Synthesis of Self-Threading Bithiophenes and their Structure–Property Relationships Regarding Cyclic Side-Chains with Atomic Precision

Yuki Ouchi,^[a, b] Kazunori Sugiyasu,^{*[a]} Soichiro Ogi,^[a] Akira Sato,^[c] and Masayuki Takeuchi^{*[a, b]}

Abstract: We have recently reported a self-threading polythiophene as a new family of insulated molecular wires. Herein, we focused on the structure-property relationships of the unique three-dimensional architecture of the monomer. We have synthesized nine self-threading bithiophene monomers that have cyclic side-chains of different size and flexibility: i.e., 21-, 22-, 23-, 24-, 26-, and 30-membered rings com-

posed of paraffinic, olefinic, or alkynic chains. To investigate their structure– property relationships, ¹H NMR spectroscopy, UV absorption, and fluorescence spectroscopy measurements were conducted. We found that cyclic side-

Keywords: molecular wires • oligomers • side-chains • structure-property relationships • thiophenes chains define the movable range of the dihedral angle of the bithiophene backbone, thereby affecting its photophysical properties. Therefore, the ability to design a structure with atomic precision as described herein would lead to the fine-tuning of the electronic properties of insulated molecular wires.

Introduction

Insulated molecular wires (IMWs) are π -conjugated polymers which are sheathed with an electronically-inactive molecular layer.^[1–3] A representative of the IMWs is polyrot-axane structures in which a π -conjugated polymer axis is threaded through many insulating cyclic molecules, such as cyclodextrins. Their structural analogy with electric power cords has aroused expectation of the realization of molecular integrated circuits.^[4] In addition, the lack of the π - π stacking interactions in the solid state could lead to advanced functions and configurations in organic electronic devices.^[5] For instance, the insulating layer prevented interwire interactions between the conjugated polymers, which could improve luminescence efficiency of organic light-emitting diodes (OLEDs).^[5a] Furthermore, the luminescence

[a]	Y. Ouchi, Dr. K. Sugiyasu, Dr. S. Ogi, Prof. Dr. M. Takeuchi
	Organic Materials Group, Polymer Materials Unit
	National Institute for Materials Science (NIMS)
	1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 (Japan)
	Fax: (+81)29-859-2101
	E-mail: SUGIYASU.Kazunori@nims.go.jp
	TAKEUCHI.Masayuki@nims.go.jp
[b]	Y. Ouchi, Prof. Dr. M. Takeuchi

- Department of Materials Science and Engineering Graduate School of Pure and Applied Sciences University of Tsukuba 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571 (Japan)
- [c] A. Sato Materials Analysis Station National Institute for Materials Science (NIMS)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201100524.

property of the IMW-based OLED was found to be affected by continuously thinning out the insulating cyclodextrin, which was quantifiable by the so-called "threading ratio".^[5c] Such a control over the optoelectronic properties of conjugated polymers—by taking advantages of the unique threedimensional structures of IMWs—enable us to not only optimize the performance of but also to unravel the fundamentals of organic electronics; in this context, understanding the structure–property relationships of IMWs is particularly important.

We have recently reported insulated polythiophenes as a new family of IMWs (Scheme 1).^[6] The unique three-dimensional architecture of the monomer is reminiscent of rotaxanes; however, the "ring" and "axis" are covalently connected. In other words, the π -conjugated molecular axis (i.e., bithiophene) is threaded through its own cyclic side-chain; accordingly, we designated the monomer as a self-threading bithiophene (**STB**_{6/6}: where the subscript "6/6" denotes that two hexyl chains (C₆H₁₂) are covering both faces of the bithiophene π -platform, see Scheme 1). Bromination at the 5,5'-positions using NBS, followed by Yamamoto reductive coupling, afforded the polymerized **STB**_{6/6} to provide a selfthreaded polythiophene (i.e., **PSTB**_{6/6}). The striking features of **PSTB**_{6/6} are as follows:

1) $\pi - \pi$ stacking between the adjacent polythiophene backbones is effectively prevented by the defect-free insulating layer even in the solid film.

2) The covalently-connected cyclic side-chains impose a co-planar conformation on the bithiophene backbone, thereby extending the effective conjugation length (ECL).

This latter feature has engaged our interest because few IMWs have such a merit.^[3a-d] In the case of previously reported **STB**_{6/6}, the cyclic side-chain corresponds to 1,8,15,22-





Scheme 1. Synthetic approach toward self-threading polythiophene: a) second-generation Grubbs catalyst, CH_2Cl_2 , b) H_2 , Pd/C, $CH_2Cl_2/MeOH$, c) NBS, $CHCl_3/AcOH$, d) $[Ni(cod)_2]$, cod, bipy, toluene/DMF. "Cyclic side-chain" (green area in the axial view) corresponds to a 22-membered ring in the case of the previously reported **STB**₆₀₆.^[6] NBS = *N*-Bromosuccinimide, DMF = *N*,*N*-dimethylformamide, cod = 1,5-cyclooctadiene, bipy = 2,2'-bipyridine.

tetraoxa[6.6]metacyclophane, which affords an overall 22membered ring (Scheme 1). Here, it occurred to us that designing the ring size of the **STB** should control the planarity of the bithiophene backbone, which in turn leads to the tuning of the electronic properties of IMWs. In fact, Mayor and co-workers have recently reported that the torsion angle (ϕ) of biphenyl derivatives determines their optoelectronic characteristics, such as band gaps,^[7a] NLO responses,^[7b] and conductance,^[7c-e] where the variations in the properties showed proportional relationships to $\cos^2 \phi$.^[7,8]

Herein, we report on the synthesis of a family of **STB**s. By varying the length of the alkyl chains, we have prepared **STB** derivatives that have 21, 22 (reported^[6]), 23, 24, 26, and 30-membered rings, through which the bithiophene backbone is threaded. We found that the ring size defines the movable range of the dihedral angle and affects the electronic properties of the bithiophene. This result means that

Abstract in Japanese:

我々は、新しい絶縁被覆分子細線として「自己貫通ポリチオフェン」を 設計・合成し、ポリチオフェン1本の特性を評価している。本論文では、 そのモノマーユニットである自己貫通ビチオフェンの構造・特性相関につ いて調べた。自己貫通ビチオフェンは、ビチオフェン骨格が自身の環状分 子側鎖を貫通した構造を有する。環のサイズが異なる自己貫通ビチオフェ ンを複数合成し、吸収および蛍光スペクトル測定を行った。その結果、環 のサイズがビチオフェンの2面角の可動域を規定し、ひいてはその電子特 性に影響することを明らかにした。すなわち、我々の自己貫通ビチオフェ ンは、絶縁被覆分子細線の物性をチューニングし得る、原子レベルの高い 設計性を有する。 we can establish a new molecular design parameter in the targeted synthesis of IMWs.

