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The Synthesis of Molecular Rods with a Transversal Push-Pull System

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The design and synthesis of the molecular cruciforms **1**–**4** consisting of an oligophenylene-ethynyl backbone with an acetyl-protected sulfur anchor group on one end and a crossing oligophenylene cross-bar with terminal trifluoromethyl and dimethylamino groups as transversal push-pull system are reported. These cruciforms **1**–**4** are model compounds to investigate electronic potential-dependent switching properties of molecular junctions. While the oligophenylene-ethynyl backbone is responsible for the electronic transport properties, the transversal push-pull system should alter the tilt angle of the rod upon alignment in an electric field. As the tunnel distance at the rods end to the opposite electrode depends on the tilt angle of the rod, a considerable dependence of the transport current on the tilt angle is expected. The investigation of such transport mechanisms with the model compounds **1**–**4** may unravel the origin of negative differential conductance phenomena in devices consisting of sandwiched self assembled monolayers between two electrodes. The reported cruciform structures display limited stability features in the presence of acids. Their assembly is based on metal catalyzed cross coupling reactions with the chromatographic separation of two, on opposite sides mono-protected regioisomers as key step.

Introduction

The concept of molecular electronics that considers the use of molecular structures to build electronic devices exhibits remarkable scientific interest recently.[1] Feasibility of molecular devices lies in our ability to understand specific properties of molecules acting individually or in self-assembled monolayers and to use these properties in the creation of a new class of devices. Of particular interest within molecular electronics are switching devices based on bistable molecular structures.[2] A molecular junction consisting of a laterally limited self-assembled monolayer between two parallel gold electrodes displayed promising electronic properties, namely a negative differential resistance (NDR).[3] However, the origin of the effect is still under investigation and numerous theoretical studies provide a variety of different hypotheses.[4] In addition, model compounds for the thorough investigation of a particular hypothesis have already been reported like e.g. the synthesis of suitably functionalized macrocycle.[5] The self-assembled monolayer forming molecule consists of a oligopheneylene-ethynyl (OPE) backbone with a terminal sulfur group for the immobilization on a gold substrate. In addition, the central phenyl ring is functionalized with a nitro and an amino group resulting in a transversal push-pull system which is tilted by 60° with respect to the axis of the OPE rod. Variations of the molecular structure unraveled that the nitro group is crucial for the observation of NDR effects in such devices.[6]

A plausible explanation for the observed decrease of the current upon applying a particular threshold voltage (NDR effect) could be the parallel alignment of the push-pull vector of the SAM-molecule in the electric field. In Figure 1 an upright molecule in the junction is displayed in A) and a tilted molecule after alignment of its push-pull vector in the electric field is displayed in B). As in the nanopore set-up the distance between both electrodes remains constant, the tilting of the molecular rod increases the distance between its end and the top electrode considerably (d_1 compared with d_0 in Figure 1). The tunnel current between the molecule and the top electrode decreases exponentially with the distance and hence, an increasing spacing between molecule and top electrode should decrease the current through the junction significantly. Electric field-dependent switching properties have already been reported for scanning tunneling microscope investigations of molecular rods with tailor-made polarities in an amide containing SAM host matrix.[7] However, the focus of these studies was rather the interplay between polarity along the rod axis and hydrogen bonding in the host environment than the alignment of a perpendicular dipole vector.

The strength of the dipole moment of the transversal push-pull system depends not only on its terminal electron-donating and electron-accepting functional groups, but also

