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Macromolecular Complexes Leading to High-Performance Energy Devices

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Summary: Dynamic interactions and electronic processes in macromolecule-metal complexes established in 1970s provided conceptual basis for the development of a new class of functional polymers. Principles of soft/multiple interaction and multi-electron processes have been pursued by exploring the macromolecule-metal complexes and polyion complexes, which gave rise to more generalized concept of macromolecular complexes. As one of the multiple interaction, reversible binding of O_2 in aqueous media and facilitated transport of O_2 were first accomplished by macromolecular metal complexes. The related oxygen technologies have led to the development of unprecedented materials to allow oxygen enrichment in cathodes of fuel cells and air batteries. Properties of electric/ionic conduction and electron transfer mediation in macromolecular complexes suggested our avenue toward the "radical batteries" as entirely organic, rare metal-free, and rechargeable burst power sources. Combination of the photoelectrochemistry of macromolecular complexes and the methods for the precision control of charge separation, transport, and storage in polymers derived from the battery research have inspired design principles of novel photovoltaic polymers useful for organic solar cells. In this paper, recent developments of energy-related materials originated from the idea of the macromolecular complexes are focused.

Keywords: electron transfer; facilitated transport; organic battery; reversible binding; solar cell

Introduction

Macromolecular complexes are defined as complexes of macromolecules (Fig. 1).[1] A typical example is macromolecule-metal complexes composed of macromolecules and metal ions. The metal ions give inorganic functionalities to an organic polymer. Intermacromolecular complexes and molecular complexes between macromolecules and organic molecules are also included in the category of the macromolecular complexes. The macromolecular complexes are thus viewed as the molecular-level composites of macromolecules, small organic molecules, and metal ions that are so labile that one could anticipate unlimited possibilities for providing a wide variety of previously unknown molecular functions.

In the macromolecular complexes, physicochemical properties and chemical reactivities of the complex moieties are often strongly affected by interactions with the polymer matrices, which surround the complex moieties as illustrated in Fig. 2. These interactions are weak but significant and act multiply and dynamically. They not only constitute the macromolecular complexes themselves, but also control their higher-order structure based on a dynamic conjugation between the complex moieties and the polymer matrices. Thus, a weak profile in the coordination reactions, a cooperative interaction between the complex moieties and a multiplied or enhanced

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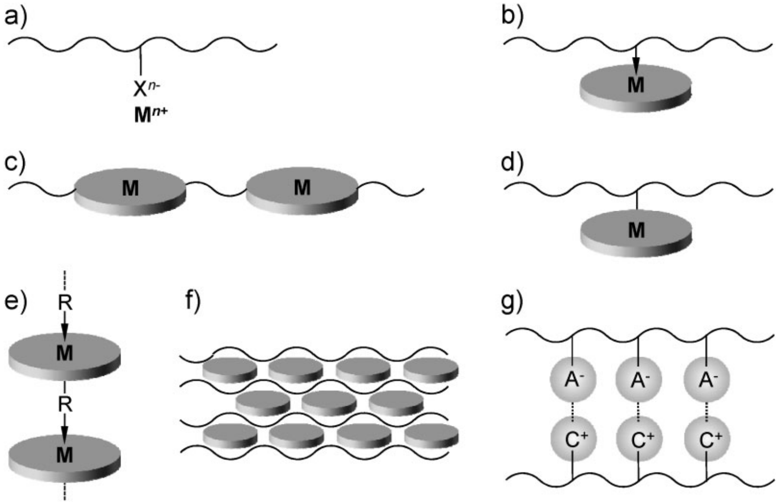


Figure 1.

Types of macromolecular complexes.[1–6] (a) Metal ions electrostatically bound to polyelectrolytes. (b) Metal complexes coordinatively bound to polymeric ligands. (c) Metal complexes as a part of polymer chains (or networks) via the ligand. (d) Metal complexes covalently bound to polymers. (e) Metal complexes as a part of polymer chains (or networks) via the metal ion. (f) Macromolecular complexes between polymer chains and molecularly dispersed organic molecules. (g) Polymer-polymer complexes, such as polyion complexes.

interaction are observed as characteristic features of the macromolecular complexes.

