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Polymerized Vesicles Derived from an Isocyano Amphiphile. Electron Microscopic Evidence of the Polymerized State

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Abstract: The synthesis and characterization of amphiphile dimethyl-*n*-hexadecyl[11-((1-isocyanoethyl)carbonyloxy)undecyl]ammonium bromide (**1**), containing a polymerizable isocyano function, are described. On dispersal in water **1** forms closed vesicles with diameters ranging from 200 to 5000 Å. Addition of nickel capronate causes polymerization of the bilayers of the vesicles. The aggregates have been studied by freeze fracture electron microscopy. The appearance of the polymerized vesicles is different from that of the unpolymerized analogues. This phenomenon is ascribed to a different fracture behavior; in the polymerized vesicles cross-links are present between the two halves of the bilayer. Both unpolymerized and polymerized vesicles of **1** behave as almost ideal osmometers. The polymerized vesicles show enhanced stability toward lysis by alcohol.

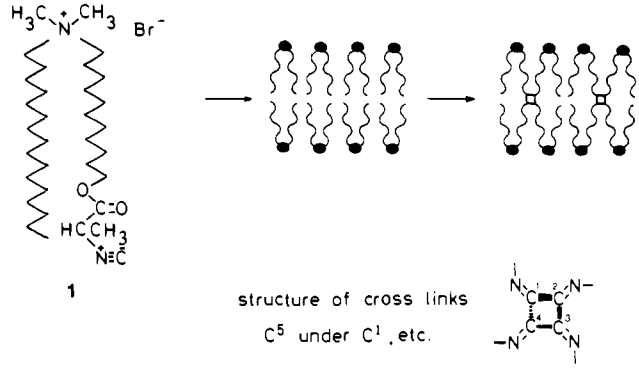
On dispersal in water double-chain synthetic surfactants are capable of forming closed vesicles.[2] These aggregates are receiving intense interest as carriers of drugs, models for biological membranes, and devices for solar-energy conversion.[2,3] As vesicles have a limited lifetime, applications based on long-term use are restricted.

Very recently, the synthesis of polymerized vesicles has been reported from surfactants containing a polymerizable residue.[4] This residue is an isopropenyl, vinyl, or diacetylenyl function.[4-6] Polymerization is effected by UV irradiation or radical initiation. The polymerized vesicles are more stable than their unpolymerized analogues.

In this paper we report on the synthesis and characterization of polymerized vesicles derived from a new amphiphile, **1**, containing an isocyano function. This function is polymerized by nickel(II) ions.[7]

$$n\mathrm{R{-}\overset{+}{N}{\equiv}\overset{-}{C}} \xrightarrow{\mathrm{Ni^{II}}} [\mathrm{R{-}N{=}C{<}}]_n$$

Scheme I



Furthermore, we wish to demonstrate that the polymerized state of our vesicles can be visualized by freeze fracture electron microscopy.[8]

Results and Discussion

Amphiphile **1** was synthesized starting from dimethylhexadecylamine.[9] This amine was reacted with 11-bromoundecanol[10] to give dimethylhexadecyl(11-hydroxyundecyl)ammonium bromide. The latter salt was coupled to *N*-formyl-L-alanine by means of the active ester method.[11] The resulting formamide was