Results and Discussion

Synthesis of Self-Threading Bithiophenes

Our synthetic strategy toward **STB** derivatives is based upon the double ring-closing metathesis (RCM) reaction. In the previously reported example, the precursor had four 1-butenyl moieties, the two pairs of which ring-close and result in two 3-hexenyl chains that cross over the bithiophene platform. After hydrogenation of the olefin moieties, **STB**_{6/6} is obtained (Scheme 1).^[6]

The main framework of **STB**s (i.e., $1(OMe)_4$) was synthesized from 3,3'-dibromo-

2,2'-bithiophene and 2,6-dimethoxyphenylboronic acid through Suzuki-Miyaura coupling under Buchwald conditions (SPhos, [Pd₂(dba)₃], and K₃PO₄ in toluene).^[9] Demethylation of 1(OMe)₄ using BBr₃ afforded 1(OH)₄ in quantitative yield. We first carried out Williamson ether synthesis for $1(OH)_4$ to introduce RCM-active olefinic side-chains (Scheme 2c: 4-bromobutene, K₂CO₃, DMF, 90 °C); however, we mainly obtained di- $(1_{04/04})$ - and tri- $(1_{04/44})$ -substituted intermediates, together with $\mathbf{1}_{44/44}$ in poor yield (<20%), which is probably because of the steric hindrance of 1(OH)₄. We thus applied the modified Mitsunobu reaction reported by Lepore and He.^[10] High-concentration conditions and sonication in the presence of 3-buten-1-ol, DIAD, and PPh₃ in tetrahydrofuran were effective against the sterically hindered reaction sites of $1(OH)_4$, thus affording $1_{44/44}$ in good yield (88%). Likewise, $\mathbf{1}_{55/55}$ and $\mathbf{1}_{66/66}$ were synthesized using corresponding olefinic alcohols. The precursors obtained through this approach (i.e., $\mathbf{1}_{44/44}$, $\mathbf{1}_{55/55}$, and $\mathbf{1}_{66/66}$) led only to symmetrical STB products, of which insulating alkyl chains were composed of even numbers of carbon atoms (i.e., STB_{6/6}, STB_{8/8}, and STB_{10/10}, respectively). In order to synthesize a variety of STBs, we made use of the products from the abovementioned Williamson ether synthesis (i.e., $\mathbf{1}_{04/04}$ and $\mathbf{1}_{04/44}$ in Scheme 2). Through the modified Mitsunobu conditions, $\mathbf{1}_{04/04}$ led to $\mathbf{1}_{34/34}$ and $\mathbf{1}_{45/45}$ by reacting with allyl alcohol and 4-penten-1-ol, respectively. Likewise, $\mathbf{1}_{04/44}$ afforded $\mathbf{1}_{34/44}$ and $\mathbf{1}_{44/45}$. Consequently, we have prepared seven precursors for the double RCM reaction, namely: $1_{34/}$ 34, 134/44, 144/45, 145/45, 155/55, and 166/66 (Scheme 2).

So far, multiple RCM reactions have successfully been applied to synthesize three-dimensional molecular architectures such as catenanes,^[11] rotaxanes,^[12] gyroscopes,^[13] and so



Scheme 2. Synthesis of precursors for the double RCM: a) SPhos, $[Pd_2(dba)_3]$, K_3PO_4 , 2,6-dimethoxyphenylboronic acid, toluene, b) BBr₃, CH_2Cl_2 , c) K_2CO_3 , 4-bromobutene, DMF, d) corresponding olefinic alcohol, PPh₃, DIAD, THF, sonication. dba=dibenzylideneacetone, DIAD=diisopropyl azo-dicarboxylate, THF=tetrahydrofuran.

forth.^[14,15] Particularliy related to our approach are the examples by Cox and co-workers^[16] and Gladysz and co-workers^[17] in which they have reported strategies to synthesize IMWs through double RCM reactions. RCM reaction using second-generation Grubbs catalyst was doubly applied on both faces of the bithiophene platform (Scheme 3). By closing the two pairs of olefinic side-chains that face each other, $\mathbf{1}_{ab/cd}$ affords $\mathbf{STB}^{\mathbf{D}}_{(a+b)-2l(c+d)-2}$ (here, the superscript "**D**" denotes the double bonds in the ring). Figure 1 shows ¹H NMR spectra taken before and after the double RCM reaction of $\mathbf{1}_{44/44}$; after 80 min reaction time, $\mathbf{1}_{44/44}$ was exclusively converted into $\mathbf{STB}^{\mathbf{D}}_{666}$ (also see the Supporting Information of $\mathbf{1}_{56}$ (also see the Supporting Information of the state of the superscript is the superscript in the state of the superscript in the state of the

mation, Figure S1). A single RCM reaction attempted using $2_{4/4}$ (Scheme 4) revealed that olefinic side-chains on the same resorcinol group cannot cyclize but polymerize by acyclic diene metathesis (ADMET) polymerization; this observation implies the selective double RCM reaction among the four olefinic side-chains in $1_{44/44}$. Furthermore, it is remarkable that $STB^{D}_{6/6}$ showed only a single olefinic peak (H_e) in the ¹H NMR spectrum, which indicates that the metathesis reaction of $1_{44/44}$ is regiospecific. We confirmed from its X-ray crystal structure that only the *trans* configuration of $STB^{D}_{6/6}$ had formed; thus, we designated this particular compound as (*E*)-STB^{D}_{6/6} (Figure 1 c). The downfield



shifts of the protons H_a, H_b, and H_c, and upfield shifts of the protons H_d and H_e, induced by the double RCM reaction, are consistent when considering enhanced ring current the effect by the planarized bithio-(Figure 1 d).^[18] phene The quantitative and regiospecific double RCM reaction of $1_{44/44}$ and the planar conformation of the product ($\mathbf{x}C_3C_2C_2'C_3'$ of (E)-STB^D_{6/6} is 179.76°) suggest that the 22-membered ring perfectly fits the girth of the bithiophene.

With the above successful ex-

ample in mind, we carried out

Scheme 3. Synthesis of $\mathbf{STB}^{\mathbf{D}}_{m/n}$ and $\mathbf{STB}_{m/n}$: a) second-generation Grubbs catalyst, CH₂Cl₂, b) H₂, Pd/C, CH₂Cl₂/MeOH.

Chem. Asian J. 2012, 7, 75-84

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemasianj.org



Figure 1. ¹H NMR spectra taken a) before and b) after 80 min of the double RCM reaction of $\mathbf{1}_{44/44}$. c) X-ray crystal structure of (*E*)-**STB**^{**b**}_{6/6}. d) Ring-current effect of the planarized bithiophene backbone; H_a: +0.29 ppm; H_b: +0.43 ppm; H_c: +0.29 and +0.17 ppm; H_d: -0.09 ppm; H_e: -0.58 ppm shifts were induced by double RCM reaction. Spectrum (b) was taken after removing the catalyst by filtering through a short silica gel pad.



mustures of the commounds discussed in the

Scheme 4. Structures of the compounds discussed in the text: ones of the enantiomers of $\mathbf{1}_{6/44}$ $\mathbf{1}_{5/34}^{D}$, and $\mathbf{UTB}_{10/10}^{D}$ are shown, which were used as racemates.