The polymer matrices also provide specific local environments around the complex moieties that contribute to modulate the electronic state of the complex moieties. A highly tailored or precisely controlled structure and/or alignment of the complex moieties have inspired the concept of multielectron transfer process and sequential potential field, which also characterize the uniqueness of the macromolecular complexes as a class of functional materials.

In this paper, the dynamic interactions and the electronic processes characteristically observed for the macromolecular complexes are reviewed, in reminiscence of the pioneering achievements by the father of the macromolecular complexes,

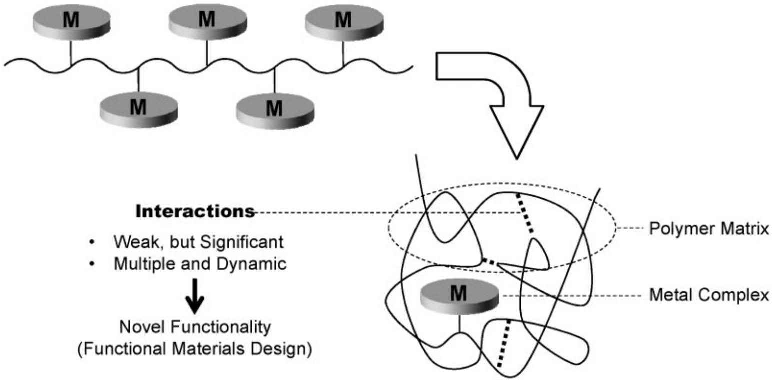


Figure 2.

Concept of functional materials designed with macromolecular complexes, based on their weak but significant interaction.[1,2]

Prof. Eishun Tsuchida (Waseda University, Tokyo), who passed away in 2010. Especially, how the earlier concept of functional design for macromolecular compleses have led to the current research on energy-related materials and devices is emphasized, focusing on the transport phenomena based on exchange reactions that are typically enhanced in the matrices of the macromolecular complexes.

Development of Novel Functionality of Macromolecular Complexes

Interactions in macromolecular complexes consist of various binding forces, such as coulombic or electrostatic force, dipole-dipole interaction, hydrogen bonding, charge-transfer interaction, and hydrophobic interaction. These interactions are featured by fast kinetics, reversibility, and multiplicity in binding, which cooperatively play important roles in determining the overall properties of the macromolecular complexes. In the earlier studies,[1] concepts of "soft interaction" and "multiple interaction" were introduced to account for the multiplicity observed for the binding force in macromolecular complexes, each of which was weak, rapid, and reversible, but was integrated in the matrices to give rise to significant interactive forces. The multiple interactions were supposed to maintain the higher structures of the macromolecular complexes and dominate their molecular-level functions such as recognition and facilitated transport of guest molecules.

The multiple interactions in macromolecular complexes are characterized by their dynamic natures. While metal complexes possess stable coordination structure with static configuration, macromolecular complexes often exhibit labile, unsaturated, and constrained coordination structures caused by dynamic changes in the conformation of the macromolecules. In the earlier studies, the dynamic processes were regarded as essential in understanding the properties of the macromolecular complexes.[1,2] Much efforts have been devoted to unraveling the dynamics of the coordination behaviors found for the macromolecular complexes, typically focusing on the allosteric or cooperative effect of the O_2 binding in hemoglobin,[7–9] by which the rational desgin principles of synthetic O_2 carrries are currently established.

A variety of electronic, magnetic, and redox properties of metal complexes were also supposed to be enhanced in the macromolecular complexes, due to the constrained coordination microenvironment caused by the dynamics of the polymer matrices and the extended site-to-site interaction as a result of the large population of the complex moieties. Along this concept, a number of macromolecular complexes have been explored to accomplish electric conduction, paramagnetism, electrochromism, redox mediation, photochemical and -physical properties, based on their multiple and dynamic interaction. Figure 3 represents how the potential applications anticipated for the macromolecular complexes in the earlier studies[1] have spread to various kinds of functional materials and devices, which clearly demonstrates that macromolecular complexes are currently taking a central role in the development of functional materials.

