

論文の内容の要旨

論文題目

Linear Heterojunctions Composed of Graphite-like Semiconducting Nanotubular Segments (グラファイト状半導体ナノチューブセグメント からなる一次元ヘテロ接合)

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Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solution as well as in the bulk. As well known, self-assembly plays an essential role in biological systems, however, it is only of recent date that these supramolecular polymers enjoy a steadily increasing interest due to the fact that these polymers exhibit unprecedented and highly useful functional properties. The present thesis contains an extensive study on a supramolecular block copolymer base on self-assembled hexabenzocoronenes.

In Chapter 1, the basic concept and recent progress concerning supramolecular polymer chemistry was introduced. The first section explained the definition and recent categorical examples. The following section focused on one-dimensional supramolecular polymers with electronic functions. Then the chirality issue including “chiral memory”, “sergeant and soldier effect” and “majority rule” was discussed. The last section introduced the chemistry of nanotubular self-assembled hexabenzocoronenes developed by our group.

In Chapter 2, a ligand attached amphiphilic hexabenzocoronenes was designed, with the expectation combining coordination chemistry to carbon rich assemblies. As the first step toward this goal, a controlled assembly of Pt(II)-ligating hexabenzocoronene derivatives into ‘graphite’ nanotubes hybridized with metal-coordination layers, which are potentially applicable as seeds for the formation of metallic nanoclusters, was presented. By using pyridyl-appended hexabenzocoronene, three different nanotubes molecularly hybridized with pyridine–Pt(II) coordination layers were successfully developed. For coordination chemistry, a wide variety of transition metal ions are available, which can be reduced into metallic clusters. Studies on seeding or templating the formation of metallic nanoclusters using metal ion-coated hexabenzocoronene ‘graphite’ nanotubes is one of the subjects worthy of further investigation.