the double RCM reactions of other precursors (Scheme 3). In the case of the smallest precursor (i.e., $1_{34/34}$), $STB^{D}_{5/5}$ was not obtainable; a pair of olefinic side-chains cyclizes but the other pair seems unable to reach each other, which yielded $STB^{D}_{5/34}$ (Scheme 4). The second-smallest precursor, $1_{34/44}$, afforded $STB^{D}_{5/6}$. Thus, the structural threshold for the double RCM reaction is very precise, and the 21-membered ring appeared to be the smallest in the **STB** family. It is interesting to note the coincidence of this size with that of the crown ether [21]crown-7 which is known as the smallest ring component for rotaxane formation.^[19] Using the same procedure, $STB^{D}_{6/7}$, $STB^{D}_{7/7}$, and $STB^{D}_{8/8}$ were obtained from $1_{44/45}$, $1_{45/45}$, and $1_{55/55}$, respectively. Interestingly, in the case of

the largest precursor $(1_{66/66})$, **STB**^D_{10/10} was obtained together with an unthreaded conformational isomer $(UTB^{D}_{10/10},$ Scheme 4), which is formed via **STB**^D_{(a+c)-2/(b+d)-2}-type mismatching double RCM. The ratio of $[STB^{D}_{10/10}]/[UTB^{D}_{10/10}]$ in the reaction mixture was about 1/0.8, and they are isolable by column chromatograpy on silica gel. In addition, these

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

two isomers were not interconvertible even after stirred at 100 °C for 24 hours, which was confirmed by ¹H NMR spectroscopy (in 1,1,2,2-[D₂]tetrachloroethane). This result indicates that the alkyl chains in the ring cannot stride over the bithiophene framework (like a jumping rope) in case they are shorter than $C_{10}H_{20}$. This observation demonstrates the well-defined structure of **PSTB**_{6/6} in our previous study. These reactions using a systematic series of the precursors revealed that the available cyclic side-chain of **STB**_{m/n} is between 21- and 30-membered rings: here, the ring-size equals to m+n+10. All the **STB**^D_{m/n} products were subjected to hydrogenation to provide the **STB**_{m/n} products. As a reference compound, we also synthesized **1**_{6/44} by stopping the double RCM reaction of **1**_{44/44} before the completion followed by hydrogenation (Scheme 4).

In addition to the double RCM approach, we have applied a double ring-closing alkyne metathesis reaction for $3_{55/55}$, which afforded $\mathbf{STB}^{T}_{6/6}$ (Scheme 5, the superscript "**T**" denotes the triple bonds in the ring).^[20] Furthermore, semi-reduction of the triple bonds of $\mathbf{STB}^{T}_{6/6}$ through standard Lindlar hydrogenation led to (*Z*)- $\mathbf{STB}^{D}_{6/6}$, a *cis* isomer of (*E*)- $\mathbf{STB}^{D}_{6/6}$.^[21] The influence of the flexibility of the ring (i.e., paraffinic, olefinic, and alkynic side-chains in $\mathbf{STB}_{6/6}$, $\mathbf{STB}^{D}_{6/6}$, and $\mathbf{STB}^{T}_{6/6}$, respectively) on photophysical properties of bithiophene is also worth considering.

Structure–Property Relationships of Self-Threading Bithiophenes

Figure 2a displays aromatic region of the ¹H NMR spectra of \mathbf{STB}_{min} . As mentioned earlier, the double RCM induces peak shifts owing to the deshielding effect by the planarized



Scheme 5. Synthesis of \mathbf{STB}^{T}_{66} and (Z)- \mathbf{STB}^{D}_{66} : a) 2-fluorophenol, Mo(CO)₆, PhCl,^[20] b) Lindlar catalyst, quinoline, H₂ gas.^[21]



Figure 2. a) ¹H NMR spectra of **STB**_{5/6} (i), **STB**_{6/6} (ii), **STB**_{6/7} (iii), **STB**_{7/7} (iv), **STB**_{8/8} (v), and **STB**_{10/10} (vi). b) Plot of the chemical shift of proton "H_a" (δ) versus the ring size.

bithiophene π -system. As shown in Figure 2b, the chemical shift of the H_a proton moved upfield by letting the ring become looser. This change plateaued with **STB**_{10/10}, the largest family. This result indicates that the population of the planar conformation decreases with increasing the ring size.

X-ray crystallographic structures of $\mathbf{STB}_{6/6}$, $\mathbf{STB}_{10/10}$, and $\mathbf{1(OMe)_4}$ are shown in Figure 3. Although it is known that ordinary β -substitutions cause the dihedral twist,^[22] all the derivatives have nearly planar bithiophene backbones in crystallized form (Figure 3). This result implies that a planar conformation can be allowed by a packing effect in the crystal. In fact, the rotational barrier at $\phi = 180^\circ$ was calculated to be $< 1 \text{ kJ mol}^{-1}$ for $\mathbf{1(OMe)_4}$, which is small enough to be overcome at room temperature. Thus, the dihedral angles of the bithiophene backbone of the $\mathbf{STB}_{m/n}$ compounds are not immobilized but fluctuating within the range determined by the cyclic side-chains in solution (see the Supporting Infor-



Figure 3. Axial views of a) STB_{666} , b) $STB_{10/10}$, and c) $1(OMe)_4$, shown with the dihedral angles of their bithiophene backbone.

mation, Figure S2). This feature seems to be different from those reported by Mayor and co-workers, in which dihedral angles are twisted even in the crystallized form.^[7] Hence, instead of ϕ , we hereafter regard the chemical shift of the proton H_a (δ H_a) as an index that reflects the movable range of the dihedral angle of **STB**s in solution: for reference, δ H_a of **1**_{44/44} is 7.00 ppm.

Having a family of STBs in hand, we evaluated the photophysical properties of $STB_{m/n}$ products in dichloromethane; Figure 4 compares their UV absorption spectra. All the $STB_{m/n}$ compounds showed identical absorption maxima at 318 nm which is longer than that of 1(OMe)₄ (285 nm) because the cyclic side-chains dictate co-planar conformation to the bithiophene backbone. Small but significant difference among the $STB_{m/n}$ compounds is that the vibrational fine structure became less pronounced as the ring-size increased. In addition, IR spectra also became less structured with increasing ring size (see the Supporting Information, Figure S3).^[23] These results indicate that the molecular motion is restricted by the cyclic side-chains. Against the ring size, a plot of the ratio of A_{318} to A_{285} showed similar tendency with that of δH_a (compare Figure 2b and 4b). We thus plotted the A_{318}/A_{285} as a function of δH_a . The plot showed a linear relationship, which suggests the structureproperty relationship of the STB_{m/n} compounds.

Because a potential-energy surface of the excited state is generally steeper than that of the ground state, more-distinct differences among the **STB**s could be observed in their fluorescence spectra. As shown in Figure 5 a, the fluorescence maxima (λ_{em}) shifted to longer wavelengths as the ring-size increased. Excitation spectra of **STB**s completely traced their absorption spectra (see the Supporting Information, Figure S4). In addition, the fluorescence of the **STB**_{m/n} compounds was independent of the solvent polarity: measured in dimethyl sulfoxide, tetrahydrofuran, chloroform, dichloromethane, and hexane. Therefore, we ruled out the "insula-



Figure 4. a) Normalized absorption spectra of **STB**_{5/6} (i), **STB**_{6/7} (iii), **STB**_{7/7} (iv), **STB**_{8/8} (v), **STB**_{10/10} (vi), and **1(OMe)**₄ (vii). Plots of the ratio between absorption intensities at 318 nm and 285 nm as a function of the ring size (b) and the δH_a (c).

tion" effect of the cyclic side-chains on the observed fluorescence difference.