For energy-related devices such as fuel cells, rechargeable batteries, and solar cells, the material design is based on the reversibility and the intersite interaction that can be significantly enhanced in the macromolecular complexes. We will raise some of the examples for this idea in the following section, tracing the history of the developments in the related materials.

Facilitated Transport of Oxygen

The concept of facilitated transport by macromolecular complex solids was inspired from the reversible binding of O_2 by hemoglobin in solutions. Multiple interaction of gaseous molecules, O_2 and N_2, with metal complexes fixed in solid macro-

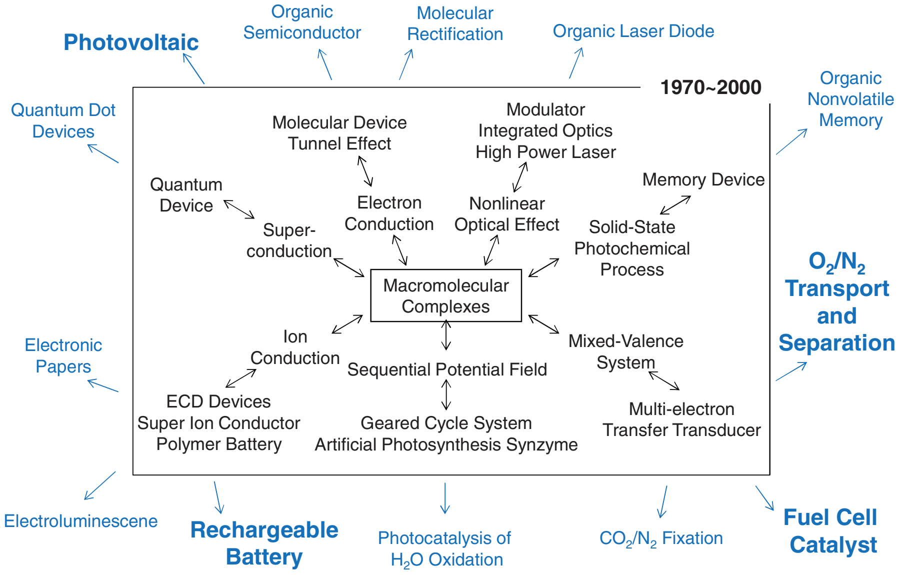


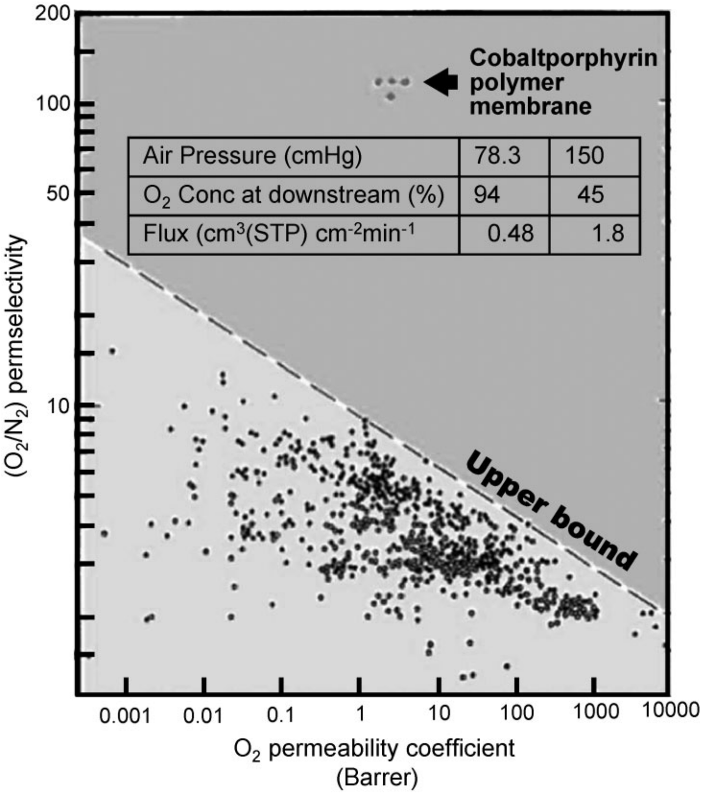
Figure 3.
Potential applications in the field of the macromolecular complexes: development of concept and current research overview.

