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Hexagonally Ordered Nanostructures Comprised of a Flexible Disk-like Molecule with High Self-Assembling Properties at Neutral and Cationic States

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Self-assembly of organic π -conjugated systems in solution can be widely utilized to construct unique, complex supramolecular structures.^{1,2} Thus, π -conjugated molecules with either electronwithdrawing groups or large π -circles and disks self-aggregate in solution by $\pi - \pi$ stacking interactions and solvophobic effects.³ On the other hand, solid state and surface organization of π -conjugated molecules is frequently applied to molecular electronics.^{4,5} To control one-, two-, or three-dimensional arrangement of the molecule in the solid state, preaggregation of conjugated π -systems plays an important part.

Recently, TTF-containing oligomers, polymers, and dendrimers have been synthesized to investigate redox-active supramolecular structures.⁶ In particular, conjugated TTF oligomers are regarded as candidates for building blocks of supramolecular systems because of their unique electronic properties at neutral, radical cationic, and polycationic states.⁷ Quite recently, gelators having TTF moieties were reported to produce electroactive nanowires,^{8,9} although all nanowires exhibit moderate to poor conductivities presumably due to the poor ability to form a good conduction path in the oxidized state. To take advantage of the stacking behavior of TTF as a driving force for constructing higher aggregates, hexakis(tetrathiafulvalenylethynyl)benzene (1) is an ideal molecule with a radial core (Chart 1). The present study deals with the synthesis of 1 and fabrication of hexagonal nanostructures using self-assembly of 1 and its cation radicals. The electric conductivities of cation radicals clearly reflect the difference of their nanostructures.

An efficient route to **1** was established by the Sonogashira coupling reaction of iodo-TTF **4** with hexaethynylbenzene **3** (Scheme 1). TTF hexamer **1** exhibits a purple color in chloroform solution with the longest absorption maximum at 559 nm. B3LYP/ 6-31G(d,p) calculations of **1** revealed that a disk-like C_6 -conformation with a small torsional angle (dihedral angle between phenyl and TTF rings = 15°) is an energy minimum. In fact, the ¹H NMR spectrum of **1** (6.7×10^{-6} M) in CDCl₃ shows the TTF proton at low field (δ 6.96) due to the closely located S····H arrangement (SH is 3.156 Å based on calculation).¹⁰

Vapor pressure osmometric (VPO) measurements of **1** in chloroform revealed that neutral **1** self-associates to form aggregates higher than dimers, although reported 1,3,5-tris(tetrathiafulvalenylethynyl)benzene shows very weak association behavior in solution.^{7a} Assuming an infinite association model, the association constant was determined with concentration dependence of electronic spectra in CHCl₃ ($K_a = 2.1 \times 10^4 \text{ M}^{-1}$ at 23 °C). Considering the fairly large K_a of **1**, association of **1** mainly depends on intermolecular attractive forces between terminal TTF groups based on weak S^{...}S and $\pi - \pi$ interactions to form a columnar structure.

When a purple solution of 1 in CHCl₃ was cast on a glass surface, a blue film was formed. UV-vis spectrum of the film shows a red shift of the longest absorption maximum (600 nm). Interestingly, when hexane was added to a solution of 1 in CHCl₃, dark blue





fibrous material with the longest wavelength absorption at 580 nm was formed. As shown in Figure 1A, a slender and frizzled wire structure (40–200 nm wide and 30–100 nm thick) more than 10 μ m long was observed by the SEM and AFM measurement.¹¹

X-ray diffraction (XRD) studies on the film and fibrous material of **1** show that the two diffraction patterns are different. The diffractogram of the film showed a couple of reflections (d = 21.4and 10.7 Å) with a broad reflection (d = 3.69 Å) corresponding to lateral order and $\pi - \pi$ stacking (Figure S15, Supporting Information),¹² whereas the diffractogram of the fibrous material exhibited a hexagonally ordered structure with a lattice constant $a_0 = 32.1$ Å (Figure 1B). Thus, an intense (100) reflection (d = 27.8 Å) with four weak higher-order reflections (d = 15.9 and 13.9 Å) allows the lattice to be indexed to a two-dimensional hexagonal arrangement. Furthermore, XRD experiments of powders prepared from the wires showed an additional reflection of d = 3.53 Å corresponding to a stacking structure (Figure S13, Supporting Information).

Oxidation of **1** measured by cyclic voltammetry in CH₂Cl₂ (1.5 × 10⁻⁵ M) shows a very broad wave of the first six-electron oxidation at -0.13 to 0.05 V (vs Fc/Fc⁺) to form 1⁶⁺ and the second sharp six-electron oxidation wave at 0.32 V to form 1¹²⁺. The very broad oxidation wave for the formation of 1⁺⁺-1⁶⁺ reflects a complex aggregation of 1, 1⁺⁺, and 1ⁿ⁺ (n = 2-6) in solution. Analytically pure 1⁺⁺·ClO₄⁻ and 1³⁺·(ClO₄⁻)₃ can be prepared by chemical oxidation of 1 with Fe(ClO₄)₃. UV-vis-NIR spectra of the cation radicals in CHCl₃ show very broad NIR absorptions at ca. 2350 nm (log $\epsilon = 3.53$) for 1⁺⁺·ClO₄⁻ and ca. 2200 nm (log $\epsilon = 3.61$) for 1³⁺·(ClO₄⁻)₃ due to mixed valence state of a stacked

Figure 1. (A) SEM image of entangled fibrous material of neutral 1 with $5000 \times$ magnification. (B) XRD pattern of hexagonal nanowires of 1 on an aluminum plate.



