Multifunction Integrated Macromolecules for Molecular-Scale Electronics

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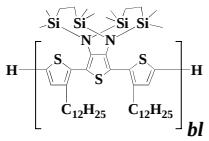
We have been developing step-wise synthetic protocols for integrating molecule-based quantum device elements (quantum dots, wells, and tunnel junctions) within a single planar macromolecule. Our strategy is based on "modular architecture" using a library of versatile molecular building blocks. The flexible functionality of our building blocks is derived from the 3,4-diaminothiophene component, which can be easily modified to tune the structural and electronic properties of the main π-conjugated chain.

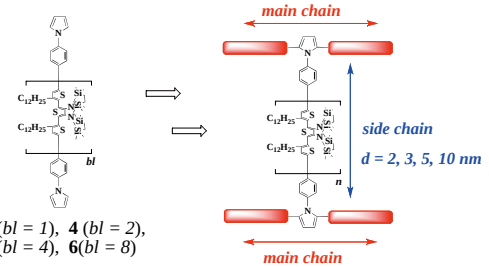
1. Step-Wise Synthesis of Molecular Wire Modules of Over 100 nm Lengths

We have finished the step-wise synthesis of precisely defined molecular wires of over 100 nm lengths (**1**-**2**). Now we have a series of wire modules of 1–166 nm lengths. These are not a final product, but a starting material for our next target system, that is, 2-dimension macromolecules of 100 × 100 nm size. As a first step, we have synthesized multi-terminal modules (**3**-**6**), and set out to build up molecular ladder structures.



1 (*bl* = *96*) [*288T, l = 110 nm,* $C_{4608}H_{8066}N_{192}S_{288}Si_{384}$*, MW = 86,185*]

2 (*bl = 144*) [*432T, l = 166 nm,* $C_{6912}H_{12098}N_{288}S_{432}Si_{576}$*, MW = 129,276*]



3 (*bl = 1*), **4** (*bl = 2*),
5 (*bl = 4*), **6**(*bl = 8*)

Figure 1. Structures of building blocks (**1**-**6**).

2. Isomeric Discriminating and Indiscriminating Assembly of Adsorbed Oligothiophenes on Ag(110)[1)]

Selective discriminating and indiscriminating assembly of isomeric oligothiophene derivatives is performed on a Ag(110) surface. The self-assembled structures are directly analyzed by using scanning tunneling microscopy. We demonstrate that the phase separation and phase mixing of s-*cis*- and s-*trans*-oligothiophenes can be controlled by "shape complementary intermolecular interactions" associated with the overall molecular shapes. The overall shapes of the s-*cis*- and s-*trans*-oligothiophenes are tuned by the length of alkyl side chains.

3. Electrical Resistance of Long Oligothiophene Molecules[2)]

The electrical resistance of single oligothiophene molecular wires with lengths ranging from 2.2 nm (5-mer) to 9 nm (23-mer) was measured by the break junction method. A linear relationship between the molecular length and resistance was found for molecules longer than 11 mer, whereas an exponential increase in the resistance was observed for molecules shorter than 11-mer. These results indicate that the carrier transport mechanism changes from tunneling to hopping at around 11–14-mer (5.6 nm).

References

1) T. Yokoyama, S. Kurata and S. Tanaka, *J. Phys. Chem. C* **112**, 12590–12593 (2008).

2) R. Yamada, H. Kumazawa, S. Tanaka and H. Tada, *Appl. Phys. Express* **2**, 025002 (3 pages) (2009).