molecules, has been described in terms of coordination kinetics and molecular diffusion. The small guest molecules have been demonstrated to be enriched by permeating through the membrane of the macromolecular complexes, based on the ligand exchange reaction of the complex moieties.[10] When a cobaltporphyrin was used as the fixed carrier in the layer, a significant increase in the permeation selectivity of O_2 was established, compared to the magnitude of the mass-transfer flux through the membrane by a physical diffusion (Fig. 4).[11,12]

The facilitated transport of O_2 have led to the O_2 enrichment from air, based on the O_2-exchange reaction between the metal centers that are highly populated in the matrices of the macromolecular complex (Fig. 5). A number of metal complexes, in addition to the cobaltporphyrins, and macromolecules that dominate the overall permeation properties of the gaseous molecules by physical diffusion have been explored to combine the high O_2/N_2 selectivity and a large flux through the membrane. Well-designed macromolecular complexes made a breakthrough in the upper bound of the O_2/N_2 permselectivity versus the O_2 permeability coefficient expected for conventional gas separation membranes (Fig. 4). The O_2 enrichment membrane is regarded as a key material for the next-generation oxygen technologies, because of its expected contribution to increase the efficiencies of fuel cells, metal-air batteries, and combustion engines that utilize O_2 as the oxidant for energy conversion. The efficient usage of O_2 in air, which is abundant everywhere with the same composition, is currently an important issue in the development of the energy conversion devices.

Optical Oxygen-Sensing Polymers

The efficient usage of O_2 is also essential in improving the performance of the fuel cells and the metal-air batteries, which is often limited by the supply of O_2 to bring about the suffocation of the devices. Measurement of O_2 concentration or O_2 partial pressure is important to optimize the



Air Pressure (cmHg)	78.3	150
O_2 Conc at downstream (%)	94	45
Flux (cm^3(STP) $cm^{-2}min^{-1}$	0.48	1.8

Figure 4.
O_2 concentration of the downstream through the CoTPP polymer membrane by supplying air (gas chromatographic measurement) at 25 °C.

material balance in the cells. Classical sensing methods for O_2 are classified into the conductivity measurements with metal oxides to detect adsorbed O_2 from the gas phase, the electrochemical methods to determine the reduction current of O_2 in solutions, and the colorimetry based on the reversible reaction of dye molecules with O_2. The advantage of the macromolecular complexes has been demonstrated in optical O_2 sensors, which is based on the luminescence quenching of organic dyes with O_2 (Fig. 6). The quenching process is a typical weak but dynamic interaction

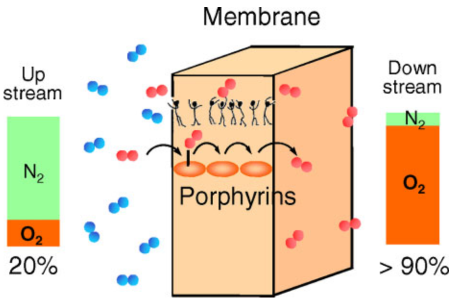


Figure 5.
Concept of facilitated O_2 transport through the fixed cobaltporphyrin carrier in the polymer membrane.

