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学 位 論 文 題 目 Design and Functions of Novel Supramolecular  
and Macromolecular Nanoarchitectures

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Studies on  $\pi$ -electronic molecules have been one of the important subjects in organic electronics and optoelectronics. Introduction of metal modules to conjugated molecules plays an important role in expanding the diversity of supramolecular self-assembly. For example, properties of metal ions such as magnetism, redox, and photochemical activities may be transcribed on the supramolecules. This thesis reports a general strategy for the integration of metal species to  $\pi$ -electronic compounds *via* conjugation. It demonstrates the first synthesis of conjugated multinuclear metallo complexes and their assemblies to form two-dimensional molecular tapes and sheets with unique electronic and photo functionalities. In relation to these hole-transporting supermolecules, this thesis reports a new kind of n-type conducting molecules with robust thermal stability, high processability, and large electron mobility. These unique properties are unprecedented and highly correlated with their well-defined supramolecular architectures.

Along this line, this thesis reports the development of novel functional macromolecules *via* topological design, by focusing on the creation of a new class two-dimensional polymers and the finding of light-harvesting effect of conjugated microporous polymers. Exploration of functional macromolecules is one of the interesting and central topics in chemistry, physics, and molecular science. Especially,  $\pi$ -electronic macromolecules are indispensable in molecular devices such as biosensors, light-emitting diodes, and plastic solar cells. Their capabilities of triggering emission, photoinduced energy/electron transfers, and charge carrier transportation are key factors that vitalize device performance. Various 1D conjugated polymers have been developed for these purposes, while the molecular design of 3D conjugated polymers has led to unique dendritic scaffolds for cascade energy transduction. To access 2D polymeric architecture, elaborate modifications of 1D conjugated polymers have led to findings of 2D anisotropic monolayers and thin films by SAM, LB, and LBL techniques. Clearly, a covalent 2D polymer assures a robust and shape-persistent polymer network with permanent order in its building blocks. Synthesis of such covalent 2D polymers has been heavily pursued since they are expected to open entirely new vistas for future science and technology. However, the existence of covalent 2D polymers has not yet been proved and the development of a realistic way to create such polymers remains a major challenge. This thesis describes the first example of the synthesis of a covalent two-dimensional (2D) conjugated polymer, which is a completely new class of polymer.

As summarized in the above, this thesis consists of the design, synthesis, and functional exploration of supermolecules and macromolecules, with an emphasis on the development of novel  $\pi$ -electronic nanoarchitectures.

**(1) The Noncovalent Assembly of Benzene-Bridged Metallosalphen Dimer: Photoconductive Tapes with Large Carrier Mobility and Spatially Distinctive Conduction Anisotropy**

In photoconduction, photo-generated charge carriers move to electrodes and produce electric current. Studies on such photo-responsive molecules have been an important part of

progress in the field of solar energy conversion. Single crystals of certain  $\pi$ -conjugated molecules, e.g., arenes, have been reported to become photoconductive as a result of exciton migration and charge separation at the molecule–electrode interface. However, small arenes absorb photons only in the ultraviolet region, while large arenes with absorption bands extending to the visible region require complicated synthesis along with tedious purification and are difficult to process. Moreover, the undesirable photoinduced dimerization and bleaching of arenes deter their application to optoelectronics. During a study on the assembly of conjugated multinuclear metallocomplexes, the author serendipitously discovered that these  $\pi$ -electronic metallo-conjugates are photo-responsive, robust against irradiation and may avoid the above drawbacks. In the first part, the author describes a newly synthesized benzene-bridged metallosalphen dimer tailored with aliphatic chains, which is demonstrated for the solution-processed assembly of a  $\pi$ -electronic tape. The tape is unique in that it shows a large intrinsic carrier mobility, is spatially anisotropic in conduction, forms *p*- or *n*-type semiconductors tunable upon doping. The author emphasizes that the tape is highly responsive to visible light irradiation, triggers prominent photocurrent generation, shows on/off ratios as high as  $9.0 \times 10^4$  and is capable of repeated on-off switching without deterioration. Molecular design of bridged dinuclear metallocomplexes has led to the findings of unusual physical properties and utilities such as catalysts, mimicry for biological enzymes, molecular magnets, building blocks for coordination polymers and MOFs. However, photo functions have been unexplored to date.

