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METAL COMPLEX MEDIATED ELECTRON TRANSPORT SYSTEM

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A series of bathophenanthroline metal complexes effectively mediated electron transport, coupled with their redox properties.

Electron transport is an essential process to simulate the artificial photosynthesis and bioenergetic systems. Of particular, synthetic photosynthetic membrane has received wide attention as means of separating two photosystems for generation of reduced and oxidized species capable of decomposing the water.[1] In such systems, it is most important to choose the combination of electron donor, electron acceptor, electron carrier, and photosensitizer.[2] Hence, a development of various type of elements is required to construct the potential artificial photosynthetic systems.

Here we report that simple lipophilic metal complexes successfully mediated electron transport through a liquid membrane. Although some metal complexes[3] have been employed as electron carrier, our examined bathophenanthroline metal complexes offer several advantages: (1) A variety of metal ions(Cu, Ni, Co, Fe, Mn, and Ru) are easily introduced into the carrier. (2) By appropriate choice of central metal ion, the redox potential of the carrier can be controlled without any structural changes. (3) Their photochemistry was well-characterized and provides a possibility of further applications.[4] (4) Their chemical stability and ready availability are also important from practical points. Electron transport experiment was performed in a cell, in which an aqueous solution of reductant is separated from an aqueous solution of oxidant(Ce^{4+}ion) by a $ClCH_2CH_2Cl$ membrane (Figure). The transport process was followed by determining reduction rates of Ce^{4+} ion.[5]

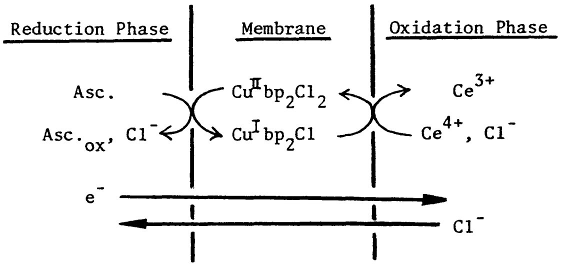

Figure. Electron Transport Liquid Membrane.
Asc.:ascorbic acid; bp: bathophenanthroline.

When the bathophenanthroline metal complex was added into the membrane, Ce^{4+} ion was effectively reduced, showing that trans-membrane electron transport occurred. Their reduction rates were almost constant until all Ce^{4+} ions were converted, and obtained rates are summarized in Table. The reduction did not occur in the absence of a carrier, or in the absence of reductant. Spontaneous transport of reductant through the carrier-containing membrane in the absence of oxidant was negligible (0.03 µmol/h).

The reduction of Ce^{4+} ion was confirmed to be coupled with redox process of metal complex by following observations. The bathophenanthroline copper(II) complex in $ClCH_2CH_2Cl$ (λ_{max}=729 nm), for example, was rapidly reduced by treating with an aqueous solution of ascorbic acid, and resulting copper(I) complex (λ_{max}=462 nm) was oxidized by contacting with an aqueous solution of Ce^{4+} ion.

A new series of metal complex carriers showed higher electron transport rates than the previously reported quinones[6] under the employed conditions: $Cu(bp)_2^{2+} > Fe(bp)_3^{3+} > Ni(bp)_2^{2+} \simeq Co(bp)_2^{2+} > Mn(bp)_2^{2+} \simeq$ p-BQ-Cl_2 > Vitamin K_3. Since used metal complexes have similar properties such as mobility, lipophilicity, and others, their electron transport abilities might be controlled by the nature of central metal ions,i.e., redox potential. Moreover, present finding is of particular interest, if, by introduction of Ru ion, metal complex could serve as both electron carrier and photosensitizer.[7]

Table. Metal Complex-Mediated Electron Transport.

Reductant	Carrier (μmol)	Oxidant	Transport Rate (μmol/h)
No	$Cu(bp)_2Cl_2$ (9.4)	Ce^{4+}, KCl	0.2
Asc.	No	Ce^{4+}, KCl	0.2
Asc.	$Cu(bp)_2Cl_2$(9.4)	Ce^{4+}	3.8
Asc.	$Cu(bp)_2Cl_2$(9.4)	Ce^{4+}, KCl	10.4
Asc.	$Cu(bp)_2Cl_2$(28.2)	Ce^{4+}, KCl	20.3
NH_2OH	$Cu(bp)_2Cl_2$(9.4)	Ce^{4+}, KCl	13.4
Asc.	$Ni(bp)_2Cl_2$(9.4)	Ce^{4+}, KCl	3.8
Asc.	$Co(bp)_2Cl_2$(9.4)	Ce^{4+}, KCl	3.8
Asc.	$Mn(bp)_2Cl_2$(9.4)	Ce^{4+}, KCl	1.7
Asc.	$Fe(bp)_3Cl_3$(9.4)	Ce^{4+}, KCl	5.4
NH_2OH	$Fe(bp)_3Cl_3$(9.4)	Ce^{4+}, KCl	11.2
Asc.	Vitamin K_3(20.0)	Ce^{4+}, KCl	0.7
Asc.	p-BQ-Cl_2(20.0)*	Ce^{4+}, KCl	4.0

Asc.(ascorbic acid) or NH_2OH, 0.25 mmol/H_2O (pH=6.00), 5ml. Ce^{4+}(sulfate), 0.07 mmol/3% H_2SO_4aq. 5 ml. KCl (0.33 mmol) was added if noted. The transport experiments were performed at room temperature, and membrane phase ($ClCH_2CH_2Cl$, 12 ml) was stirred by a magnetic stirrer. Under the employed conditions, the metal ion leakage was usually negligible. Reproducibility: ± 10% or better. *p-BQ-Cl_2: 2,6-dichloro-p-benzoquinone.

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