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Interconvertible Oligothiophene Nanorods and Nanotapes with High Charge-Carrier Mobilities

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Molecular designs leading functional π-conjugated oligomers into well-defined nanoarchitectures through noncovalent interactions are crucial for the realization of miniaturized organic electronic devices based on the bottom-up approach.[1] In particular, the bottom-up construction of electronically addressable 1D nanostructures has received a great deal of attention, owing to their potential as effective pathways for charge carriers.[1] If such nanostructures have stimuli-responsive properties in their morphologies and chromophore packing motifs, they could be used as smart nanomaterials in which their electronic properties can be controlled at will. Several fibrillar nanostructures have been reported to exhibit morphological change induced by guest[2] and solvent.[3] On the other hand, temperature is one of the most convenient variables to control, but its use to regulate well-defined nanostructures remains challenging,[4] because most enthalpy-driven noncovalent assemblies in solution dissociate into monomers upon increasing temperature. Here we report thermally interconvertible semiconductive nanorods and nanotapes comprising π-conjugated oligothiophenes,[5,6] displaying high charge-carrier mobilities in their condensed states (Scheme 1).

Recently, we have shown that merocyanine dyes equipped with barbituric acid can be loaded into diverse self-organized nanoarchitectures upon complexation with flexible bismelamine receptors (**BM**, see Scheme 1) through complementary hydrogen-bonding interactions.[7–9] Our next challenge is to corroborate the validity of our strategy to extended π-conjugated systems and to offer more practical nano- to microarchitectures, as functional modules for miniaturizing electronic devices. We prepared quaterthiophene (**1a**), functionalized on one end by a barbituric acid (BA) headgroups[10] and the other end by a tridodecyloxyphenyl (TDP) tail (Scheme 1). Compound **1a** was synthesized according to Scheme S1 (in the Supporting Information) and fully characterized.[11] Barbituric acid group is a well-known ditopic triple-hydrogen-bonding module that complementarily binds with diaminopyridine or melamine modules.[8] However, the examples that demonstrate its capability to lead π-conjugated molecules into well-defined nanostructures without assistance are scant.[12] The UV/Vis spectra of **1a** ($1\times10^{-6}\,\text{M} < c < 5\times10^{-3}\,\text{M}$) in methylcyclohexane (MCH) showed the absorption maximum at $\lambda = 439$ nm, which was strongly blue-shifted ($\nu = 3474\,\text{cm}^{-1}$) from that in dichloromethane ($\lambda = 518$ nm).[13] Furthermore, a significant drop in the fluorescence intensity was observed.[13] These optical changes are typical for the H-type aggregation of oligothiophenes in nonpolar and aqueous conditions,[6c,14] but not observed for *N,N'*-dimethylated derivative **1b**. This demonstrates that the BA group of **1a** plays a crucial role in the aggregation. The H-aggregate showed a pronounced thermal stability: it remained intact upon heating to 80 °C in MCH, above which reversible transition to monomeric state was observed.[13]

Dynamic light scattering of **1a** in MCH ($c = 5\times10^{-5}\,\text{M}$) showed the presence of large aggregates with hydrodynamic diameters around 400 nm.[13] Atomic force microscopy (AFM) of H-aggregated **1a** exhibited uniform rodlike nanostructures with hundreds of nanometers in length, which are