## **(2) Noncovalently Netted, Photoconductive Sheets with Extremely High Carrier Mobility and Conduction Anisotropy from Triphenylene-Fused Metal Trigon Conjugates**

Studies on conjugated molecules have been one of the central subjects in organic electronics and optoelectronics. Introduction of metal modules to conjugated molecules plays an important role in expanding the diversity of supramolecular self-assembly. For example, properties of metal ions such as magnetism, redox, and photochemical activities may be transcribed on the supramolecules. In this context, triphenylene, a typical conjugated planar molecule, is an intriguing motif for such a purpose due to its utility in supramolecular assembly. However, up to date, metal-containing triphenylene derivatives have been limited to only thioligated bismuth and silver crystalline solids. In relation to the first part, here, the author reports the first example of triphenylene-fused metal trigon conjugates, where multinuclear metal sites are connected to one another via conjugation with triphenylene core. The metal trigon upon self-assembly forms well-defined 2D sheet, which harvests a wide range of photons, converts them to bright emission, and allows exciton migration. Moreover, the 2D sheet is semiconducting with a high carrier mobility and capable of repetitive on–off current switching at room temperature. The noncovalent 2D sheet is photoconductive to exhibit a quick response to visible light irradiation with large on/off ratio. Spatial anisotropy in conductivity reveals that the sheet assembly favors a conduction path perpendicular to the stacked sheets other than the one along the sheet planes. These characters are unique and clearly originate from the highly ordered molecular structure of the noncovalent sheet assembly.

### **(3) Pyrene-Fused Phenazine Bisimides as Robust, Solution Processable and Chemically Addressable *n*-Channel Organic Semiconductors**

Organic semiconductors have attracted great interests in relation to their utilities in optoelectronics and molecular electronics. In contrast to rich varieties of *p*-type semiconductor, *n*-type organic semiconductor has been very limited in numbers to certain electron-withdrawing  $\pi$ -conjugation systems including perfluorinated aromatic compounds, heteroaromatic compounds, and fullerene derivatives. Due to electronic deficient nature, *n*-type organic semiconductors are usually unstable and air sensitive in conducting condition. Recently, bisimides with aromatic cores such as anthracene, naphthalene, perylene, and tetrathiafulvalene moieties have been reported to function as *n*-type semiconductor, which allows supramolecular self-assembly upon tailoring at bisimide terminals with alkyl chains to fabricate various nanostructured devices. Very recently, phenazine compounds have been demonstrated to be *n*-type semiconductor with high carrier mobility due to the presence of electron-withdrawing imine units. In this part, the author reports a molecular system combining three structural parameters (1) bisimide terminals, (2) phenazine linkages, and (3) an extended  $\pi$ -conjugation pyrene core, *i.e.*, pyrene-fused phenazine bisimide as a novel *n*-type organic semiconductor. The author highlights that such a topological design allows a multiple combination of high thermal and air stability, ordered crystalline packing together with facile solution processability. Moreover, protonation of phenazine units leads to the generation of quadruple cationic bisimide, thus converting the conjugated neutral skeleton to positively charged backbone. We found that bisimide and cationic bisimide are *n*-type semiconducting with the largest charge carrier mobility of  $4.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and capable of stable repetitive on/off current switching in ambient condition.

### **(4) Synthesis of Covalent Two-Dimensional Polymers Using a Topological Approach**

Conjugated polymers are commonly used for a wide variety of applications. Extensive research has led to the realization of one-dimensional linear and three-dimensional hyperbranched and dendritic conjugated polymers. Despite tremendous efforts, a fully-characterized covalent two-dimensional conjugated polymer has not yet been achieved and its creation remains a substantial challenge. In this part the author reports the synthesis of a two-dimensional conjugated poly(para-phenylene), by covalently 'knitting' one-dimensional linear conjugated chains, based on a specific topological two-dimensional cross-coupling polycondensation reaction. This 2D polymer is crystalline and consists of flat square sheets with very clear and smooth edges. It holds extremely dense interwoven longitudinal and latitudinal straight chains of  $6.6 \times 10^6$  cubic micrometer and possesses persistent, long-range, periodic repeating-unit order. Electronic experiments and transient conductivity measurements predict that two-dimensional conjugated polymers would exhibit completely novel properties when used in molecular electronics and optoelectronics.