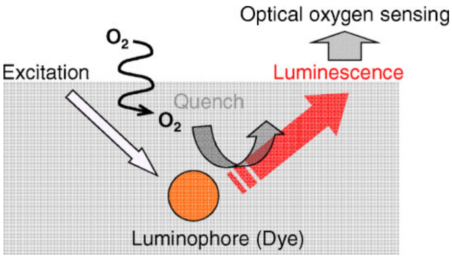


Figure 6.
Optical O_2 sensor based on luminescence from luminophores dispersed in polymer matrices as coating materials.

between the dye and O_2 in macromolecular matrices. Aromatic dyes such as pyrene and quinoline, metal complexes such as ruthenium and osmium polypyridine complexes and metalloporphyrins immobilized in membranes of matrix polymers have been employed for the real-time two-dimensional visualization of O_2 concentration in the fuel cells, which greatly contributed to unravel the mass-transfer process of the operating O_2 cathode.[13]

Charge Transport in Macromolecular Complexes for Energy Storage

The macromolecular complexes have been employed for electrode modification in pursuit of electrocatalytic surfaces for the multielectron reactions[14–17] of small molecules such as O_2, N_2, and CO_2, and various electrochemical devices such as electrochromic cells, sensors, and electrochemiluminescent devices.[18] The motivation for the use of the macromolecular complexes was given by the discovery of significant electroactivity of various polyelectrolyte layers by the incorporation of oppositely charged redox-active metal complexes.[18] Interestingly, the incorporation was observed as an irreversible process for multiply charged complexes, such as $Fe(CN)_6^{4-/3-}$, in poly(vinylpyridine) (Fig. 7), giving rise to redox-active layers immobilized on electrodes. One of the important findings for this class of materials was the redox mediation effect of the incorporated metal complexes, allowing the redox process of the guest molecules to proceed in the layer with substantial thickness by successive bimolecular exchange reactions. A number of cationic and anionic polyelectrolytes and redox-active guest molecules have been examined, which gave insights into the nature of charge propagation and the dynamics of solvent and electroneutralization in macromolecules bathed in electrolyte solutions.

A concept of reversible, facile and high-density charge storage has been inspired by the studies on the modified electrodes. It was found that the charge propagation in the redox-active layers went to completion, when the electroneutralization was accomplished throughout the layer. In that case, the amount of charge stored in the layer was equvalent to the electroactive coverage.[19]

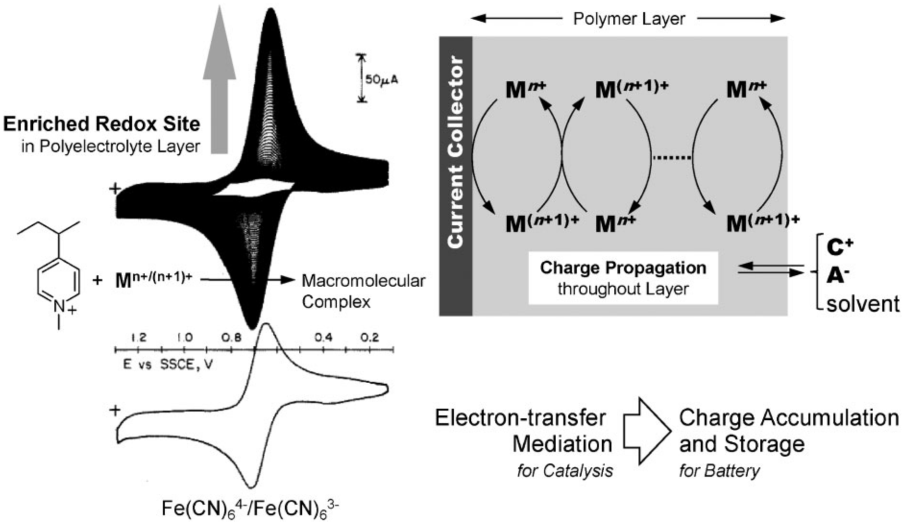


Figure 7.
Macromolecular complexes for highly populated redox sites: From redox mediation for electrcatalytic applications to the concept of energy storage.