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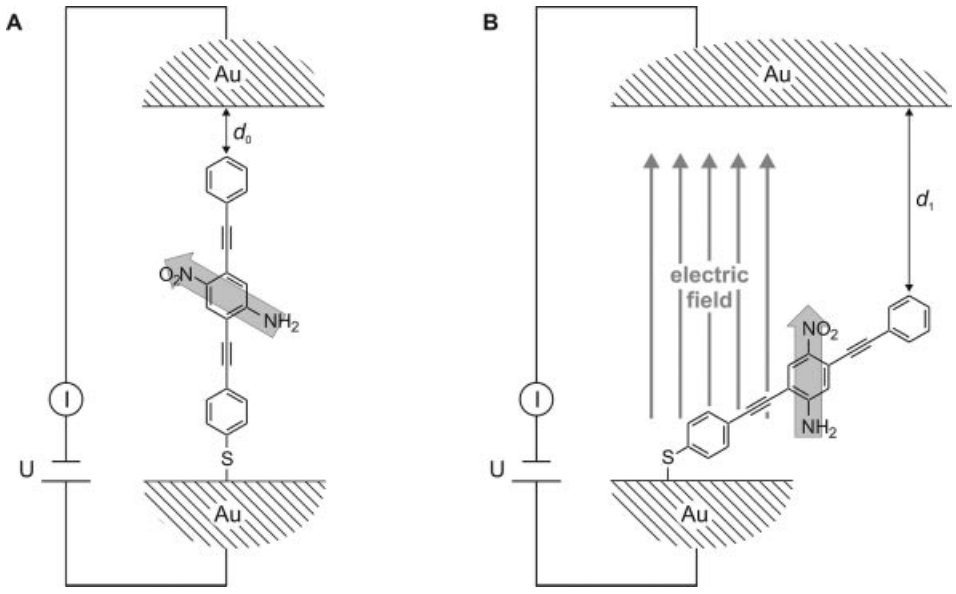
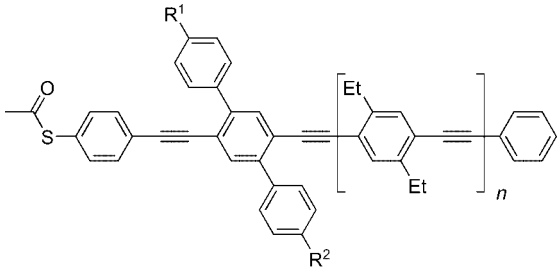


Figure 1. Sketch of a hypothetical switching mechanism of the reported NDR device. At low voltages the molecule stands more or less upright in the SAM with the distance d_0 for the tunnel current between the top electrode and the terminal π-system of the molecular rod (**A**). Upon applying an electric field, the *para* nitro aniline push-pull system of the central ring subunit aligns resulting in an increased distance d_1 between the top electrode and the end of the molecule (**B**).

on their separation. As model compounds to investigate the proposed electric field-dependent switching mechanism, molecular rods with a considerable transversal dipole moment due to an increased spacing between donor and acceptor group are appealing.

Here we report the synthesis and characterization of cruciform molecules **1**–**4** (Figure 2) consisting of oligophenylene-ethynylene (OPE) backbones of varying length and transversal oligophenylene (OP) rods. While one end of the longer OPE rod substructure is terminally functionalized with an acetyl-protected sulfur group for immobilization on noble metal surfaces, the transversal OP substructure acts as a push-pull system with an electron-donating dimethylamino group on one end and a chemically inert electron-accepting trifluoromethyl group on the opposite end. A particular advantage of these cruciforms is that the direction of the transversal push-pull vector can be inverted by chemical synthesis allowing a more detailed investigation of the polarization direction. Furthermore, the length of the OPE rod can be adjusted to the electrode spacing of a particular device.

Functionalized cruciform π-systems have already been reported as test structures for molecular electronics,[8] as electro-optically active chromophore in self-assembled thin films,[9] as chromophores with tunable bandgaps,[10] as metal ion sensors[11] and as building blocks of coordination polymers.[12] Some of these cruciform structures have either an OP-[8] or an OPE-substructure[10–12] in common with the here presented cruciforms. Furthermore, the combination of OP and OPE rods in a cruciform structure has been reported from Swager and co-workers as precursors of extended fused-ring systems in molecules[13,14] as well as in polymers.[14]



1: $n = 0$, $R^1 = CF_3$, $R^2 = NMe_2$
2: $n = 0$, $R^1 = NMe_2$, $R^2 = CF_3$
3: $n = 1$, $R^1 = CF_3$, $R^2 = NMe_2$
4: $n = 1$, $R^1 = NMe_2$, $R^2 = CF_3$

Figure 2. Cruciform target structures **1**–**4** consisting of an OP push-pull system crossing a terminal acetylsulfanyl-functionalized OPE rod.