### **(5) Light-Harvesting Conjugated Microporous Polymers: Spatial Confinement and Inner Surface-Interfered Energy Transduction**

Conjugated microporous polymers (CMPs) are amorphous polymers with conjugated

framework and inherent three-dimensional porous structure. Owing to their unique pore sizes which could be tuned through molecular design, CMPs serve as a bridge between zeolites and MOFs/COFs. However, most studies to date have mainly focused on the gas storage and separation properties. The author envisioned that the highly dense  $\pi$ -electronic components of CMPs framework could serve as antennae for collecting photons, while the well-defined inner pores could embed and spatially confine energy-accepting counterparts, thus leading to the fabrication of a supramolecular system for energy transduction mediated by the large inner surface of CMPs. In the last part of this thesis, the author reports the first example of light-harvesting CMPs, which consist of microporous polyphenylene framework as antennae and coumarin 6 noncovalently encapsulated within the pore as energy-accepting pool. The CMP-based light-harvesting system not only allows the creation of a novel noncovalent energy donor-acceptor array but much importantly makes it possible a directional pinpoint energy transfer from the framework to the energy converter. These characters together with a large inner surface facilitate the energy transduction process and result in an almost 100% energy transfer quantum efficiency. These unique properties constitute an important step to the utility of CMPs in sensing and optoelectronics.

Exploration of functional supramolecular and macromolecular nanoarchitectures is a subject that has a high probability to lead to the development of new materials. In summary, the author has developed a series of novel  $\pi$ -electronic supermolecules and macromolecules. The author designed and synthesized a series of new  $\pi$ -electronic multinuclear metallo conjugates and *n*-type conjugated molecules and succeeded in the construction of  $\pi$ -electronic two-dimensional assemblies. By using topological molecular design, a new class of polymers, *i.e.*, covalent two-dimensional polymer was created. By exploration of the porous channel, a novel light-harvesting antenna based on conjugated microporous polymers was established. These  $\pi$ -electronic organic architectures show unique photo and electrical functions that clearly originate from their highly ordered structures and thus open a new way to molecular optoelectronics and electronics.

光機能性ナノ物質の開拓は、エネルギー利用の観点から極めて重要な課題である。光機能性物質を構築するには、いかに分子秩序を作り上げ、長距離にわたって維持することがキーポイントである。本研究では、構成ユニットの配列制御に着目し、超分子と高分子の両戦略からアプローチし、新規な機能性ナノ物質の設計に挑戦した。具体的に、新規な有機小分子やビルディングブロックを設計し、超分子相互作用及び高分子重縮合反応を用いて、様々な低次元光・電子機能性物質群を創出し、その構造に由来する特異な光機能について検討した。

第一章は機能性ナノ物質の構築に関して、これまでの超分子および高分子アプローチについて記述してある。第二章は拡張  $\pi$  共役系であるベンゼンサロフェンを配位子として用いて、共役二核金属錯体を設計・合成し、自己組織化により軸配比の極めて高いベルトの構築、その光機能、キャリア移動機能について述べてある。第三章はトリフェニレンをコアとして有する共役三核金属錯体を設計・合成し、その自己組織化能を検討すると共に、形成された二次元超分子シートの構造解析、光伝導機能、キャリア運搬機能について記述してある。第四章は新規な  $n$  型半導体の合成を目指して、フェナジンとイミドを組み込んだ  $\pi$  電子系分子を合成し、その自己組織化及び酸化還元特性、キャリア移動能について記述してある。第五章は二次元共役高分子の合成、構造解析、光機能及びキャリア伝導機能について記述されている。第六章はマイクロ孔を有する共役高分子を合成し、光捕集アンテナ系の構築及び光エネルギー移動について記述されている。第七章は全体まとめと展望について記述している。

多核金属共役電子系を用いた自己組織化アプローチは、金属の多彩な光機能や酸化還元機能を活かすことができる。特に、構造特異な低次元機能性ナノベルトや二次元シートを構築することに成功し、これまでに類のない高いキャリア移動能や光伝導性を見いだしている。一方、高分子アプローチでは、世界に先駆けて共役二次元高分子を合成することに成功した。共役二次元高分子は重縮合反応によりポリフェニレン鎖を規則正しく二次元的に織り込んだ構造を有し、また積層することにより四角プリズムを形成していることを見出している。特に、二次元的に共役しているため、構造に由来する特異な機能が期待できる。実際、キャリア移動度を計測したところ、従来の直線状高分子に比べて、百万倍も高い移動度を有することを突き止めた。本研究は、『共役二次元高分子』の初めての例として注目され、新しい光・電子機能性物質として大いに期待できる。

以上のように、本論文では、様々な  $\pi$  電子系分子を合成し、新規な低次元ナノ構造体及び共役二次元高分子の合成及び機能開拓に成功している。特に、共役二次元高分子の合成は極めて独創的であり、皆無である。審査会では Chen 氏の研究に対する取り組みや努力が伺われた。世界初の共役二次元高分子の合成およびその機能開拓を通じて、新しい分子科学を開拓する上で重要なベースとなり得る物質を創出したことで、国際的にも高い水準の研究であると判定された。よって、審査委員会は出願論文が博士（理学）の授与に値すると全員一致で判断した。