The charge-storage density was thus maximized by minimizing the redox-equvalent weights.[20] For this purpose, "radical polymers" have been developed as a new class of electroactive polymers.[21] The radical polymers are characterized by the presence of organic robust radicals, such as nitroxides, 2,6-di-*tert*-butylphenoxyls, galvinoxyls, verdazyls, and nitronyl nitroxides, populated in ultimate density as pendant groups per repeating unit of aliphatic polymers.[22–28] These radicals are viewed as the "greener" substitute of heavy metal ions to take the role of the redox functionality. The chargeless or neutral radical polymers undergo positive (or p-type) charging to polycations and/or negative (or n-type) charging to polyanions, according to the radical groups.[29–33] For many types of the radical polymers, reversible charging processes throughout the polymer layer have been established by the electron self-exchange reaction between the populated radicals, resulting in the storage of positive or negative charges equivalent to the magnitude expected from the formula weight-based theoretical redox capacities of the radical polymers. Interestingly, it was found that the p-type and n-type chargings are likely to proceed at relatively positive and negative potentials, respectively (Fig. 8),[21] which prompted the studies on electrical energy storage with organic polymers. Entirely organic rechargeable devices has been fabricated by sandwiching an electrolyte layer with a couple of neutral polymers different in redox potentials,[34] which suggested new avenues for battery developments in future to release the conventional limitations of resources, safety concern, and inflexibilities in shapes and sizes.

A curious feature of the so-called radical battery is the capability of burst power

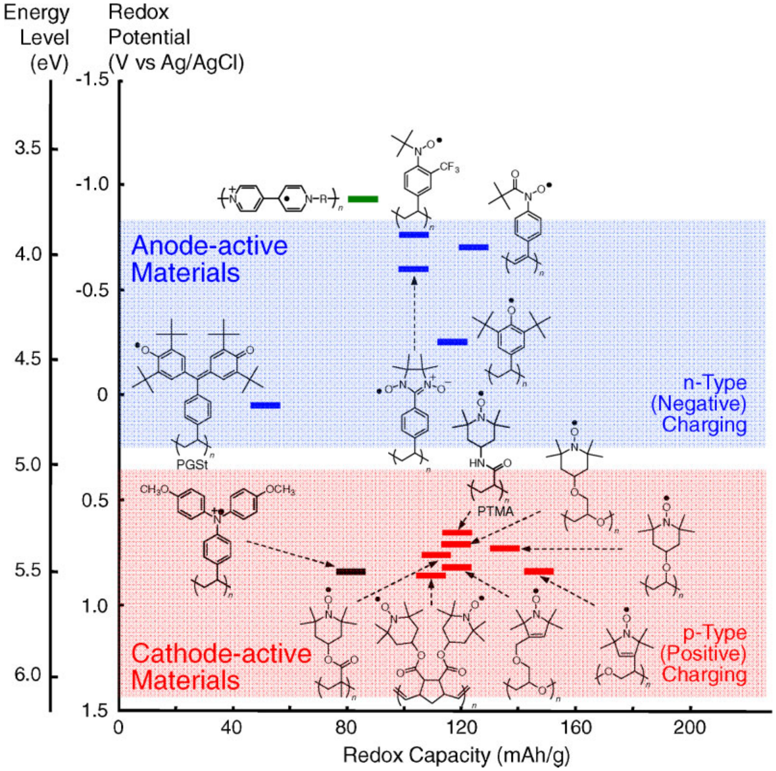


Figure 8.
Map of redox potentials versus formula weight-based theoretical redox capacity of radical polymers.

generation, which allow instant full charging. Radical batteries are characterized by the excellent rate performance and the moderate energy density. The mass-specific energy density is placed between those of polyacetylene- and disulfide-based organic batteries, but the power density is much larger and comparable to those of supercapacitors.

The radical battery is being developed for sub-battery and smart card applications.[35] A 100 mAh-class aluminum-laminated-film-packaged radical battery with a poly(1-oxy-2,2,6,6-tetramethylpiperidinyl-methacrylate) (PTMA)/carbon composite cathode[36] and a graphite anode has been fabricated (Fig. 9).[35] The fabricated battery was half of a business card with 4.3 mm in thickness and weighed only 22 g. A battery pack consisting of four batteries connected in series operated a 200 W-class desktop computer. A rate capability test demonstrated that the battery pack had a 13 A (130 C-rate) discharge capability. The radical batteries are expected as high-power energy sources, not only for electronic devices but also for electric vehicles, replacing the electric double-layer capacitors and nickel metal hydride batteries.