Synthetic Strategy

While the OPE backbone of the cruciform target structures **1**–**4** is assembled sequentially by acetylene scaffolding steps like Sonogashira cross-coupling reactions[15] and acetylene protection group chemistry, the transversal OP push-pull system is formed gradually by Suzuki cross-coupling reactions.[16] Both cross-coupling reactions have palladium catalysts in common and display comparable chemo selectivities like the preference of iodine as leaving group compared with bromine. Thus starting with 1,4-dibromo-2,5-diiodobenzene, either the OPE or the OP rod might be assembled in first place. In Figure 3 the here investigated fraction of the possible retrosynthetic pathways are dis-

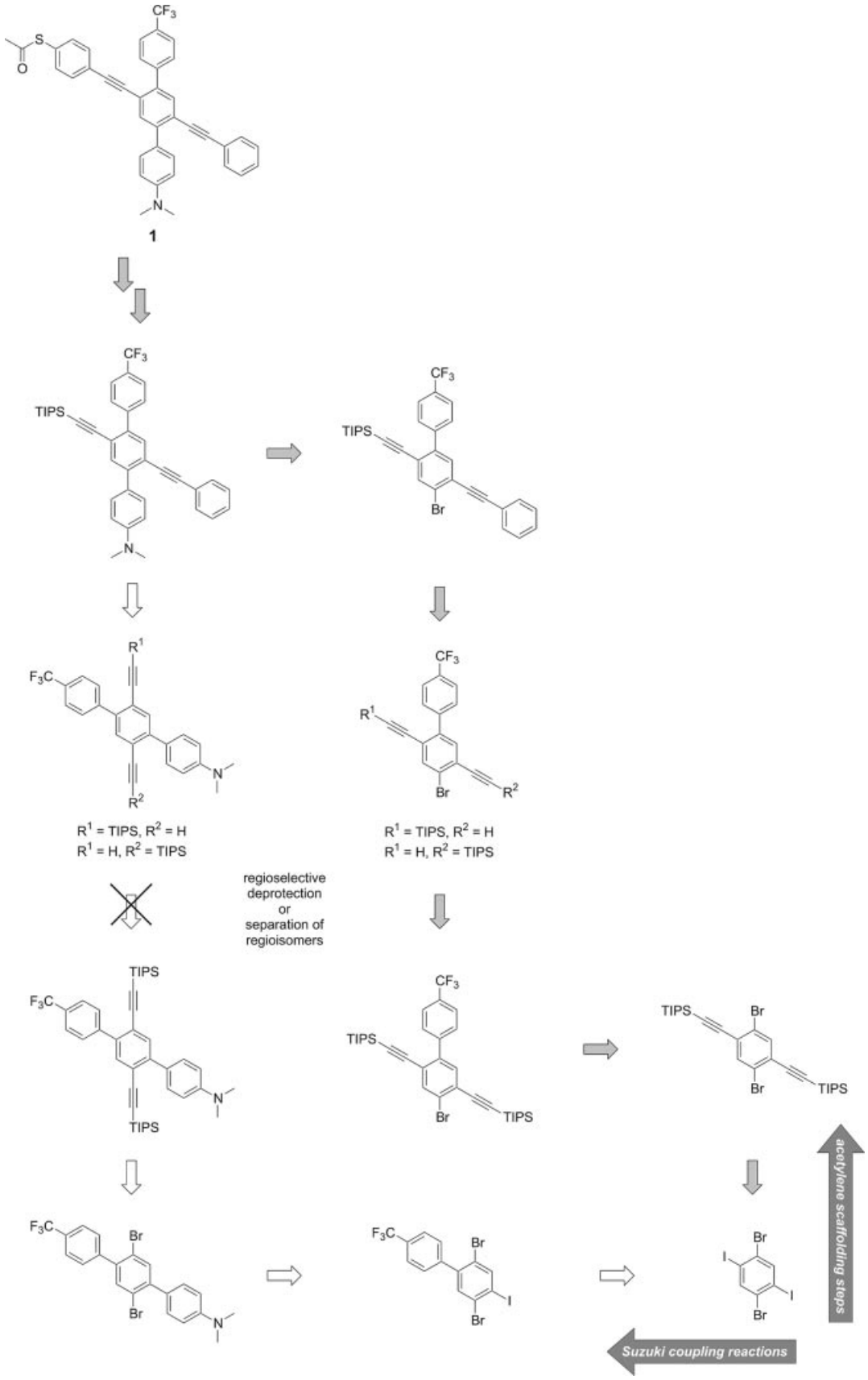


Figure 3. Retrosynthetic strategy to assemble the target structure **1**. Horizontal retrosynthetic arrows represent Suzuki coupling steps and vertical retrosynthetic arrows represent acetylene scaffolding steps like Sonogashira coupling reactions or acetylene deprotections. The white retrosynthetic arrows represent the pathway *A*, while the light grey retrosynthetic arrows display the synthetic path *B* which led to the target structure **1**.

played. While acetylene scaffolding reaction steps are displayed vertically, Suzuki coupling reactions are represented by horizontal retrosysnthetic arrows. After the introduction of both silyl-protected acetylenes, the key step of the retrosynthetic Scheme is the differentiation of both acetylene