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学位論文題目 DESIGN, SYNTHESIS, AND FUNCTIONS OF NOVEL
CONJUGATED MICROPOROUS POLYMERS

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論文内容の要旨

Nanoporous materials that have large specific surface areas are of broad interest in relation to their outstanding functions and wide applications in various fields such as gas adsorption and storage, catalysis, light-emitting diodes, semiconductors, and light energy conversions. Among various porous materials thus far developed, conjugated microporous polymers (CMPs) represent a new class of porous architectures because CMPs are purely organic polymers that can be composited with light-weight elements via strong covalent bonds. One significant feature of CMPs is that the molecular skeleton is p conjugated, thus making a sharp contrast to other families of porous materials. Most studies on CMPs to date have focused on the development of synthetic approaches for the control of pore size and surface area. However, the functions of CMPs, apart from gas storage, have not yet been well explored. In this thesis, the author focused on the design, synthesis, and functional exploration of CMPs.

(1) Three-dimensionally Interlocked Architecture for the Construction of Conjugated Polymers

Conjugated polymers play a vital role in lasing, light-emitting diodes, flexible transistors, and solar cells. Owing to their rigid conformation, they have a high tendency to aggregate in solution and the solid state. Such aggregation leads to the dissipation of excitation energy and ultimately limits their utility as light-emitting motifs. In Chapter 2, the author describes the design, synthesis, and functions of new light-emitting conjugated polymers.

The author developed a strategy for the design of highly luminescent conjugated polymers by restricting rotation of the polymer building blocks through a microporous network architecture. The author demonstrated this concept using tetraphenylethene (TPE) as a building block to construct a light-emitting conjugated microporous polymer. The interlocked network successfully restricted the rotation of the phenyl units, which are the major cause of fluorescence deactivation in TPE, thus providing intrinsic luminescence activity for the polymers.

To monitor the development of the porous network and the growth in p -conjugation, time-dependent Yamamoto reactions of tetrakis(4-bromophenyl)ethene were carried out at different reaction times to produce a series of TPE-CMPs. TPE- have high surface area and possess homogeneous micropores with a size of about 0.8 nm. The TPE-CMP network grows larger with increasing reaction time to achieve large surface area but with retained pore size.

The absorption bands of TPE-CMPs redshifted as the reaction time was increased, which indicates a progressed extension of p -electronic conjugation. Fluorescence spectroscopy shows that the emission bands of the TPE-CMP samples were increasingly redshifted. Fluorescence anisotropy measurements showed that the fluorescence of TPE-CMPs were significantly depolarized in comparison with linear polymer analogue, indicating that the CMP structure can facilitate exciton migration over the three-dimensional network.

The absolute quantum yield of fluorescence (Φ_{FL}) of monomer and linear polymer analogue were only 0.20% and 0.65%, respectively. In sharp contrast, the Φ_{FL} value of TPE-CMPs was as high as 40% under identical condition. Therefore, the interwoven CMP scaffold can efficiently enhance luminescence activity. More significantly, the TPE-CMP samples are highly luminescent even in the solid state, without showing deterioration in light-emitting activity or with any apparent differences between the samples prepared over different reaction time.

The CMP network with three-dimensionally interlocked skeleton suppresses the rotation of building blocks, promotes p -electronic conjugation, facilitates exciton migration, and enhances luminescence irrespective of the solvent and material state. These positive “CMP effects” on p -electronic conjugation feature CMPs as a unique platform for the design of de novo conjugated materials, which can be difficult to achieve with conventional linear polymers. Because emission losses induced by rotation are ubiquitous among chromophores, this network approach can be generalized for the development of various efficient light emitters and wavelength converters.

(2) Core-Shell Architecture for the Construction of Conjugated Polymers

Core-shell structuring is a fascinating approach that combines two materials to produce an onion-like morphology. This approach has been well established for constructing inorganic nanoparticles, organic-inorganic hybrids, and macromolecular assemblies, and it has shown its high potential for achieving unique architectures and outstanding functions. However, core-shell-structured p -conjugation system is unprecedented and remains a synthetic challenge.

In Chapter 3, the author describes a strategy for the core-shell structuring of p-conjugated systems based on CMP architectures. The author demonstrates this concept through a consecutive polymerization of two different CMP networks to form the core and shell parts of the polymer skeleton. A one-pot, two-step polycondensation system was newly developed to initially construct a blue-luminescent polyphenylene CMP network as the core, onto which another yellow-luminescent polytetraphenylethene CMP skeleton is grown to form the shell. The different chromophores in the core and shell allow monitoring of the core-shell structural development.

As revealed by absorption and fluorescence spectroscopy together with nitrogen sorption isotherm measurements, the core-shell structure enhances the porosity, develops a progressed extension of the p-conjugation, and promotes exciton migration. These CMPs are highly luminescent with a Φ_{FL} of about 30%, and retain their emission colors irrespective of the solvent including CH_2Cl_2 , $CHCl_3$, hexane, DMF, THF, dioxane, benzene, methanol, and water. Interestingly, the core-shell-structured CMPs are highly luminescent even in the solid state and give emission colors similar to their solutions. In this sense, the core-shell-structured CMPs represent a new class of light-emitting materials, which not only allow the tuning of fluorescence over a wide range of wavelengths but they are also robust in that they retain both the emission color and brightness, irrespective of the solvent and state. Moreover, a change in the content of the shell or the inversion of the core and shell components tunes the color of the emitted light over a wide range of wavelengths, from deep-blue to near-white, green, and deep-yellow.