Figure 2. (A) SEM image of a fibrous material of $1^{\bullet+}$ ·ClO₄⁻ with 5000× magnification. (B) Powder XRD patterns of a hexagonal columnar structure of $1^{\bullet+}$ ·ClO₄⁻; the inset shows the region of $17.5 < 2\theta < 30^{\circ}$.

 $(\text{TTF})_2^{\bullet+}$ unit, and the association constants of $1^{\bullet+}\cdot\text{ClO}_4^-$ and $1^{3+}\cdot(\text{ClO}_4^-)_3$ in CHCl₃ have been estimated to be $K_a = 2.3 \times 10^6$ and $2.5 \times 10^6 \text{ M}^{-1}$ (23 °C), respectively. Although a large cylinder structure of the stacked $1^{\bullet+}$ and 1^{3+} can be expected in solution, ¹³ ESR spectra of $1^{\bullet+}\cdot\text{ClO}_4^-$ and $1^{3+}\cdot\text{ClO}_4^-$ in CHCl₃ (23 °C) exhibit the existence of 100% spin for $1^{\bullet+}$ (g = 2.0068) and 33% spin for 1^{3+} (g = 2.0073), respectively, suggesting weak intermolecular spin—spin interaction in $1^{\bullet+}$ and strong intramolecular spin—spin interaction in 1^{3+} .

Interestingly, deep green fibrous material was formed when a solution of $1^{\bullet+}$ ·ClO₄⁻ in CHCl₃ was mixed with large amounts of hexane (Figure 2A). The nanowires are 40–80 nm wide and more than 20 μ m long. In contrast, a deep green film was formed when a CHCl₃ solution of $1^{\bullet+}$ ·ClO₄⁻ was cast on a glass surface. UV– vis–NIR spectra of the nanowires and film are very similar to that of $1^{\bullet+}$ ·ClO₄⁻ in CHCl₃ presumably due to their multistacking structures. It is noteworthy that nanowires of $1^{\bullet+}$ ·ClO₄⁻ (Figure 2A) seem to be loose probably due to Coulomb repulsion between the cationic charges, whereas nanowires of 1 (Figure 1A) prefer to gather to form an entangled structure.

XRD studies on the wires and drop-cast film of $1^{\bullet+} \cdot \text{ClO}_4^-$ exhibit the remarkable structural differences, although their absorption and ESR spectra are very similar. The diffractograms of the wires of $1^{\bullet+} \cdot \text{ClO}_4^-$ showed one intense (d = 27.5 Å) and four weak reflections based on a hexagonally ordered lamellar structure $(a_0 = 31.8 \text{ Å})$ with the $\pi-\pi$ stacking distance of 3.51 Å (Figure 2B). In contrast, the diffractogram of the film of $1^{\bullet+} \cdot \text{ClO}_4^-$ exhibited a couple of reflections (d = 25.5 and 13 Å) corresponding to laterally stacking arrangement. The longer distance (d = 25.5 Å) of the film of $1^{\bullet+} \cdot \text{ClO}_4^-$ compared to that of 1 (d = 21.4 Å) may reflect more overlapping structure of $1^{\bullet+} \cdot \text{ClO}_4^-$ which rises perpendicularly from the surface of the aluminum plate. Another point which should be noted is that the lattice constants (a_0) of nanowires of $1^{\bullet+} \cdot \text{ClO}_4^$ are smaller than that of **1** despite the presence of a $\text{ClO}_4^$ counteranion.

The electric conductivities of the wires and film of 1^{++} -ClO₄⁻ exhibit a considerable difference according to their different

molecular arrangement. Thus, a small tape $(0.24 \times 0.10 \times 0.005 \text{ mm})$ prepared from wires of $1^{\bullet+} \cdot \text{ClO}_4^-$ showed a conductivity of $\sigma_{rt} = 1.1 \times 10^{-3} \text{ S cm}^{-1}$, suggesting more effective conduction due to a hexagonally ordered columnar structure, whereas the film of $1^{\bullet+} \cdot \text{ClO}_4^-$ showed a conductivity of $\sigma_{rt} = 3.1 \times 10^{-5} \text{ S cm}^{-1}$.

In summary, we have synthesized a novel TTF hexamer 1 with a flexible disk-like structure, weak amphiphilic nature, and strong self-aggregation properties. Nanowires fabricated from 1 in a CHCl₃/hexane solution have a hexagonal columnar structure, reflecting the lateral and $\pi - \pi$ stacking interactions of its disk-like frame. Furthermore, we have also succeeded in formation of fibrous material with a hexagonal columnar structure from 1^{++} ·ClO₄⁻. We believe this is a quite rare example of nanowires prepared from organic ion radical salts. The electric conductivity of the wire of 1^{++} is 2 orders of magnitude higher than that of the film of 1^{++} , reflecting their nanostructured, one-dimensional morphologies.

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Supporting Information Available: Details of the synthesis, aggregation behavior, and characterization of nanostructures of 1, $1^{+} \cdot \text{CIO}_4^-$, and $1^{3+} \cdot (\text{CIO}_4^-)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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- (12) The film of **1** exhibits weak FET properties, reflecting a lamellar structure vertical to the substrate (Figure S16, Supporting Information).
- (13) Small-angle X-ray scattering (SAXS) analysis of 1⁺⁺ and 1³⁺ in THF reveals cylinder structures with 11 Å radius and 14–16 Å high, and hence three to five disk-like 1⁺⁺ and 1³⁺ stacks on average, although 1 shows no self-aggregation in THF (Figure S24, Supporting Information).

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