functions. Distinguishing chemically between both acetylenes is crucial to control the position of the sulfur anchor group and hence also the direction of the transversal push-pull rod with respect to the backbone of the immobilized molecule. This can either be achieved by regioselective deprotection or by separation of both regioisomers from a statistical mixture after partial removal of the silyl protection groups of the acetylenes.

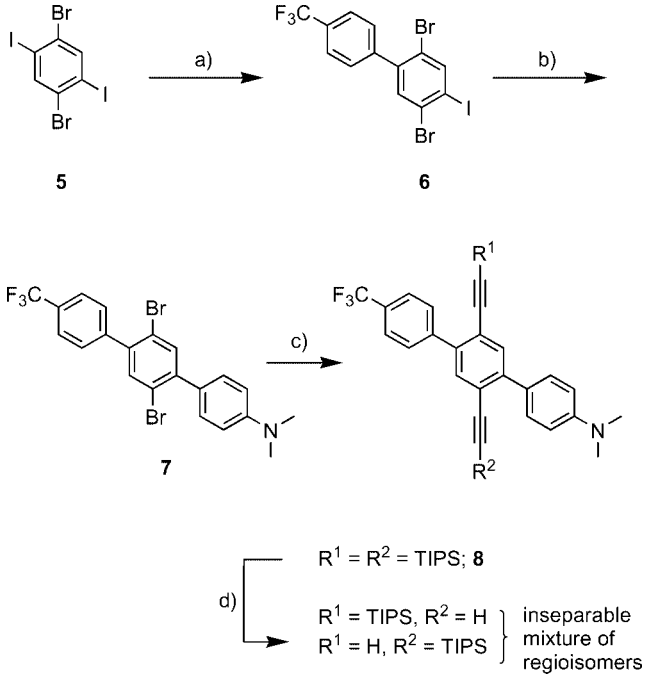
As displayed in Figure 3, the synthetic strategy has been investigated along two alternative pathways for both shorter rods **1** and **2**. However, the modular synthesis of the OPE backbone allows to assemble the longer rods **3** and **4** from the same building blocks.

In pathway *A*, the OP based push-pull rod was first synthesized by consecutive Suzuki coupling reactions substituting both iodine atoms of the starting tetrahalobenzene. Subsequently both bromine atoms were substituted by silyl-protected acetylenes. After either regioselective deprotection of one of both acetylenes or separation of the regioisomers, the OPE backbone comprising a sulfur anchor group on one end should be assembled gradually to provide access to the desired target structures. However, for the silyl-protected diacetylene with the perpendicular terphenyl push-pull system neither suitable reaction conditions for the regioselective deprotection nor a chromatographic system for the separation of both regioisomers have been found.

