts of TFPB in dichlor methane, where the curves (a), (b), (c), and (d) correspond to those of BuPP$^+$, Pr(PP$^+$)$_2$, Np(MePP$^+$)$_2$, and MV^{2+}, respectively.

In conclusion, the protonated forms of BuPP$^+$ and Pr(PP$^+$)$_2$ showed the redox potentials comparable to that of MV^{2+} in an aqueous phase, and were proved to work as electron carriers as efficiently as MV^{2+}. The ion pairs of the present pyridylpyridinium TFPB were highly lipophilic to be retained quantitatively in the organic phase. The protonated forms of $BuPP^+$ and $Pr(PP^+)_2$ were seemingly capable to work catalytically as electron-proton (an equivalent of hydrogen radical) carriers in a hydrophobic organic liquid membrane, so far as the redox potential and lipophilicity were concerned. The applications of the ion pairs to the reduction reactions are under way in this laboratory.

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