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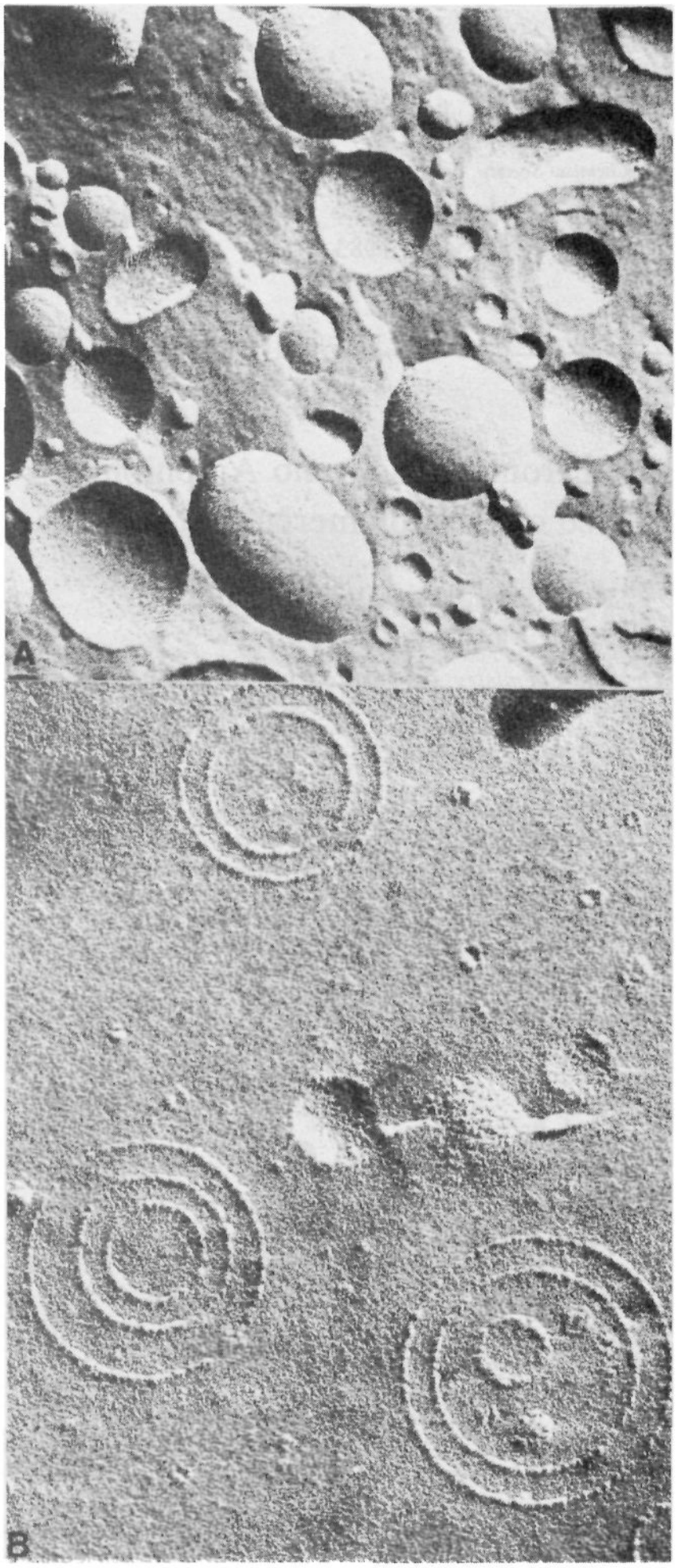

Figure 1. Freeze fracture electron micrographs of unpolymerized (A) and polymerized (B) vesicles. Magnification, ×100 000.

dehydrated with phosphorus oxychloride and base to give isocyanide **1**.[12]

Closed vesicles were obtained by dispersing amphiphile **1** in water. Electron micrographs taken by the freeze fracture technique of unsonicated dispersions revealed the presence of aggregates having diameters ranging between 200 and 5000 Å (Figure 1A). For the major part these aggregates are unilamellar vesicles. On sonication for 30 min at 35 °C the dispersions became optically clear. According to electron micrographs these solutions contained vesicles of smaller but more uniform size (~500 Å). The phase-transition temperature of the vesicles was determined by

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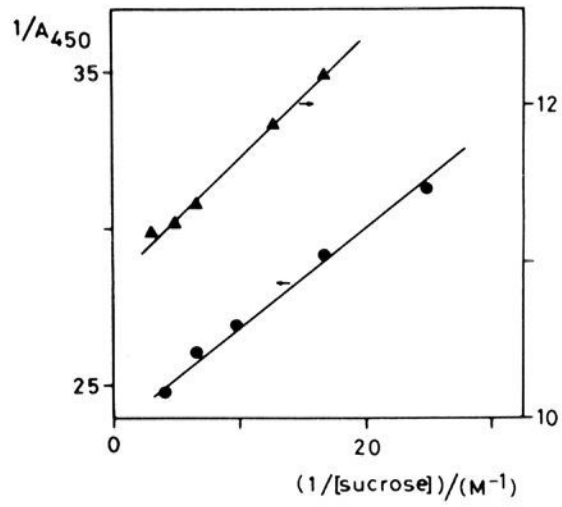

Figure 2. Relationship between the reciprocal of the absorbance at 450 nm of unpolymerized (●) and polymerized (▲) vesicle dispersions and the reciprocal of the concentration of sucrose in solutions in which the vesicles are osmotically treated until equilibrium.

following changes in ^{1}H NMR line widths as a function of temperature. The transition occurred at 30 °C.