To increase the difference between both regioisomers, in pathway *B* the perpendicular push-pull system was only partially assembled. Again starting from 1,4-dibromo-2,5-diiodobenzene, a subunit of the OPE backbone is first synthesized by substituting both iodines with silyl-protected acetylenes in a Sonogashira coupling reaction. Subsequently the electron-accepting subunit of the OP push-pull rod is introduced by a Suzuki coupling. Partial deprotection of the silyl-protected acetylenes provides a reaction mixture containing both regioisomers. The considerable difference of both sides of the OP rod at this stage of the synthesis enhances their physical difference and facilitates their separation and indeed, classical column chromatography allowed to distinguish between both regioisomers. After separation of both regioisomers, the first branch of the OPE backbone is introduced in a Sonogashira coupling reaction to get rid of the rather reactive deprotected acetylene subunit. Subsequently, the OP push-pull system is completed by substituting the remaining bromine with a corresponding dimethylaniline boronic acid derivative in a Suzuki reaction step. Finally, the second acetylene is deprotected and the remaining part of the OPE backbone comprising the acetyl-protected sulfur anchor group is assembled. In both strategies the acetyl-protected sulfur terminus is introduced at the end of the synthesis as this rather labile functional group would restrict considerably the possible reaction conditions for both palladium catalyzed coupling reactions required to assemble the OP and the OPE rods.

Synthesis and Characterization

The required starting compound 1,4-dibromo-2,5-diiodobenzene **5** was synthesized following a reported synthetic protocol.[17] Our first attempts towards the target structure **1** were following the retrosynthetic pathway *A*, represented by white retrosynthetic arrows in Figure 3. The synthetic steps are displayed in Scheme 1.



Scheme 1. Synthetic steps towards **1** following the retrosynthetic pathway *A* depicted in Figure 3: a) 4-(trifluoromethyl)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, DME/H_2O, 75 °C, 16 h, 48%; b) 4-(dimethylamino)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, DME/H_2O, 75 °C, 16 h, 15%; c) TIPSA, $Pd(PPh_3)_2Cl_2$, $(iPr)_2NH$, CuI, THF, room temp., 16 h, 98%; d) TBAF, THF/AcOH, room temp.

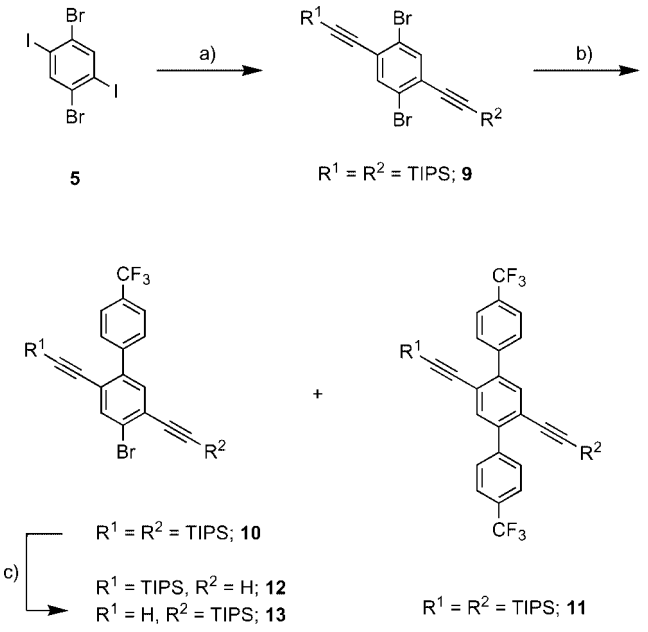
Applying Suzuki coupling conditions, commercially available 4-(trifluoromethyl)phenylboronic acid together with the starting material **5** provided the monosubstituted derivative **6**. In a 1,2-dimethoxyethane (DME) water mixture 1.5 equivalents of **5** were treated with an equivalent of 4-(trifluoromethyl)phenylboronic acid and a tenfold excess of potassium carbonate (K_2CO_3) in the presence of 5 mol-% tetrakis(triphenylphosphane)palladium(0) ($Pd(PPh_3)_4$) as catalyst at 75 °C. After workup, the doubly substituted terphenyl derivative and the desired singly substituted trihalobiphenyl compound **6** were isolated as white solids by column chromatography (CC) in 41% and 48% yield respectively. To keep the reaction temperature at 75 °C turned out to be crucial as at higher temperature considerable deiodination of the starting material was observed. Comparable reaction conditions applied to the monoiodo derivative **6** and commercially available 4-(dimethylamino)-phenylboronic acid provides the push-pull terphenyl system