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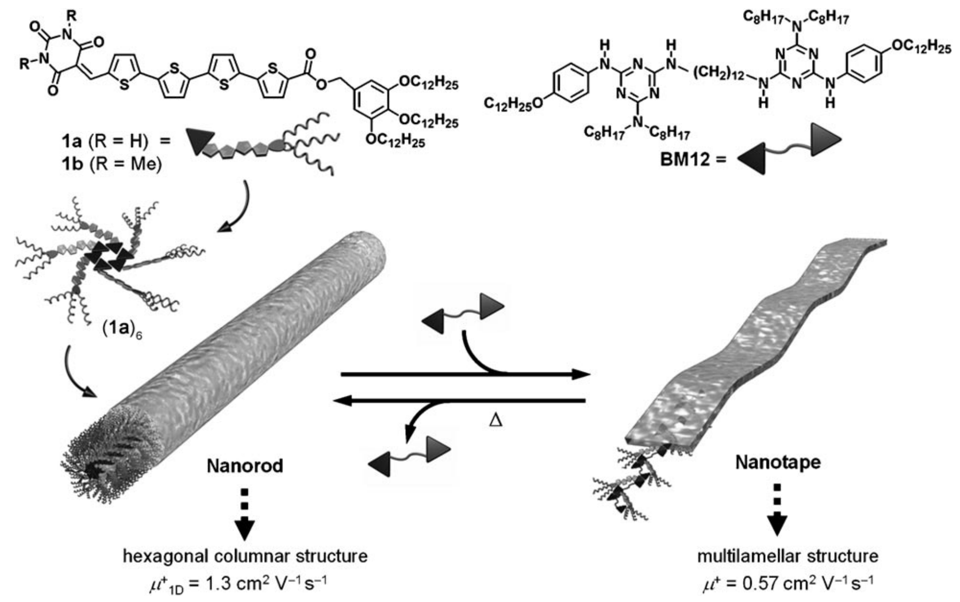

Scheme 1. Schematic representation of interconversion between nanorod and nanotape.

arranged in monolayered fashion (Figure 1a). Owing to the side-by-side interaction between rods, the body-to-body distance of 7.3±0.3 nm estimated by cross-sectional analysis would be a reliable width of rods (panel *i* in Figure 1b). In some parts, bilayered rods were observed with orthogonal (line *ii*) or parallel (line *iii*) orientation between layers. The former bilayers provides the height of 7.0±0.4 nm for the upper layers (full height = 13±0.4 nm), which corresponds to the reliable longitudinal diameter of rods because the height of the bottom layers (6.0±0.3 nm) may involve alkyl chains deformed by the interaction with graphite surface (panel *ii* in Figure 1b). These analyses revealed that **1a** self-assemble into a cylindrical nanostructure with a diameter of 7 nm. On the other hand, the bilayers with the parallel orientation provide the average height of 12±0.4 nm (panel *iii* in Figure 1b), indicative of the closest (hexagonal) packing of cylindrical rods. The interlayer spacing is roughly estimated to be 6 nm.