According to the Franck-Condon principle, all electronic transitions are vertical; namely, they proceed without a change in the molecular geometry.^[24] In general, in the ground state, oligoaromatic conjugation is more or less twisted owing to the steric hindrance between the sidechains.^[7,22] In contrast, co-planar conformation is favored in the excited state because the lowest unoccupied molecular orbital (LUMO) is delocalized over the quinonoid-type conjugation.^[25,26] Thus, after the vertical transition processes (i.e., absorption and emission), the conjugation backbone undergoes geometrical rearrangements, which loses excitation energy as much as the so-called reorganization energy (also referred to as relaxation or equilibration energy). One can observe this as Stokes' shifts: the energy space between the absorption and fluorescence maxima. This value can reflect the charge carrier mobility along a polythiophene backbone because aromatic/quinonoid structural rearrangement is also accompanied throughout the charge-carrier transport.^[27]

As shown in Figure 5b (filled circles), Stokes' shifts of the **STB**_{*mln*} bithiophenes decreased as the ring became smaller.^[28] **STB**_{6/6} showed the smallest Stokes' shift because thermal fluctuation of its dihedral angle is limited by the symmetrical and tight alkyl chains, and the co-planar conformation is favored even at the ground state.^[28] As such, structural similarity between the ground and excited states of **STB**_{6/6} results in the small reorganization energy. Importantly, we confirmed that Stokes' shifts of **STB**_{*mln*} in polystyrene (PS) matrix—where molecular motion is rather restricted—were each smaller than those measured in solution (compare the filled circle and lozenge in Figure 5b). The difference in the Stokes' shifts between in solution and PS matrix should be related to the molecular mobility, which is indeed dependent on the ring size and proportional to δH_a (Figure 5c). Thus,



Figure 5. a) Normalized fluorescence spectra of **STB**_{5/6} (i), **STB**_{6/7} (iii), **STB**_{7/7} (iv), **STB**_{8/8} (v), **STB**_{10/10} (vi), and **1(OMe)**₄ (vii) displayed in a stacked mode: in CH₂Cl₂ (0.05 mM) excited at 340 nm. b) Plots of Stokes' shift of **STB**_{m/n} as a function of δ H_a in solution (circle) and in PS film (square). c) Plot of the difference between the Stokes' shifts observed in solution and PS film as a function of δ H_a.

80 www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

the smaller the ring size is, the less the geometrical rearrangement at the excited state is accompanied. We, therefore, expect that tuning of the electronic functions of the **STB** family is possible with atomic precision by designing the movable range of the dihedral twist.^[7,29-31]

Finally, comparisons among $STB_{6/6}$, (E)- $STB^{D}_{6/6}$, (Z)-STB^D_{6/6}, and STB^T_{6/6} did not confirm significant differences in absorption and fluorescence spectra (Figure 6). In fact, their δH_a values are 7.383, 7.379, 7.376, and 7.370 ppm, respectively, thus indicating that they have more or less the same movable range of dihedral angle in-between STB_{5/6} $(\delta H_a = 7.398 \text{ ppm})$ and **STB**_{6/7} $(\delta H_a = 7.360 \text{ ppm})$; see the Supporting Information, Figure S5 for ¹H NMR spectra of STB_{6/6} derivatives. It is interesting to note that the photophysical properties of $1_{6/44}$ (Scheme 4) are different from those of $STB_{6/6}$ but rather close to those of $STB_{7/7}$ (Figure 6b, c). This result demonstrates the privilege of the doubly-strapped structure. We conclude that the most-favored conformation is achieved with 22-membered cyclic side-chains and flexibility of the ring is less influential in the structure-property relationships than the size. This finding should be of importance when designing advanced IMWs from STB monomers, such as the ones suggested in the following conclusions.



Figure 6. a) Normalized absorption and fluorescence spectra of **STB**_{6/6} (blue), (*E*)-**STB**^D_{6/6} (green), (*Z*)-**STB**^D_{6/6} (orange), **STB**^T_{6/6} (red), and **1**_{6/44} (dotted black) in CH₂Cl₂ (0.05 mM): λ_{ex} = 340 nm. Their fluorescence quantum yields are 0.13, 0.15, 0.14, 0.14, and 0.13, respectively. Plots of the b) A_{318}/A_{285} and c) Stokes' shift of **STB**_{6/6} brothers as a function of δ H_a, which are overlaid with those of **STB**_{m/n} family.

Conclusions

We have synthesized a family of self-threading bithiophenes having cyclic side-chains in different size: i.e., 21-, 22-, 23-, 24-, 26-, and 30-membered rings. Structure-property relationships revealed that STB_{6/6} has the smallest reorganization energy because its conjugated backbone is imposed to be co-planar by the symmetric and the most fitting alkyl chains. Hence, the two hexyl chains in $STB_{m/n}$ (i.e., m=n=6) are optimal in respect of effective conjugation, which supports our previous results where the PSTB_{6/6} showed an excellent hole mobility along the polythiophene wire $(0.9 \text{ cm}^2/$ Vs measured by a TRMC method).^[6,32] The subtle difference in the size and symmetry of the cyclic side-chains would therefore enable fine-tuning of the resistivity of the IMWs.^[7,8,33] Furthermore, by using $STB_{6/6}$, (Z)- $STB^{D}_{6/6}$, (E)- $STB^{D}_{6/6}$, and $STB^{T}_{6/6}$, we demonstrated that the electronic characteristics can be preserved intact with a fixed ring-size. These olefins and alkynes in STB^D_{6/6} and STB^T_{6/6}, respectively, can be used as a "buckle" to functionalize the surface of IMWs through, for example, epoxidation and 1,3-dipolar cycloaddition.^[34] As such, this finding motivated us to design more functional IMWs without disturbing the optimized coplanar conformation of STB_{6/6}. For instance, coaxial cables, in which electron- and hole-transporting pathways are separated by the insulating layer, would find use in photovoltaics and ambipolar transistors (see Scheme 6, cartoon). The designability of the $STB_{m/n}$ family is unique in realization of such advanced molecular wires; the synthesis is now underway in our laboratory.



Scheme 6. A potential advanced molecular wire made by surface-functionalization of our insulated molecular wires derived from \mathbf{STB}^{T}_{66} .

Experimental Section

Air- and water-sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. All chemicals were purchased from Aldrich, Kanto Chemical, or Wako and used as received. NMR spectra were recorded on Bruker Biospin DRX-600 spectrometer, and all chemical shifts are referenced to (CH₃)₄Si (0 ppm for ¹H) or residual CHCl₃ (77 ppm for ¹³C). MALDI-TOF-MS spectra were obtained with SHIMADZU AXIMA Confidence. UV absorption spectra and fluorescence spectra were obtained on a Hitachi U-2900 spectrophotometer and a Hitachi F-7000 spectrophotometer, respectively. Relative fluorescence quantum yields were determined using quaterthiophene (F_F =0.18, in benzene^[35]) as standards. Melting points were determined with Yanako NP-500P micro melting point apparatus. Fluorescence lifetime was recorded on HORIBA FluoroCube UltraFast-3000U.