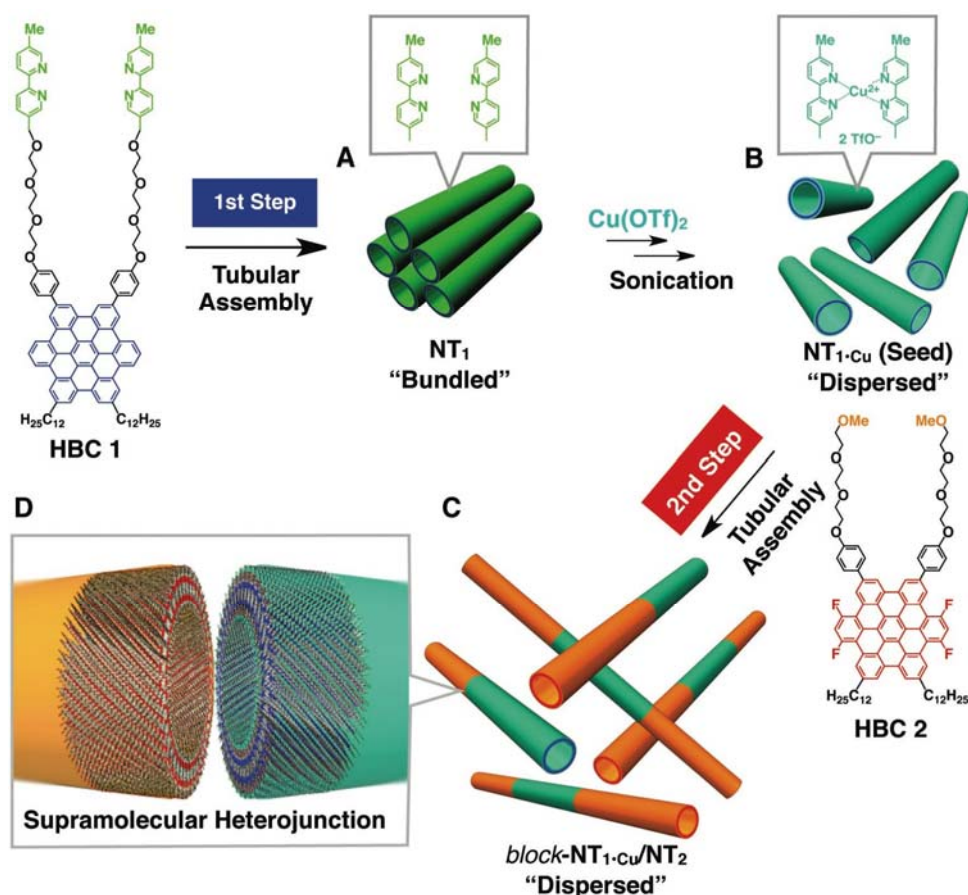


Fig. 1. Molecular structures of **HBCs 1** and **2**, and schematic illustrations of the preparation of (A) **NT₁** (bundled) by MeOH vapor diffusion into a THF solution of **HBC 1**, (B) seed **NT₁-Cu** (dispersed) by post-functionalization of **NT₁** with $\text{Cu}(\text{OTf})_2$ in MeOH, and (C) **block-NT₁-Cu/NT₂** (dispersed) by cooling a hot acetone solution of **HBC 2** in the presence of **NT₁-Cu** as the seed. (D) Schematic illustration of an idealized cross section of **block-NT₁-Cu/NT₂** at the heterojunction interface.

Based on this metal-ion coated nanotubular assembly, Chapter 3 presented the first success in constructing a linear organic heterojunction at nanoscale by stepwise coassembly of dissimilar molecular graphenes, where a graphite-like nanotube was used as a seed for the subsequent growth of the second nanotubular segment (Fig. 1). The research in this chapter overcame the essential problem arising from the dynamic nature of molecular assembly. It is also noteworthy that, the long range excited electron and energy migration is remarkable, considering that they are brought about only by non-covalent connection of two different homotropic blocks with an extremely thin (≈ 3 nm) facet. In particular, the nearly perfect fluorescence quenching of one of its block substantiates that electronic effects of heterojunctions can indeed propagate over a micrometer-long distance through a great number of π -stacks in semiconducting organic materials.