These outstanding features are not achieved by the conventional linear conjugated polymer architectures and are highly correlated with the three-dimensional architecture of the CMP scaffolds. This methodology is compatible with other cross-coupling reactions and is applicable to various p-building blocks. Therefore, the core-shell-structured CMPs offer significant potential in both the architectural and functional design of light-emitting and semiconducting materials.

(3) Fused Network Architecture for the Construction of Conjugated Polymers

In Chapter 4, the author describes the design, synthesis, and functional exploration of conjugated polymers with fused network architecture. By extending the strategy established in Chapters 2 and 3, the author extended the study to the fused network structure, with an aim to constructing a conjugated polymer with exceptional conducting properties.

The author developed hexaaminotriphenylene and pyrene tetranone as monomers for the construction of phenazine-fused porous network polymers. The tuning of reaction conditions allows the synthesis of the networks with high surface areas and extended p-conjugation. These fused network polymers are useful for photoenergy conversions and electric energy storages.

As summarized above, through the three-year work, the author demonstrated that the three-dimensional CMPs with p conjugated skeletons together with well-defined nanopores enable the development of novel materials that are completely different from traditional linear conjugated polymers without porous structures and conventional porous materials lacking p correlations among the building blocks. Especially, the author has developed new principle and strategy for the molecular design of light-emitting conjugated polymers, which are completely different from molecular approaches based on site isolations with bulky polymeric matrices that have been developed to prevent the aggregation of conjugated polymers. Those approaches provide highly luminescent polymers, but at the price of a loss in interchain electronic communications. In contrast, the three-dimensional CMPs are highly active in mediating exciton migration and charge carrier transport, thus proving a novel platform for lasing, chemical sensing, and energy storage.

博士論文の審査結果の要旨

共役多孔性高分子 (Conjugated Microporous Polymers; CMPs) は従来の共役高分子にはない多孔構造を持ち、また、通常の多孔性材料にはない π 共役を有しているため、新しい物質として期待されている。許氏は、本研究において、様々なモノマーを合成し、C-C 結合反応という戦略からアプローチし、多孔性共役高分子の設計に挑戦した。具体的には、新規な π ビルディングブロックを設計し、重縮合 C-C 結合カップリング反応を用いて、様々な共役多孔性高分子物質群を創出し、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、共役多孔性高分子に関する背景、すなわち、これまでの分子設計、合成反応、構造解析、及びガス吸着、機能開拓について記述してある。第二章は、 π 共役分子であるテトラフェニレンエテン誘導体をモノマーとして設計し、Yamamoto 反応により重縮合を行い、新規な蛍光発光性高分子を合成したこと、さらに、その共役構造、多孔構造、ガス吸着、蛍光発光能について述べてある。第三章は、共役多孔性高分子の三次元骨格構造を活かして、コア-シェル構造を有する共役多孔性高分子を構築したこと、および、その共役多孔構造、蛍光特性、及び構造による蛍光発光特性の制御について記述してある。第四章は、新規な縮環型共役多孔性高分子の合成を目指して、トリフェニレンヘキサアミンとケトン類を用いた π 電子系多孔性分子の合成について記述してある。第五章は、全体のまとめと展望について記述してある。

多孔構造を用いることで、 π 共役を促進できること、励起子を移動できること、さらに蛍光発光能を著しく改善できることを発見している。従来の共役高分子とは対照的に、共役多孔性高分子は溶媒や状態に依存せず、強く発光できることを実証している。コア-シェル構造を有する共役多孔性高分子は、コアとシェルに異なる共役系を導入することができる。さらに、コアとシェル成分を調整することで、高い蛍光発光能を保ちながら、幅広い波長領域にわたって蛍光波長をチューニングすることができ、コア-シェル構造を用いてバンドギャップを制御できることを発見している。縮環型共役多孔性高分子は共役構造に多数の窒素原子を規則正しく導入することができ、新しい蓄電材料としての可能性が秘められている。許氏の研究は、『共役多孔性高分子の構造制御と光機能』の代表的な例として注目されている。許氏の研究は、共役高分子の新しい設計指針を与えるとともに、従来の多孔性材料にはない新しい機能発現に成功している。

以上のように、本論文では、モノマーの分子設計を通じて、新規な共役多孔性高分子の合成及び機能開拓に成功している。特に、蛍光発光性共役多孔性高分子の合成は極めて独創的である。審査にて許氏の研究に対するねばりづよい努力や、真剣な取り組みが伺われた。様々な共役多孔性高分子の合成およびその構造制御を通じて、新しい光機能を開拓したことで、国際的にも高い水準の研究であると判定された。公開発表も内容、質疑応答ともにきちんとしており、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。