Chem. Asian J. 2012, 7, 75-84

Synthesis

Synthesis of the self-threading bithiophenes (**STB**_{*m*(*n*)}) were performed according to the same method reported in our previous paper.^[6] Also, see the Supporting Information for details. Characterization of the final compounds used to evaluate structure–property relationships are shown below.

STB 5/6

m.p. > 300 °C. ¹H NMR (CDCl₃, TMS): δ =0.98–1.55 (m, 14H), 3.54 (m, 2H), 3.85 (m, 2H), 4.05 (m, 2H), 4.28 (m, 2H), 6.73 (d, *J*=8.4 Hz, 2H), 6.77 (d, *J*=8.4 Hz, 2H), 6.79 (d, *J*=4.8 Hz, 2H), 7.00 (d, *J*=4.8 Hz, 2H), 7.40 ppm (t, *J*=4.8 Hz, 2H) ¹³C NMR (CDCl₃): δ =23.32, 26.66, 29.34, 30.49, 70.45, 71.54, 109.07, 109.39, 119.06, 122.83, 129.53, 130.24, 131.42, 133.39, 158.99, 158.99 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₃₁H₃₂O₄S₂: 532.17; found: 532.86 [*M*+H]⁺. Elemental analysis: calcd (%) for C₃₁H₃₂O₄S₂: C 69.89, H 6.05. found: C 70.21, H 5.82.

STB_{6/6}

m.p. > 300 °C. ¹H NMR (CDCl₃, TMS): δ =0.93 (m, 4H), 1.17 (m, 4H), 1.50 (m, 8H), 3.75 (tt, *J*=4.8, 8.4 Hz, 4H), 4.05 (dt, *J*=4.8, 6.6 Hz, 4H), 6.70 (d, *J*=8.4 Hz, 4H), 6.73 (d, *J*=4.8 Hz, 2H), 6.97 (d, *J*=4.8 Hz, 2H), 7.38 ppm (t, *J*=8.4 Hz, 2H). ¹³C NMR (CDCl₃): δ =27.23, 30.26, 69.73, 107.10, 117.45, 122.57, 129.36, 130.00, 131.03, 133.35, 158.93 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₃₁H₃₂O₄S₂: 546.19; found: 546.13 [*M*+H]⁺. Elemental analysis: calcd (%) for C₃₂H₃₄O₄S₂+0.2 CH₂Cl₂: C 68.60, H 6.15. found: C 68.91, H 6.45.

STB_{6/7}

m.p. > 300 °C. ¹H NMR (CDCl₃, TMS): δ =0.92–1.50 (m, 18H), 3.72 (m, 2H), 3.86 (m, 2H), 4.01 (m, 4H), 6.61 (d, *J*=8.4 Hz, 2H), 6.68 (d, *J*=8.4 Hz, 2H), 6.72 (d, *J*=5.4 Hz, 2H), 6.96 (d, *J*=5.4 Hz, 2H), 7.36 ppm (t, *J*=8.4 Hz, 2H). ¹³C NMR (CDCl₃): δ =26.14, 27.75, 28.312, 29.04, 29.86, 69.08, 69.63, 105.30, 106.85, 116.51, 122.20, 129.73, 129.80, 158.69, 159.28 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₃₃H₃₆O₄S₂: 560.21; found: 561.33 [*M*+H]⁺. Elemental analysis: calcd (%) for C₃₃H₃₆O₄S₂: C 70.68, H 6.47. found: C 70.66, H 6.33.

$STB_{7/7}$

m.p. > 300 °C. ¹H NMR (CDCl₃, TMS): δ =1.03–1.10 (m, 8 H), 1.19–1.23 (m, 4 H), 1.51–1.55 (m, 8 H), 3.85 (m, 4 H), 3.95 (m, 4 H), 6.66 (d, *J*= 8.4 Hz, 4 H), 6.71 (d, *J*=5.4 Hz, 2 H), 6.97 (d, *J*=5.4 Hz, 2 H), 7.35 ppm (t, *J*=8.4 Hz, 2 H). ¹³C NMR (CDCl₃): δ =25.03, 27.15, 28.17, 69.29, 106.49, 117.0, 121.90, 129.57, 130.31, 133.56, 159.00 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₃₄H₃₈O₄S₂: 574.22; found: 575.33 [*M*+H]⁺. Elemental analysis: calcd (%) for C₃₄H₃₈O₄S₂+0.25 CH₂Cl₂: C 69.02, H 6.51. found: C 68.83, H 6.27.

$STB_{8/8}$

m.p. 199.2–200.9 °C. ¹H NMR (CDCl₃, TMS): δ =1.09–1.21 (m, 16H), 1.43–1.60 (m, 8H), 3.92–3.94 (m, 8H), 6.61 (d, *J*=8.4 Hz, 4H), 6.68 (d, *J*=4.8 Hz, 2H), 6.95 (d, *J*=4.8 Hz, 2H), 7.34 ppm (t, *J*=8.4 Hz, 2H) ¹³C NMR (CDCl₃): δ =24.11, 27.42, 28.46, 67.70, 104.48, 109.39, 121.88, 129.34, 130.05, 158.73 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₃₆H₄₂O₄S₂: 602.25; found: 603.29 [*M*+H]⁺. Elemental analysis: calcd (%) for C₃₆H₄₂O₄S₂: C 71.72, H 7.02. found: C 71.60, H 6.81.

STB_{10/10}

m.p. 130.2–131.5 °C. ¹H NMR (CDCl₃, TMS): δ =1.09–1.33 (m, 24H), 1.43–1.56 (m, 8H), 3.84 (m, 4H), 3.97 (m, 4H), 6.61 (d, *J*=8.4 Hz, 4H), 6.68 (d, *J*=4.8 Hz, 2H), 6.95 (d, *J*=4.8 Hz, 2H), 7.33 ppm (t, *J*=8.4 Hz, 2H) ¹³C NMR (CDCl₃): δ =23.49, 25.07, 27.35, 27.56, 68.16, 104.53, 121.98, 129.27, 129.96, 158.69 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₄₀H₄₆O₄S₂: 658.28; found: 659.32 [*M*+H]⁺. Elemental analysis: calcd (%) for C₄₀H₃₀O₄S₂: C 72.91, H 7.65. found: C 72.93, H 7.66.

m.p. > 300 °C. ¹H NMR (CDCl₃, TMS): δ =2.14 (m, 8H), 3.80 (m, 4H), 4.00 (m, 4H), 5.11 (dt, *J*=1.2, 1.8 Hz, 4H), 6.71 (d, *J*=8.4 Hz, 4H), 6.73 (d, *J*=4.8 Hz, 2H), 6.98 (d, *J*=4.8 Hz, 2H), 7.38 ppm (t, *J*=8.4 Hz, 2H). ¹³C NMR (CDCl₃): δ =32.63, 68.45, 107.40, 117.61, 122.62, 128.39, 129.13, 129.97, 130.73, 133.55, 158.79 ppm. MALDI-TOF-MASS: *m/z*: calcd for C₃₂H₃₀O₄S₂: calculated 542.16; found: 542.04. Elemental analysis: calcd (%) for C₃₂H₃₀O₄S₂+0.25 CH₂Cl₂: C 68.69, H 5.45. found: C 68.70, H 5.31.