The osmotic behavior of the vesicles was studied in aqueous media containing different concentrations of sucrose. To this end vesicles were prepared containing 0.1 M sucrose. Small aliquots of these solutions were added to solutions containing 0.01–0.4 M sucrose. Osmotic swelling and shrinkage were measured by recording the absorbance (turbidity) at 450 nm. The existence of a proportionality between $1/A_{450\ nm}$ and 1/osmolarity indicates ideal osmotic behavior of the vesicles.[13] Figure 2 shows the results of a typical experiment. A straight line is obtained except for very high and very low concentrations of sucrose. Under the latter conditions deviations from ideal behavior can be expected.[13]

On polymerization isocyanides form a 4^1 helical polymer.[7] Polymerization in the vesicle bilayers was achieved by addition of nickel capronate to the aqueous vesicle suspensions. The process is schematically depicted in Scheme I. The reaction was followed by recording the line broadening in the ^{1}H NMR spectrum of the system. Polymerization was complete after 12 h. The infrared spectrum of a freeze-dried sample of the polymerized vesicles showed an N=C stretching vibration at 1640 cm^{-1} and the absence of an isocyanide vibration. Further evidence that polymerization had taken place came from the UV spectrum which revealed a band at 340 nm (ϵ = 45 M^{-1} cm^{-1}) indicative of the imino chromophore in the polymer.[14]

In Figure 1B a freeze fracture electron micrograph of an unsonicated polymerized vesicle sample is given. Aggregates are visible having diameters ranging between 200 and 4500 Å. These diameters are of the same order of magnitude as found for the unpolymerized samples. Very remarkably, the electron microscopic appearance of the polymerized vesicles is different from that of the unpolymerized analogues. Instead of the common convex and concave half-balls and ellipsoids (Figure 1A), circles and ellipses are visible. This phenomenon can be explained from a different fracturing behavior of the two types of vesicles.

The freeze fracture technique is known to generate two complementary fracture faces of a bilayer membrane. It is widely assumed that these fracture faces are the result of a splitting of the bilayer into two monolayers.[15] The fracture plane is determined by the hydrophobic interface. It runs between the ends of the fatty chains through the middle of the bilayer. Freeze fracture electron microscopy has been used to characterize polymerized vesicles.[16,17] For instance, Wagner et al.[17] have applied

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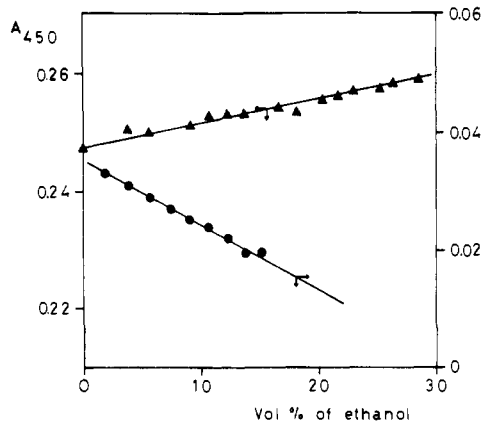

Figure 3. Plot of absorbance at 450 nm as a function of the percentage of ethanol for unpolymerized (●) and polymerized (▲) vesicles.

this technique to vesicles and polymerized vesicles of the sulfolipid **2**. Electron micrographs before and after polymerization show

$$(CH_3(CH_2)_{12}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOCH_2CH_2)_2\overset{+}{N}(H)CH_2CH_2SO_3^-$$

2

morphologies similar to that of Figure 1A, suggesting that the fracture planes are identical in both cases. This result can be explained from the fact that the polymerizable unit of **2** is situated in the middle of the surfactant chain, thus allowing polymerization to occur only within the monolayer. In our compound **1** the polymerizable group is at the end of the surfactant chain which enables the monolayers as well as the bilayer to cross-link. The special structure of the polymeric links that are formed, i.e., a rigid 4^1 helix with side chains pointing toward both monolayers, will promote this process (Scheme I). The fracture plane of our polymerized vesicles will no longer run through the middle of the bilayer. The particles are cross-fractured, generating the morphology of circles instead of balls. Thus, the electron micrograph of Figure 1B provides direct evidence of cross-linking of the bilayer. To our knowledge such visualization of the *polymerized* state of vesicles has not been reported before.

Polymerization of the vesicles leads to a restricted mobility of the hydrocarbon core. In line with this our polymerized vesicles show no phase transition anymore.[17]

On sonication and subsequent polymerization with nickel capronate dispersions of **1** yield aggregates of uniform size with average diameters of about 300 Å.