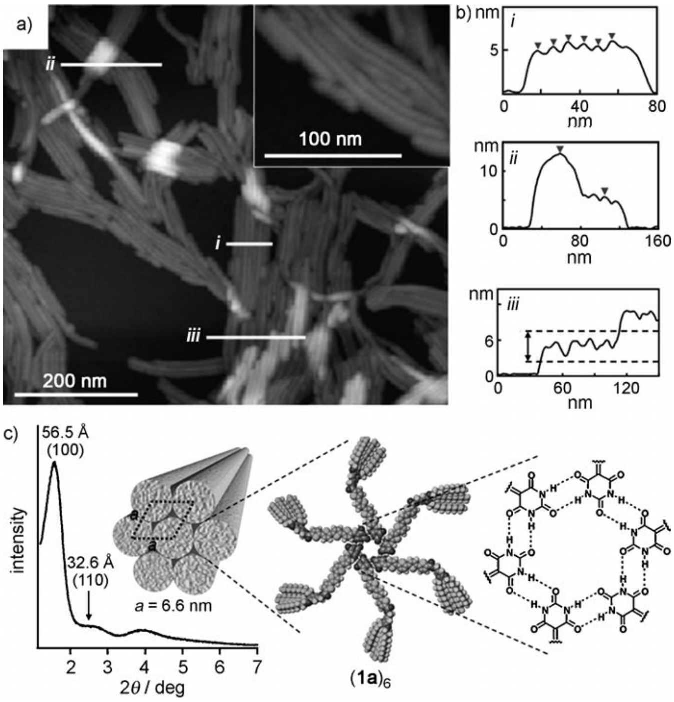

Figure 1. a) AFM height image of self-assembled **1a** spin-cast from hot (>60°C) MCH solution ($c = 5\times10^{-5}$ M) onto highly-oriented pyrolytic graphite (HOPG). *z* scale = 20 nm. Inset shows a magnified image. b) Cross sectional analysis along the lines *i–iii* in a). The triangles (▼) in panel *i* indicate the body-to-body distance between rods (7.3 nm). The triangles (▼) in panel *ii* indicate the height of the upper layer (7.0 nm). The distance between dotted lines in panel *iii* corresponds to the interlayer spacing (6.0 nm). c) X-ray diffraction pattern of a thin film of **1a** (prepared from 1×10^{-4} M solution) and a proposed packing motif of **1a** to form hexagonally-ordered nanorods.

Of reported crystal structures of BA derivatives,[8b] one-dimensional tapelike and ribbonlike motifs are most comparable to the organization of **1a** (Figure S6).[13] However, these flat structures do not fit with the observed cylindrical morphology. Furthermore, molecular modeling demonstrated that the distances between neighboring oligothiophene segments in tapes and ribbons exceed 9 and 6 Å, respectively, which do not allow the strong electronic interactions shown by the UV/Vis study. X-ray diffraction of thin films of **1a** revealed a hexagonal columnar packing with a lattice constant of $a = 6.6$ nm (Figure 1c). Assuming a density of 1 g cm^{-3}, the number of molecules per cylindrical stratum of 3.5 Å (typical π–π stacking distance) is 6.8. Furthermore, the UV/Vis spectrum of the thin film confirmed the presence of the chromophore packing to be identical to that observed in solution (H-type aggregation). We thus propose the oligomerization of **1a** into a supermacrocyclic architecture (rosette) through double hydrogen bonds, which subsequently π stacks into nanorods (Figure 1c).[12b,15,16] Molecular mechanics calculations provided energetically stable hexameric rosettes $(\mathbf{1a})_6$ with diameters of 7–8 nm, depending on the conformation of TDP tails (Figure 1c).

The addition of 1 equiv of **BM12** to a yellow MCH solution of H-aggregated **1a** ($c > 5\times10^{-5}$ M) induced a very slow spectral change indicating the disruption of H-aggregates ($\lambda_{max} = 439 \rightarrow 510$ nm, Figure 2a).[17] The spectral change almost finished after 15 h in the case of 1×10^{-4} M solution (Figure 2b), and the resulting red solution contained polymeric assemblies whose hydrodynamic diameters range from 50 to 100 nm.[13] These results corroborates the forma-