Synthesis of STB_{6/44}

Before the completion of the RCM reaction of 1_{44/44} (200 mg, 0.33 mmol) (15 min of reaction time) the reaction mixture was passed through short silica gel pad to remove the catalyst. The solution was concentrated and solid residue was obtained. Pd/C (50 mg) and THF (30 mL) was added and the mixture was stirred under H₂ atmosphere for 5 hrs. The mixture was passed through Celite and concentrated. The product was purified by column chromatography on silica gel to yield white powder. m.p. 126.0-127.6 °C. ¹H NMR (CDCl₃, TMS): $\delta = 0.75$ (t, J = 7.5 Hz, 6H), 1.02 (m, 2H), 1.19 (m, 4H), 1.34 (m, 2H), 1.48-1.60 (m, 8H), 3.72 (dd, J=2.4, 9.9 Hz, 2H), 3.90 (m, 4H), 4.00 (m, 2H), 6.61 (d, J=8.4 Hz, 2H), 6.67 (d, J=8.4 Hz, 2H), 6.69 (d, J=4.8 Hz, 2H), 6.94 (d, J=4.8 Hz, 2H), 7.36 ppm (t, J = 8.4 Hz, 2H). ¹³C NMR (CDCl₃): $\delta = 13.58$, 18.86, 27.68, 29.78, 31.14, 68.38, 69.00, 104.94, 105.93, 115.95, 122.12, 129.62, 129.65, 130.39, 133.68, 158.78, 159.00 ppm. MALDI-TOF-MASS: m/z: calcd for $C_{34}H_{40}O_4S_2$: 576.24; found: 577.05 [*M*+H]⁺. Elemental analysis: calcd (%) for $C_{34}H_{40}O_4S_2$: C 70.80, H 6.99. found: C 70.79, H 6.99.

Synthesis of $STB_{6/6}^T$

A solution of $3_{55/55}$ (200 mg, 0.31 mmol), Mo(CO)₆ (16.3 mg, 20 mol%), and 2-fluorophenol (69.3 mg, 200 mol%) in chlorobenzene (20 mL) was refluxed for 6 h under an Ar atmosphere. Upon cooling, the solution was diluted with CH₂Cl₂ and passed through silica gel to remove the catalyst. The solution was concentrated, to which methanol was added to obtain precipitate of the product. Analytical sample was purified by column chromatography on silica gel. m.p. > 300°C. ¹H NMR (CDCl₃, TMS): δ = 2.25–2.30 (m, 4H), 2.35–2.38 (m, 4H), 3.84–3.87 (m, 4H), 3.95–3.98 (m, 4H), 6.89 (d, *J*=8.4 Hz, 4H), 6.73 (d, *J*=5.4 Hz, 2H), 7.02 (d, *J*=5.4 Hz, 2H), 7.36 ppm (t, *J*=8.4 Hz, 2H). ¹³C NMR (CDCl₃): δ =20.05, 67.55, 77.57, 107.88, 117.88, 122.88, 129.08, 129.98, 158.61 ppm. MALDI-TOFFMASS: *mlz*: calcd for C₃₂H₂₆O₄S₂+0.3 CH₂Cl₂ : C 68.77, H 4.75. found: C 68.79,H 5.04.

Synthesis of (Z)-STB^D_{6/6}

A suspension of Lindlar catalyst (50 mg) and \mathbf{STB}^{T}_{66} (100 mg, 0.19 mmol), and quinoline (0.1 mL) in THF (10 mL) were stirred under H₂ atmosphere for 5 h. The reaction mixture was passed through Celite and concentrated. The solid residue was purified by column chromatography on silica gel to give a white powder. m.p. > 300 °C. ¹H NMR (CDCl₃, TMS): $\delta = 2.07-2.08$ (m, 4H), 2.16–2.17 (m, 4H), 3.84–3.87 (m, 4H), 3.98–4.02 (m, 4H), 5.08 (t, J = 4.5 Hz, 4H), 6.90 (d, J = 5.4 Hz, 2H), 6.40 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 5.4 Hz, 2H), 7.38 ppm (t, J = 8.4 Hz, 2H). ¹³C NMR (CDCl₃): $\delta = 27.83$, 71.04, 109.77, 122.32, 127.42, 129.77, 129.97, 130.52, 133.94, 159.25 ppm. MALDI-TOF-MASS: m/z: calcd for C₃₂H₃₀O₄S₂: 542.16; found: 542.38. Elemental analysis: calcd (%) for C₃₂H₃₀O₄S₂+0.15 CH₂Cl₂: C 69.52, H 5.50. found: C 69.71, H 5.74.

Acknowledgements

This work was supported by KAKENHI (No. 20750097 and No. 23655108), the Shorai Foundation for Science and Technology, and The Association for the Progress of New Chemistry for K.S. The authors thank Nanotechnology Network Project of the Ministry of Education, Culture, Sports, Science, and Technology Japan (MEXT).