The osmotic behavior of the polymerized vesicles when brought into hypotonic and hypertonic media is very similar to that of the unpolymerized ones (Figure 2). This indicates that the main properties of the aggregates are retained on polymerization. However, with respect to stability the polymerized vesicles favorably compete with the unpolymerized analogues. Both sonicated and unsonicated dispersions of the former particles can be kept for months. Also, the stability toward lysis by alcohol has considerably increased (Figure 3).[18]

This investigation has shown that very stable and well-defined closed bilayer systems can readily be prepared on the basis of isocyano surfactants. As the latter compounds are accessible in great variety from the corresponding amines, new vesicle systems for different purposes can be envisaged. Our efforts in this field are directed toward the synthesis of membrane models for cation transport.[19]

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Experimental Section

Infrared and UV–vis spectra were recorded on Perkin-Elmer 283 and 555 spectrometers, respectively. ^{1}H NMR spectra were obtained on Varian EM 390 and Bruker WP 200 instruments. Chemical shifts are given downfield from internal Me_4Si. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, and b = broad. Sonication was performed with a Sonicar SC-50-22 bath, sonic power 55W. Electron microscopy was carried out with a Philips EM 301 instrument. Samples were frozen in a slash of liquid and solid nitrogen, fractured with a Denton freeze etch apparatus, and replicated with Pd/C according to standard procedures.[20] Glycerol was added up to 25% to prevent freeze damage.

Dimethylhexadecyl(11-hydroxyundecyl)ammonium Bromide. Dimethylhexadecylamine[9] (5.57 g, 0.021 mol) and 11-bromoundecanol[10] (5.20 g, 0.021 mol) were dissolved in toluene (50 mL) and refluxed for 18 h. The solvent was evaporated and the resulting solid washed with ether: yield 9.4 g (87%) of almost pure product; mp 101–102 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3 H, CH_3), 1.05–1.85 (m, 46 H, CH_2), 3.35–3.70 (m, 12 H, CH_3N, CH_2N, CH_2O). Anal. Calcd for $C_{29}H_{62}BrNO.{}^1/_2H_2O$: C, 65.75; H, 11.99; N, 2.64. Found: C, 65.89; H, 11.92; N, 2.69.

Dimethylhexadecyl[11-((1-*N*-formylaminoethyl)carbonyloxy)undecyl]ammonium Bromide. The preceding compound (8 g, 0.015 mol) and dry triethylamine (1.55 g, 0.015 mol) were dissolved in chloroform (50 mL) and added dropwise at 0 °C to a solution of *N*-formyl-L-alanine *p*-nitrophenyl ester[21] (7.32 g, 0.031 mol) in chloroform (50 mL). The mixture was stirred at room temperature for 72 h. The solvent was evaporated and the resulting solid purified by column chromatography (silica gel, eluent chloroform–methanol 9:1, v/v): yield 5.5 g (60%) of oil; IR (neat) 1740 (CO), 1675 (NHCO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3 H, CH_3), 1.15–1.85 (m, 49 H, CH_2 and CH_3), 3.33–3.65 (m, 10 H, CH_3N and CH_2N), 4.13 (t, 2 H, CH_2O), 4.63 (m, 1 H, CHN), 6.67–6.87 (b, d, 1 H, NH), 8.2 (2, 1 H, CHO). Anal. Calcd for $C_{33}H_{67}BrN_2O_3{\cdot}H_2O$: C, 62.14; H, 10.90; N, 4.39. Found: C, 62.46; H, 10.99; N, 3.82.

Dimethylhexadecyl[11-((1-isocyanoethyl)carbonyloxy)undecyl]ammonium Bromide (1). To a solution of the preceding formamide (0.8 g, 1.3 mmol) and triethylamine (0.76 g, 7.5 mmol) in methylene chloride (25 mL) was added dropwise at 0 °C phosphorus oxychloride (0.59 g, 3.8 mmol) in methylene chloride (10 mL). The mixture was stirred at room temperature for 20 h. Aqueous $NaHCO_3$ (40 mL, 7.5% solution) was added and the organic layer was separated, dried (Na_2SO_4), and concentrated under vacuum. The product was purified by column chromatography (silica gel, eluent chloroform–methanol 9:1 v/v): yield 0.5 g (64%) of almost pure isocyanide; IR (neat) 2145 (NC), 1750 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3 H, CH_3), 1.10–1.80 (m, 49 H, CH_2), 3.30–3.63 (m, 10 H, CH_3N and CH_2N), 4.17 (t, 2 H, CH_2O), 4.30 (m, 1 H, CH). Anal. Calcd for $C_{33}H_{65}BrN_2O_2{\cdot}{}^1/_2H_2O$: C, 63.03; H, 10.90; N, 4.45. Found: C, 63.36; H, 11.00; N, 4.24.