Thin radical batteries are being developed for application to smart cards.[35] A prototype battery with a thickness of 800 μm has been fabricated and tested, which is composed of a composite electrode containing poly(2,2,6,6-tetramethylpiperidin-1-oxy-4-yl vinyl ether) and a lithium metal anode. The discharge capacity of the battery was 6.0 mAh. The direct current resistance of the battery was only 1.5 Ω, and the maximum power output was 2.0 W. This output power is sufficient for high-power applications such as LED flash devices.

Efforts have been directed toward further increasing the theoretical energy density of the radical batteries. Various radical polymers with even smaller formula weights per repeating unit are under development.

Photosensitized Electron Transfer in Macromolecular Complexes

Photosensitized electron transfer processes in macromolcular complexes has been the topics of research as one of their functionalities relevant to energy-related technologies. In the earlier studies, much efforts were devoted to developing synthetic enzymes for artificial photosynthetic systems.[1] The geared cycles and sequential potential fields expected for macromolecular complexes (Fig. 3) were widely explored, in analogy to the organized multistep electronic processes in natural photosynthesis that involved dye excitation, charge separation, redox mediation, reduction of NADP$^+$, and sugar synthesis by the Calvin cycle. The photochemistry of macromolecular complexes was also explored with a view to mimic the natural energy-conversion systems, such as the photocatalytic H_2O_2 generation accomplished with the $Ru(bpy)_3^{2+}$ complex embedded in a particle of chelate resin (Fig. 10),[37] and photovoltaic cells fabricated with the combination of macromolecular complex dyes and redox mediators in solution (Fig. 11).[38] Indeed, these pioneering works by Tsuchida et al. must be

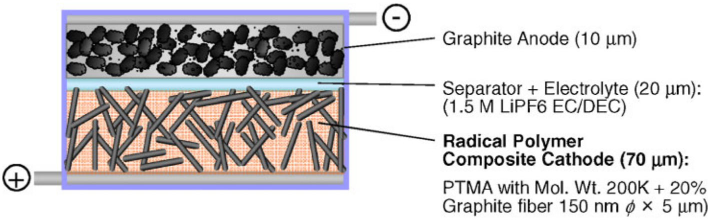


Figure 9.
Prototype of radical battery.

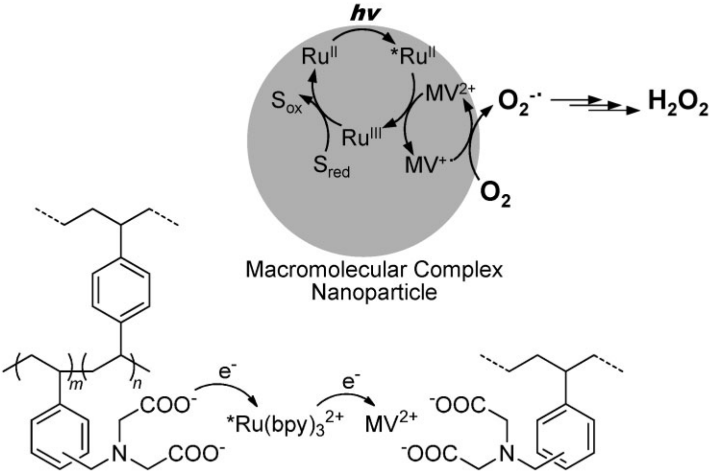


Figure 10.
Photo-sensitization and charge separation by macromolecular complexes.[37].

engraved on our heart as the important milestone of the research on dye-sensitized solar cells (DSSC)[39] that are approaching a conversion efficiency of >12%.