- For reviews on IMWs, see: a) M. J. Frampton, H. L. Anderson, Angew. Chem. 2007, 119, 1046; Angew. Chem. Int. Ed. 2007, 46, 1028; b) D. J. Cardin, Adv. Mater. 2002, 14, 553; c) S. Brovelli, F. Cacialli, Small 2010, 6, 2796; d) M. Numata, J. Inclusion Phenom. Macrocyclic Chem. 2010, 68, 25; e) A. Harada, A. Hashidzume, H. Yamaguchi, Y. Takashima, Chem. Rev. 2009, 109, 5974; f) D. Lee, T. M. Swager, Synlett 2004, 149.
- [2] For representative examples of IMWs, see: a) S. Anderson, H. L. Anderson, Angew. Chem. 1996, 108, 2075; Angew. Chem. Int. Ed. Engl. 1996, 35, 1956; b) J. E. H. Buston, F. Marken, H. L. Anderson, Chem. Commun. 2001, 1046; c) P. N. Taylor, M. J. O'Connell, L. A. McNeill, M. J. Hall, R. T. Aplin, H. L. Anderson, Angew. Chem. 2000, 112, 3598; Angew. Chem. Int. Ed. 2000, 39, 3456; d) K. Yoshida, T. Shimomura, K. Ito, R. Hayakawa, Langmuir 1999, 15, 910; e) H. Okumura, Y. Kawaguchi, A. Harada, Macromol. Rapid Commun. 2002, 23, 781; f) J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martin-Alvarez, F. Hempel, J. A. Gladysz, Angew. Chem. 2002, 114, 1951; Angew. Chem. Int. Ed. 2002, 41, 1871; g) A. D. Schlüter, J. P. Rabe, Angew. Chem. 2000, 112, 860; Angew. Chem. Int. Ed. 2000, 39, 864; h) T. Kaneko, T. Horie, M. Asano, T. Aoki, E. Oikawa, Macromolecules 1997, 30, 3118; i) R. Tang, Y. Chuai, C. Cheng, F. Xi, D. Zou, J. Polym. Sci. Part A 2005, 43, 3126; j) W.-S. Li, D.-L. Jiang, T. Aida, Angew. Chem. 2004, 116, 3003; Angew. Chem. Int. Ed. 2004, 43, 2943; k) J.-S. Yang, T. M. Swager, J. Am. Chem. Soc. 1998, 120, 11864; l) R. Fiesel, J. Huber, U. Scherf, Angew. Chem. 1996, 108, 2233; Angew. Chem. Int. Ed. Engl. 1996, 35, 2111; m) J. Terao, S. Tsuda, Y. Tanaka, K. Okoshi, T. Fujihara, Y. Tsuji, N. Kambe, J. Am. Chem. Soc. 2009, 131, 16004; n) J. Terao, Y. Tanaka, S. Tsuda, N. Kambe, M. Taniguchi, T. Kawai, A. Saeki, S. Seki, J. Am. Chem. Soc. 2009, 131, 18046; o) Y. Liu, J. Shi, Y. Chen, C.-F. Ke, Angew. Chem. 2008, 120, 7403; Angew. Chem. Int. Ed. 2008, 47, 7293.
- [3] For IMWs based on oligo- or polythiophenes, see: a) S. Tanaka, Y. Yamashita, Synth. Met. 1999, 101, 532; b) S. Tanaka, Y. Yamashita, Synth. Met. 2001, 119, 67; c) Y. Ie, A. Han, T. Otsubo, Y. Aso, Chem. Commun. 2009, 3020; d) T. Otani, M. Hachiya, D. Hashizume, T. Matsuo, K. Tamao, Chem. Asian J. 2011, 6, 350; e) A. Wakamiya, D. Yamazaki, T. Nishinaga, T. Kitagawa, K. Komatsu, J. Org. Chem. 2003, 68, 8305; f) T. Nishinaga, A. Wakamiya, D. Yamazaki, K. Komatsu, J. Am. Chem. Soc. 2004, 126, 3163; g) P. R. L. Malenfant, J. M. J. Fréchet, Macromolecules 2000, 33, 3634; h) T. Otsubo, S. Ueno, K. Takimiya, Y. Aso, Chem. Lett. 2004, 33, 1154; i) T. Ikeda, M. Higuchi, D. G. Kurth, J. Am. Chem. Soc. 2009, 131, 9158; j) M. van den Boogaard, G. Bonnet, P. van't Hof, Y. Wang, C. Brochon, P. van Hutten, A. Lapp, G. Hadziioannou, Chem. Mater. 2004, 16, 4383; k) K. Sakamoto, Y. Takashima, H. Yamaguchi, A. Harada, J. Org. Chem. 2007, 72, 459; 1) C. Lagrost, K. I. C. Ching, J.-C. Lacroix, S. Aeiyach, M. Jouini, P.-C. Lacaze, J. Tanguy, J. Mater. Chem. 1999, 9, 2351; m) Y. Takashima, Y. Oizumi, K. Sakamoto, M. Miyauchi, S. Kamitori, A. Harada, Macromolecules 2004, 37, 3962; n) C. Li, M. Numata, A.-H. Bae, K. Sakurai, S. Shinkai, J. Am. Chem. Soc. 2005, 127, 4548; o) S. S. Zhu, P. J. Caroll, T. M. Swager, J. Am. Chem. Soc. 1996, 118, 8713; p) J. Buey, T. M. Swager, Angew. Chem. 2000, 112, 622; Angew. Chem. Int. Ed. 2000, 39, 608; q) T. Ikeda, M. Higuchi, Langmuir 2011, 27, 4184; r) T. Ikeda, M. Higuchi, A. Sato, D. G. Kurth, Org. Lett. 2008, 10, 2215.
- [4] a) R. Yamada, H. Kumazawa, T. Noutoshi, S. Tanaka, H. Tada, *Nano Lett.* 2008, *8*, 1237; b) R. Yamada, H. Kumazawa, S. Tanaka, H. Tada, *Appl. Phys. Express* 2009, *2*, 025002; c) M. Taniguchi, Y. Nojima, K. Yokota, J. Terao, K. Sato, N. Kambe, T. Kawai, *J. Am. Chem. Soc.* 2006, *128*, 15062.
- [5] a) F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorí, J. P. Rabe, M. J. O'Connell, P. N. Taylor, H. L. Anderson, *Nat. Mater.* 2002, *1*, 160; b) A. Petrozza, S. Brovelli, J. J. Michels, H. L. Anderson, R. H. Friend, C. Silva, F. Cacialli, *Adv. Mater.* 2008, *20*, 3218; c) S. Brovelli, G. Latini, M. J. Frampton, S. O. McDonnell, F. E. Oddy, O. Fenwick, H. L. Anderson, F. Cacialli, *Nano Lett.* 2008, *8*, 4546; d) S. Brovelli, F. Meinardi, G. Winroth, O. Fenwick, G. Sforazzini, M. J. Frampton, L. Zalewski,

J. A. Levitt, F. Marinello, P. Schiavuta, K. Suhling, H. L. Anderson, F. Cacialli, *Adv. Funct. Mater.* **2010**, *20*, 272; e) S. Brovelli, T. Virgili, M. M. Mroz, G. Sforazzini, A. Paleari, H. L. Anderson, G. Lanzani, F. Cacialli, *Adv. Mater.* **2010**, *22*, 3690.