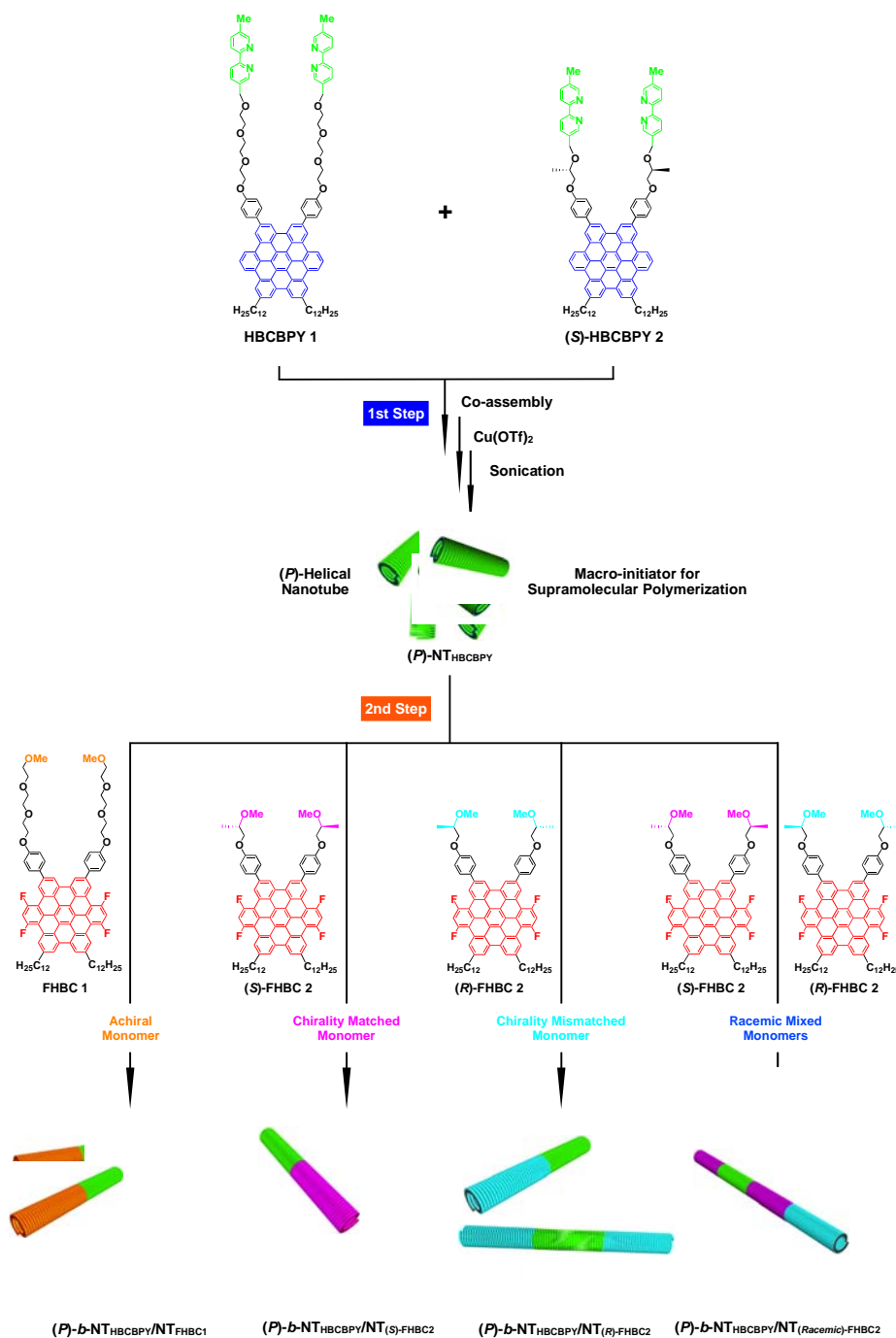


Fig. 2. Molecular structures of **HBCBPY**, **FHBC** and the schematic illustration of the stereo-selective and stereo-elective supramolecular polymerization process.

Chapter 4 demonstrated the introducing a helical chirality into this nanotubular assembly and observed a non-volatile chiral memory in this nanoscale molecular assembly. Through a translation of chirality of a molecular level to supramolecular level, diastereomerically enriched nanotubular assemblies were obtained, which were then converted into enantiomeric forms by removing of the chiral auxiliary. While the nanotubes result from a dynamic mixture of the building blocks, they deviate from equilibrium with the growth, most likely

except their edge parts, which may still take participate in dynamic events. Based on the conventional understanding of supramolecular chirality, the non-volatility of chiral memory observed in the nanotube is remarkable and might provoke new researches on chirality issue at the nanoscale.

Then a systematic study in Chapter 5 revealed the stereo-elective and stereo-selective feature in this supramolecular block copolymerization process (Fig. 2). Helicity is one of the essential structural elements in biological macromolecules and has been considered to correlate with a long-lasting question of the origin of homochirality in nature. In this chapter, we reported that helical handedness is inherited in sequential two-stage supramolecular polymerization of different molecular graphenes. The macro initiator was prepared by co-assembling of graphene molecules and stabilized by wrapping in a metal-ion coordination shell. The second segment of the polymer has to follow the same helical sense with the initiator, even the monomer is a chiral. In another word, the supramolecular helical chiral information from the nanotubular seed could be replicated and imprinted into the growth segment during the block copolymerization initiated by macroinitiator process. When a chiral monomer was used during the copolymerization, the helical sense of the second segment was still determined by the helical sense of the macroinitiator only.