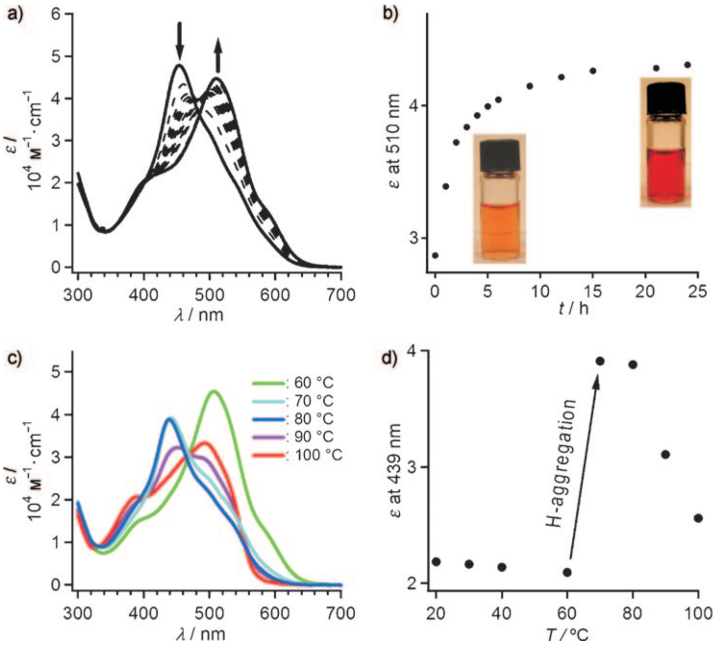

Figure 2. a) Time-dependent UV/Vis spectral change of **1a** in MCH ($c=1.0\times10^{-4}$ M) at 25 °C induced by the addition of 1 equiv of **BM12**. b) Time-dependent change of ε at $\lambda=510$ nm in a) and the color change of the solution (yellow at $t=0$ and red at $t=15$ h). c) Temperature-dependent (60–100 °C) UV/Vis spectra of an equimolar mixture of **1a** and **BM12** ($c=1.0\times10^{-5}$ M) in MCH. d) Change of ε at $\lambda=439$ nm (λ_{max} of H-aggregates) by temperature.

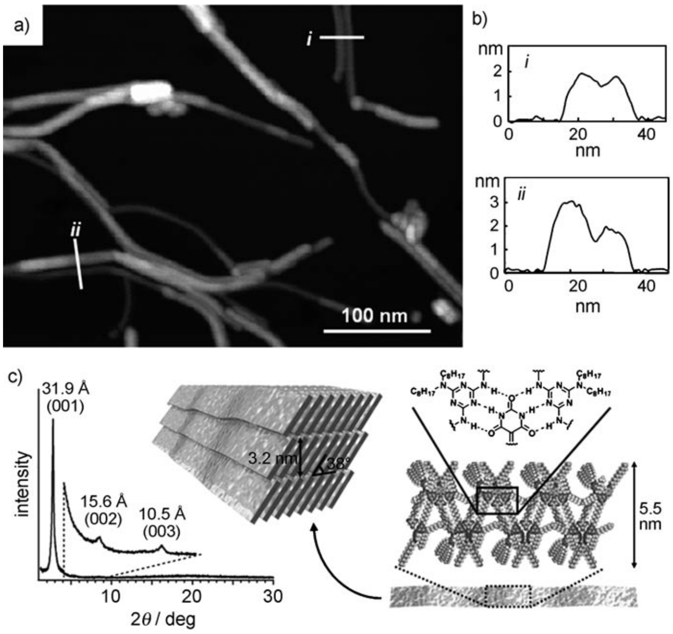

Figure 3. a) AFM height image of coaggregated **1a·BM12** spin-cast from MCH ($c=5\times10^{-5}$ M) on HOPG. z scale = 7 nm. b) Cross sectional analysis along the lines *i* and *ii* in a). c) X-ray diffraction pattern of a thin film of **1a·BM12** (prepared from 5×10^{-3} M solution) and a proposed packing motif of **1a·BM12** to form a lamellar structure.

tion of supramolecular copolymers **1a·BM12** through complementary triple hydrogen bonds.[7,18,19] AFM of the coaggregates displayed flat, tapelike nanostructures with an average thickness of 1.7 ± 0.1 nm and the width of ≈5.5 nm (Figure 3a and panel *i* in Figure 3b). Most tapes exist as two-ply strips (the height of brighter tapes is 3.3 ± 0.2 nm, see panel *ii* in Figure 3b), implying that π stacking is operative between tapes upon drying. This trend leads to the formation of a multilamellar superstructure with an interlayer spacing of 3.2 nm upon increasing concentration, as revealed by the X-ray diffraction pattern of a solvent-free film (Figure 3c). Taking the width of nanotapes (≈5.5 nm) into account, the inclination by an angle of ≈38° is suggested for the stacking of nanotapes within a lamella. The UV/Vis spectrum of the solvent free-film showed slight increase of absorption at around $\lambda=450$ and 600 nm,[13] revealing the presence of interchain electronic interactions between oligothiophene segments.