- [6] K. Sugiyasu, Y. Honsho, R. M. Harrison, A. Sato, T. Yasuda, S. Seki, M. Takeuchi, J. Am. Chem. Soc. 2010, 132, 14754.
- [7] a) D. Vonlanthen, J. Rotzler, M. Neuburger, M. Mayor, *Eur. J. Org. Chem.* 2010, 35, 120; b) J. Rotzler, D. Vonlanthen, A. Barsella, A. Boeglin, A. Fort, M. Mayor, *Eur. J. Org. Chem.* 2010, 35, 1096; c) D. Vonlanthen, A. Mishchenko, M. Elbing, M. Neuburger, T. Wandlowski, M. Mayor, *Angew. Chem.* 2009, *121*, 9048; *Angew. Chem. Int. Ed.* 2009, *48*, 8886; d) A. Mishchenko, D. Vonlanthen, V. Meded, M. Bürkle, C. Li, I. V. Pobelov, A. Bagrets, J. K. Viljas, F. Pauly, F. Evers, M. Mayor, T. Wandlowski, *Nano Lett.* 2010, *10*, 156; e) A. Mishchenko, L. A. Zotti, D. Vonlanthen, M. Bürkle, F. Pauly, J. C. Cuevas, M. Mayor, T. Wandlowski, *J. Am. Chem. Soc.* 2011, *133*, 184; f) J. Rotzler, H. Gsellinger, M. Neuburger, D. Vonlanthen, D. Häussinger, M. Mayor, *Org. Biomol. Chem.* 2011, *9*, 86.
- [8] a) S. Woitellier, J. P. Launay, C. Joachim, *Chem. Phys.* **1989**, *131*, 481; b) L. Venkataraman, Y. S. Park, A. C. Whalley, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* **2007**, *7*, 502; c) L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nature* **2006**, *442*, 904.
- [9] S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, Angew. Chem. 2004, 116, 1907; Angew. Chem. Int. Ed. 2004, 43, 1871.
- [10] S. D. Lepore, Y. He, J. Org. Chem. 2003, 68, 8261.
- [11] a) B. Mohr, M. Weck, J.-P. Sauvage, R. H. Grubbs, Angew. Chem.
 1997, 109, 1365; Angew. Chem. Int. Ed. Engl. 1997, 36, 1308;
 b) D. A. Leigh, P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, Angew. Chem. 2001, 113, 1586; Angew. Chem. Int. Ed. 2001, 40, 1538.
- [12] a) J. A. Wisner, P. D. Beer, M. G. B. Drew, M. R. Sambrook, J. Am. Chem. Soc. 2002, 124, 12469; b) X.-Z. Zhu, C.-F. Chen, J. Am. Chem. Soc. 2005, 127, 13158.
- [13] a) T. Shima, F. Hampel, J. A. Gladysz, Angew. Chem. 2004, 116, 5653; Angew. Chem. Int. Ed. 2004, 43, 5537; b) A. J. Nawara, T. Shima, F. Hampel, J. A. Gladysz, J. Am. Chem. Soc. 2006, 128, 4962; c) L. Wang, F. Hampel, J. A. Gladysz, Angew. Chem. 2006, 118, 4479; Angew. Chem. Int. Ed. 2006, 45, 4372.
- [14] a) D. H. Camacho, E. V. Salo, J. W. Ziller, Z. Guan, Angew. Chem.
 2004, 116, 1857; Angew. Chem. Int. Ed. 2004, 43, 1821; b) M. Lautens, G. Hughes, Angew. Chem. 1999, 111, 160; Angew. Chem. Int. Ed. 1999, 38, 129; c) R. Wakabayashi, Y. Kubo, K. Kaneko, M. Takeuchi, S. Shinkai, J. Am. Chem. Soc. 2006, 128, 8744; d) A. Ohashi, A. Satake, Y. Kobuke, Bull. Chem. Soc. Jpn. 2004, 77, 365; e) T. Inomata, K. Konishi, Chem. Commun. 2003, 1282.
- [15] S. Monfette, D. E. Fogg, Chem. Rev. 2009, 109, 3783.
- [16] S. M. E. Simpkins, B. M. Kariuki, L. R. Cox, J. Organomet. Chem. 2006, 691, 5517.
- [17] a) L. de Quadras, E. B. Bauer, J. Stahl, F. Zhuravlev, F. Hampel, J. A. Gladysz, *New J. Chem.* **2007**, *31*, 1594; b) L. de Quadras, E. B. Bauer, W. Mohr, J. C. Bohling, T. B. Peters, J. M. Martín-Alvarez, F. Hampel, J. A. Gladysz, *J. Am. Chem. Soc.* **2007**, *129*, 8296; c) G. R. Owen, J. Stahl, F. Hampel, J. A. Gladysz, *Chem. Eur. J.* **2008**, *14*, 73.
- [18] R. S. Macomber, A Complete Introduction to Modern NMR Spectroscopy, Wiley, 1998.
- [19] a) C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li, F. Huang, Org. Lett. 2007, 9, 5553; b) C.-C. Hsu, N.-C. Chen, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu, Angew. Chem. 2008, 120, 7585; Angew. Chem. Int. Ed. 2008, 47, 7475.
- [20] V. Sashuk, J. Ignatowska, K. Grela, J. Org. Chem. 2004, 69, 7748.
- [21] M. G. Nilson, R. L. Funk, Org. Lett. 2010, 12, 4912.
- [22] É. Naudin, N. El Mehdi, C. Soucy, L. Breau, D. Bélanger, Chem. Mater. 2001, 13, 634.
- [23] a) J. Gierschner, H.-G. Mack, H.-J. Egelhaaf, S. Schweizer, B. Doser, D. Oelkrug, *Synth. Met.* 2003, 138, 311; b) P. Hermet, J.-L. Bantignies, A. Rahmani, J.-L. Sauvajol, M. R. Johnson, F. Serein, *J. Phys. Chem. A* 2005, 109, 1684.

- [24] J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 3rd ed., Springer, 2006.
- [25] Handbook of Thiophene-based Materials, Vol. 1: Synthesis and Theory (Eds.: I. F. Perepichka, D. F. Perepichka), Wiley, 2009.
- [26] a) J. Gierschner, J. Cornil, H.-J. Egelhaaf, Adv. Mater. 2007, 19, 173;
 b) M. Kertesz, C. H. Choi, S. Yang, Chem. Rev. 2005, 105, 3448;
 c) J. L. Brédas, G. B. Street, Acc. Chem. Res. 1985, 18, 309;
 d) J. Roncali, Chem. Rev. 1997, 97, 173;
 e) J. Gierschner, H.-G. Mack, L. Lüer, D. Oelkrug, J. Chem. Phys. 2002, 116, 8596.
- [27] C. Alemán, L. Julia, J. Phys. Chem. 1996, 100, 14661.
- [28] The exception in the relationship between Stokes' shift and the ring size was the case of $STB_{5/6}$, where almost the same as or even larger Stokes' shift than that of $STB_{6/6}$ was observed. This is probably because tightly-fixed asymmetric structure of $STB_{5/6}$ sensitively reflects the stability of the co-planar conformation in the excited state.
- [29] Optical properties including fluorescence lifetimes (τ) and quantum yields (Φ_f) of **STB**_{m/ns} are summarized in the Supporting Information, Table S1. We could not find significant differences and systematic relationships between those data of excited state dynamics (τ and Φ_f) and the ring size.
- [30] B. D. Allen, A. C. Benniston, A. Harriman, I. Llarena, C. A. Sams, J. Phys. Chem. A 2007, 111, 2641.
- [31] Contribution of the molecular orbital of resorcinol moieties might need to be considered; however, this contribution should be insignif-

icant because these two π -systems are orthogonally connected; dihedral angles (and $\cos^2 \phi$) between the thiophene and resorcinol groups in the crystallized form of **STB₆₆₆**, **STB_{10/10}**, and **1(OMe)**₄ are 70° (0.12), 82° (0.019), and 85° (0.008), respectively. Considering the cosine-squared relationship.^[7,8] the conjugation between these two aromatic rings should be negligibly small.

- [32] A. Saeki, S. Seki, Y. Koizumi, T. Sunagawa, K. Ushida, S. Tagawa, J. Phys. Chem. B 2005, 109, 10015.
- [33] a) A. Salleo, R. J. Kline, D. M. DeLongchamp, M. L. Chabinyc, *Adv. Mater.* 2010, *22*, 3812; b) Y.-K. Lan, C. H. Yang, H.-C. Yang, *Polym. Int.* 2010, *59*, 16; c) F. C. Grozema, P. Th. Van Duijnen, Y. A. Berlin, M. A. Ratner, L. D. A. Siebbeles, *J. Phys. Chem. B* 2002, *106*, 7791; d) M. Hultell, S. Stafström, *Phys. Rev. B* 2007, *75*, 104304.
- [34] a) M. Jurícek, P. H. J. Kouwer, A. E. Rowan, *Chem. Commun.* DOI: 10.1039/c1cc10685f; b) C. R. Becer, R. Hoogenboom, U. S. Schubert, *Angew. Chem.* 2009, *121*, 4998; *Angew. Chem. Int. Ed.* 2009, *48*, 4900; c) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* 2001, *113*, 2056; *Angew. Chem. Int. Ed.* 2001, *40*, 2004.
- [35] R. S. Becker, J. S. de Melo, A. L. Macanita, F. Elisei, J. Phys. Chem. 1996, 100, 18683.

Received: June 9, 2011 Published online: November 16, 2011