Topics of current research on DSSC include the recent development of so-called radical solar cells, which has been inspired from the radical batteries (Fig. 12). Photovoltaic effect has been accomplished by employing the electrode configuration of the entirely organic radical batteries[34] and placing dyes in-between the p- and n-type polymers, allowing photoexcitation and charge separation at the p-n junction and redox-gradient-driven charge transport through the polymer layer to the current collectors. The amorphous radical polymers have provided optically transparent charge transport layers which proved to be highly compatible with various organic dyes such as indoline-containing molecules. Perspectives of high conversion efficiency have been obtained from the large power density demonstrated for the radical batteries.

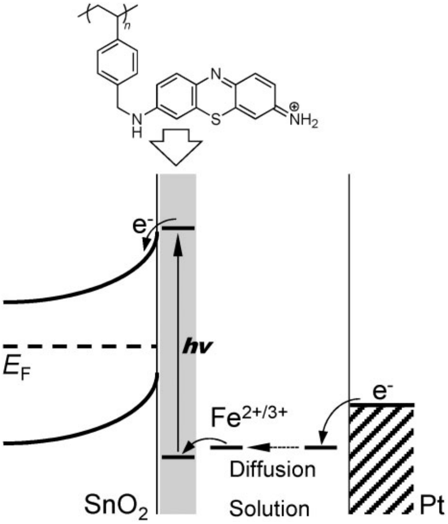


Figure 11.
Dye-sensitization by macromolecular complex systems for photovoltaic cells.[38].

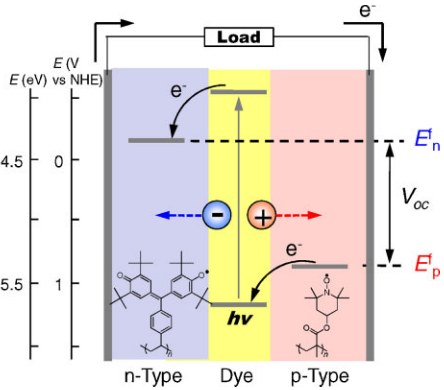


Figure 12.
Electrode configuration in a radical solar cell.

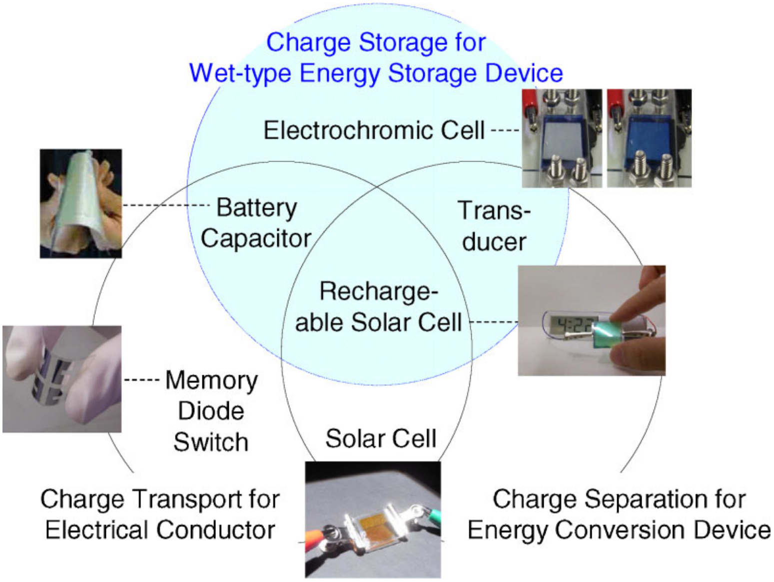


Figure 13.
Energy-related devices along the extension of the development of macromolecular complexes.

Conclusion

A new class of functional polymers have been developed for energy-related application, based on the concept of dynamic interactions and electronic processes in the macromolecular complexes. Insights into the multiple interaction in macromolecular complexes have led to the idea of enhanced exchange interaction between the complexes populated in the matrices of the macromolecules, which have spawned a variety of energy-related materials and devices such as the O_2 enriching membranes and sensors for the fuel cell cathodes, the charge transport and storage materials in organic batteries, and organic photoelectrodes for photovoltaic cells. Increasing types of devices accomplished by the use of the macromolecular complexes (Fig. 13) demonstrate their unlimited possibility as the functional materials.

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