

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



Title of Project : Development of Novel Functional Supramolecules based on the Control of Energy Landscapes

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Research Area : polymer chemistry

Keyword : self-assembly, coordination, ferroelectricity, photon up-conversion, nanointerface

【Purpose and Background of the Research】

Supramolecular polymers show a rich variety of constituent elements, higher degree of designing nanoarchitectures and concomitant functions. Accordingly, the ability to self-assemble functional units into well-organized nanoarchitectures holds promise to tailor and improve their properties for technologically important applications. We have developed nanowires and nanoparticles which were self-assembled from a variety of molecules including metal ions, metal complexes, organic and bio-molecules. Based on these studies, the present project aims further to develop functions of social requests, i.e., supramolecular ferroelectrics and photon up-conversion of near-infrared light, by exploiting methodologies to control energy landscapes of supramolecular polymers.

【Research Methods】

To achieve a breakthrough innovation in supramolecular science, we develop methodologies to control landscapes of coordination polymers both in the ground and the excited states.

First, novel coordination polymers which consist of lipophilic metal complexes and ditopic linkers with large permanent dipole moment will be synthesized (Fig. 1). They are designed to be dispersed in organic media, and hierarchical self-assembly from coordination polymers to liquid crystals and solid microfibers will be achieved. The rotation of the ditopic ligands will be investigated by ¹H-NMR and ferroelectric properties of cast films. The use of free-rotating coordination bonding would lead to decrease of the electric field which is required to invert macroscopically aligned dipole moments of

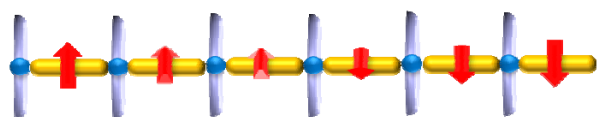


Fig. 1. A schematic illustration of the coordination polymer which consists of metal complexes and ditopic ligands (molecular shafts). The permanent dipole moments are expressed by red arrows.

existing ferroelectrics.

Second, novel supramolecular systems with photon upconversion of near-infrared (NIR) light will be designed based on the triplet-triplet annihilation (TTA) mechanism. As NIR sensitizers (S), Pt(II) or Pd(II) porphyrins will be employed. Emitter molecules (annihilator, A) are selected from organic chromophores such as diphenylanthracene. These sensitizer and emitters are chemically modified in order to add solubility and self-assembling property. It is expected that regular self-assembly of these sensitizers and emitters will maximize the triplet-triplet energy transfer from (S) to (A) as well as the triplet energy migration among (A), which would enhance efficiency of the TTA process.

【Expected Research Achievements and Scientific Significance】

Although recently supramolecular ferroelectrics have been shown for hydrogen-bonded crystals, the present supramolecular polymers are envisaged to give thin films in which macroscopic orientation of aligned dipole moments are controllable at lower applied electric fields. In the supramolecular TTA systems, efficient TTA upconversion will be widely applied to photovoltaics, photocatalysis, and many other light-driven photophysical and photochemical processes.

【Publications Relevant to the Project】

1. R. Kuwahara, S. Fujikawa, K. Kuroiwa, N. Kimizuka, *J. Am. Chem. Soc.*, **2012**, 134, 1192-1199.
2. J. Liu, M-a. Morikawa, N. Kimizuka, *J. Am. Chem. Soc.*, **2011**, 133, 17370-17374.

【Term of Project】 FY2013-2017

【Budget Allocation】 192,000 Thousand Yen

【Homepage Address and Other Contact Information】

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