【Grant-in-Aid for Scientific Research(S)】
Science and Engineering (Chemistry)

Title of Project : Development of Novel Photo- and Electro-functional Polymers by SOMO Design of Organic Radicals

Hiroyuki Nishide
(Waseda University, Faculty of Science and Engineering, Professor)

Research Area : polymer chemistry
Keyword : polymer synthesis, organic radical, functional polymer, charge storage, photovoltaic

【Purpose and Background of the Research】

We have been focusing on reversible and rapid electron transfer processes of organic robust radicals and developing "radical polymers" as a new class of functional polymers, which gave insights into the nature of high density energy storage with excellent power-rate capabilities. Based on these results, the present research aims at establishing the chemistry of materials for charge transport and storage exploiting redox gradient-driven electron self-exchange reactions, with a projection as a departure from the conventional conducting polymers which are dominated by the properties based on π-conjugation. The concept of using the non-conjugated polymers for electroactive applications will be broadened by (i) developing highly efficient transporting systems and (ii) precisely designing transport properties by incorporating specific interfacial structures such as heterojunctions. Physical organic chemistry of the electroactive polymers will be explored by (iii) further enhancing the rate properties and pursuing pn bipolar characteristics by expanding the organic radical species, in order to establish (iv) SOMO (singly-occupied MO)-π conjugated systems. The research is expected to provide a breakthrough for organic electronics, and practical insights to affect the fields of organic photovoltaic and rechargeable devices.

【Research Methods】

We have found that oxidation and reduction of organic robust radicals by 1e$^-$ electrode reaction on SOMO both provide stable and isolable closed shell molecules, and that the redox exchange reaction is accomplished throughout the bulk of the radical polymer layer to allow charging and discharging for more than 10^3 times. In the present research, the idea will be generalized, as follows, to provide design principles for highly efficient electroactive polymers, placing emphasis on the physical chemistry of unpaired electrons that are densely populated on polymer chains (Fig. 1).

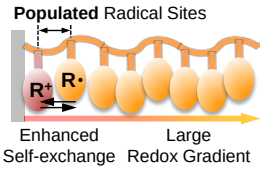

Fig. 1 Charge transport and storage by redox-condensed materials.

First, the charge transport properties will be maximized by increasing the radical concentration and controlling the redox gradient in the polymer layer. Then, the polymers will be examined as materials for charge separation at well-designed dissimilar interfaces. Based on the synthetic chemistry of radical polymers, SOMO-π conjugated and dye-incorporated systems will be developed to upgrade the charge separation, transport and storage properties.

【Expected Research Achievements and Scientific Significance】

Development of polymers with excellent electric and photochemical properties (Fig. 2) and control of their higher order structures at various levels from molecules to bulk scale are expected to maximize the unpaired electron-based functionalities, contributing to establish many types of energy-related materials for next generation radical batteries and organic solar cells.

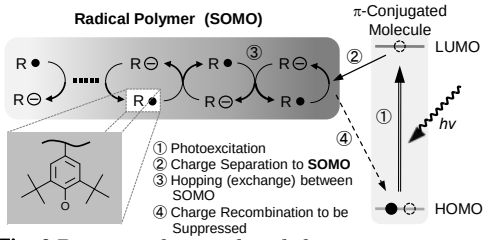

Fig. 2 Deriving photo-induced charge separation properties via exchange reactions on SOMO.

【Publications Relevant to the Project】

- H. Nishide, et al., "Morphology-driven modulation of charge transport in radical/ion containing, self-assembled block copolymer platforms", *Adv. Mater.*, **23**, 5545-5549 (2011).
- H. Nishide, et al., "Radical polymer-wrapped SWNTs at a molecular level: high-rate redox mediation through a percolation network for a transparent charge-storage material", *Adv. Mater.*, **23**, 4440-4443 (2011).

【Term of Project】 FY2012-2016

【Budget Allocation】 150,300 Thousand Yen

【Homepage Address】
http://www.appchem.waseda.ac.jp/~polymer/index.html