Preparation of Vesicles. Amounts of 10–40 mg of **1** were dispersed in 1 mL of triple-distilled water by means of a vortex mixer. Optically clear solutions were obtained on sonication for 30 min at 35 °C: ^{1}H NMR (D_2O) δ 0.90 (b, t, 3 H, CH_3), 1.10–1.80 (b, m, 49 H, CH_2), 3.1–3.5 (b, m, 10 H, CH_3N and CH_2N), 4.2 (b, t, 2 H, CH_2O), 4.6 (b, m, 1 H, CH).

Polymerization of Vesicles. Dispersions of **1** (10–40 mg, 0.02–0.08 mmol) in 1 mL of triple-distilled water, containing a suspension of 0.5–1 mg (1.7–2.4 × 10^{-3} mmol) of nickel capronate, were vortexed and kept at 30 °C for 12 h: UV (H_2O) 340 nm (ϵ 45 M^{-1} cm^{-1}); ^{1}H NMR (D_2O) δ 0.5–1.7 (b, m, 52 H, CH_2 and CH_3), 2.9–3.5 (b, m, 10 H, CH_2N and CH_3N), 4.2 (b, 2 H, CH_2O), 4.6 (b, 1 H, CH). A freeze-dried sample had IR ($CHCl_3$) 1740 (CO), 1640 (N=C) cm^{-1}.

Osmotic Experiments.[13] A stock solution was prepared by vortexing 35 mg (0.06 mol) of compound **1** in 0.6 mL of water containing 0.1 M sucrose. Small aliquots (0.005 mL) of this stock solution were added to 0.25 mL of solutions containing 0.01–0.4 M sucrose. Three minutes after mixing the turbidity was measured at 450 nm. A stock solution of polymerized vesicles was prepared as follows. Compound **1** was dispersed in 0.1 M sucrose as described above. Subsequently 1 mg (2.4 × 10^{-3} mmol) of nickel capronate was added and the mixture was kept at 30 °C for 12 h. With this stock solution the same experiments were performed as described above.

Stability Experiments.[18] Stabilities of vesicles were investigated by adding 5-μL aliquots of ethanol to 0.25 mL of the vesicle or polymerized

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vesicle solutions (10 mg/mL) and then mixing the resulting solutions and measuring the turbidity at 450 nm. A total amount of 100 μL of ethanol was added. The following equation was used to correct for turbidity change due to dilution: corrected turbidity = observed turbidity × (volume of aqueous vesicle solution + volume of ethanol added)/(volume of aqueous vesicle solution).

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Registry No. 1, 85850-53-9; **1** homopolymer, 85850-54-0; L-dimethylhexadecyl[11-((1-*N*-formylaminoethyl)carbonyloxy)undecyl]ammonium bromide, 85850-57-3; *N*-formyl-L-alanine *p*-nitrophenyl ester, 61167-49-5; dimethylhexadecyl(11-hydroxyundecyl)ammonium bromide, 85850-56-2; 11-bromoundecanol, 1611-56-9; nickel capronate, 16034-23-4; dimethylhexadecylamine, 112-69-6.

Redox Conduction in Mixed-Valent Polymers

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Abstract: The redox conduction of thin films of Os and Fe polypyridine polymers was measured by steady-state voltammetry in the electrochemical cell Pt electrode (electron acceptor)/polymer film/porous Au electrode (electron donor)/electrolyte solution/SCE. The redox conduction becomes turned on at potentials near E° of the polymer M(III/II) couple and is dependent on generating the mixed-valent state of the polymer, and the current achieves a limiting value at an overall 1:1 M(III)/M(II) polymer film composition. The limiting current occurs because the 1:1 composition gives maximal M(III) and M(II) concentration gradients in the film, not because the 1:1 composition has an intrinsically greater conductivity. The sandwich electrode assembly is also used to explore certain characteristics of bilayer electrodes.

Organic and organometallic polymers that have significant electrical conductivity are of interest both for their potential technological utility and as models for gaining a more cathodic understanding of the electronic conductivity of materials.[1-5] Polymers incorporating discrete electron donor/acceptor (i.e., electron transfer) sites are an important class of conducting materials, and have recently been intensively investigated as electroactive films on electrodes.[6-32] In many such polymers, electron transport is thought[31] to occur by a hopping mechanism, and this mechanism has been dubbed "redox conduction".

In previous investigations[10,11,21,24,26,31,33-50] of redox conduction

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