The morphological features of the present oligothiophene assemblies imply that they should act as efficient pathways for mobile charge carriers.[6a,d,h,20] Intrinsic charge-carrier mobilities of hexagonally-packed nanorods of **1a** and lamellarly-packed nanotapes of **1a·BM12** were thus evaluated by flash-photolysis time resolved microwave conductivity (FP-TRMC) measurements.[21] For this purpose, the thin films of the assemblies were prepared on quartz substrate, and irradiated with a $\lambda=355$ nm laser pulse. The irradiation resulted in the generation of long-lived charge carriers showing maximum transient conductivities ($\phi\Sigma\mu$ in cm^{2}V^{-1}s^{-1}) of 1.0×10^{-4} for **1a** and 0.67×10^{-4} for **1a·BM12** (Figure 4). Negligible influence of the TRMC signal under SF_6 atmosphere in-

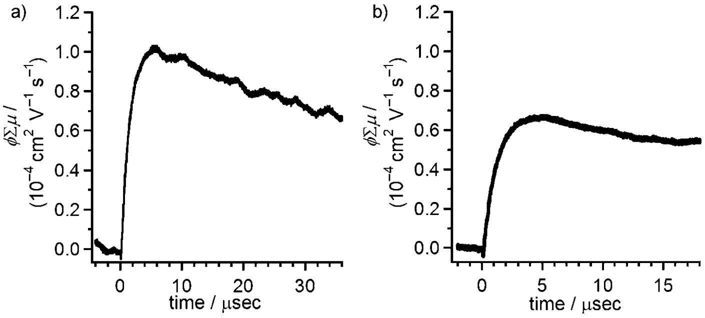

Figure 4. Transient conductivities observed for films of a) **1a** and b) **1a·BM12** under an excitation at $\lambda=355$ nm by 1.8×10^{16} photons cm^{-2} pulse^{-1}. The samples were prepared from cyclohexane solutions (gels) of $c=4\times10^{-3}$ M.

dicates the *p*-type semiconducting properties of the materials. The quantum efficiencies of the charge-carrier generation (ϕ) were determined as 1.5×10^{-4} for **1a** and 1.2×10^{-4} for **1a·BM12**, by the integration of photocurrent under an excitation of the materials overcoated onto an interdigitated electrode at $\lambda=355$ nm.[13] Thus, hole mobility (μ^+) of **1a·BM12** was calculated as 0.57 cm^{2}V^{-1}s^{-1}, whereas for **1a** the value of one-dimensional hole mobility (μ^+_{1D}) of 1.3 cm^{2}V^{-1}s^{-1} was estimated by taking its morphological feature into account.[13] These values are one-order of magnitude higher than the mobility observed for lamellarly-organized poly(hexylthiophene)s,[22] and represent the highest intrinsic hole mobilities among those reported for self-organized materials determined by TRMC techniques.[21] Although the high mobility of **1a** is accomplished along the long axis of nanorods, the interchain transportation of charge carriers within a lamella may play an dominant role for that of **1a·BM12**.[22]

Interestingly, H-aggregation of **1a** was observed by UV/Vis spectroscopy ($\lambda_{max} = 510 \rightarrow 439$ nm) upon heating a MCH solution of coaggregates **1a·BM12** ($c = 1 \times 10^{-5}$ M) to 70°C (Figure 2c,d). Above 80°C, the resulting H-aggregates started to dissociate into monomers. AFM images of the samples prepared from the solution heated at 80°C indeed show the formation of nanorods instead of nanotapes.[13] Released **BM12** molecules are thus considered to exist in a molecularly-dissolved state. The mixture of nanorods of **1a** and monomeric **BM12** regenerated nanotapes when the solution was kept at room temperature. Although the formation of nanorods from the molecularly dissolved **1a** is an enthalpy-driven process, the formation of nanorods from coaggregates (**1a·BM12**) upon heating is apparently an entropy-driven process, in which the release of closely-packed **BM12** contributes to the reorganization of **1a**.[23]

In summary, we have shown that a BA-functionalized oligothiophene undergoes self-aggregation and co-aggregation with a bismelamine receptor, affording nanorods and nanotapes with remarkable charge-carrier mobilities in their condensed states. Furthermore, we have demonstrated that selective formation of either of two nanostructures is possible by regulating the temperature of the coaggregated solution. Such smart self-assemblies composed of electronically addressable components contribute to a step forward toward switchable electronic nanomaterials.

Keywords: conductivity · conjugation · hydrogen bonds · nanostructures · self-assembly

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