7 in poor yields of 15%. The assembly of the terphenyl system was accompanied by several side products that have neither been isolated nor identified. Substitution of both bromines of **7** by (triisopropyl)acetylene (TIPSA) has been achieved applying Sonogashira coupling conditions. Thus the dibromide **7** was treated with TIPSA in tetrahydrofuran (THF) with diisopropylamine ($(i\text{Pr})_2\text{NH}$) as base and dichlorobis(triphenylphosphane)palladium ($Pd(PPh_3)_2Cl_2$) and copper iodide (CuI) as catalysts at room temperature to provide the doubly protected diacetylene **8** in 98% yield as a white solid after CC. Monodeprotection of the doubly silyl-protected diacetylene **8** was achieved with tertabutylammonium fluoride (TBAF) as source of fluorine anions. Compound **8** was dissolved in THF and after addition of a drop of acetic acid (AcOH) as proton source 0.7 equiv. of TBAF were added. After stirring overnight at room temperature, a mixture of starting material, both monodeprotected regioisomers and traces of the fully deprotected diacetylene were obtained. While the starting material **8** and the fully deprotected derivative could be separated by CC, the very comparable polarities of both regioisomers did not allow separating them by CC. Even though numerous solvent systems have been investigated, hardly any differences in polarities have been observed for both regioisomers.

The difficulties in separation of both regioisomers together with the poor yield in the assembly of the terphenyl push-pull system considerably reduced the attractivity of the so far followed synthetic pathway *A*. In order to enhance the differences between both regioisomers, the gradual assembly of the push-pull system and the OPE rod as displayed in Figure 3 as pathway *B* has been envisaged.

In similarity to the synthetic pathway *A*, also in the second pathway *B* the desired target structure **1** is developed from 1,4-dibromo-2,5-diiodobenzene **5** as starting material. As displayed in Scheme 2, first exclusively both iodine's of the tetrahalo derivative **5** were substituted by TIPSA to provide the doubly silyl-protected diacetylene **9** in a yield of 77%, demonstrating the chemoselectivity of the Sonogashira coupling. The synthesis of **9** followed the protocol already reported by Tovar and Swager.[18]

The chemical robustness of both TIPS protection groups opened a wide space of potential reaction conditions for the subsequent Suzuki coupling reactions. To introduce the electron withdrawing trifluoromethylphenyl group equimolar amounts of the dibromide **9** and the commercially available 4-(trifluoromethyl)phenylboronic acid with catalytic amounts of $Pd(PPh_3)_4$ and an excess of K_2CO_3 were kept at 80 °C in a DME/water mixture for 14 h. After work up the desired monosubstituted biphenyl derivative **10** and the doubly substituted terphenyl system **11** were isolated both as white solids in 46 and 32% yields respectively by CC. Comparable reaction conditions applied to the doubly silyl-protected diacetylene **10** as described above for **8** resulted in a statistical mixture of the fully protected starting material **10**, both regioisomers **12** and **13** together with traces of the doubly deprotected diacetylene. The starting material **10** was dissolved in THF and after addition of a



Scheme 2. Synthesis of both regioisomers **12** and **13**. a) TIPSA, $Pd(PPh_3)_2Cl_2$, $(i\text{Pr})_2\text{NH}$, CuI, THF, room temp., 40 h, 77%; b) 4-(trifluoromethyl)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, DME/H_2O, 80 °C, 14 h, 46%; c) TBAF, THF/AcOH, room temp.

drop of acetic acid 0.74 equiv. of TBAF was added. After work up by filtration through a silica short plug the different reaction products were isolated by CC. Fortunately, both regioisomers turned out to be separable by CC on silica gel with pure hexane as eluent. Both regioisomers **12** and **13** were isolated as colorless oils in 29 and 21% yields, respectively. Both compounds displayed rather limited stability properties indicated by a color change to brown upon extended drying. Nevertheless, both compounds were stable over several weeks when kept at –20 °C in the dark. Due to these stability restrictions we were not able to provide correct elemental analysis of these two compounds.

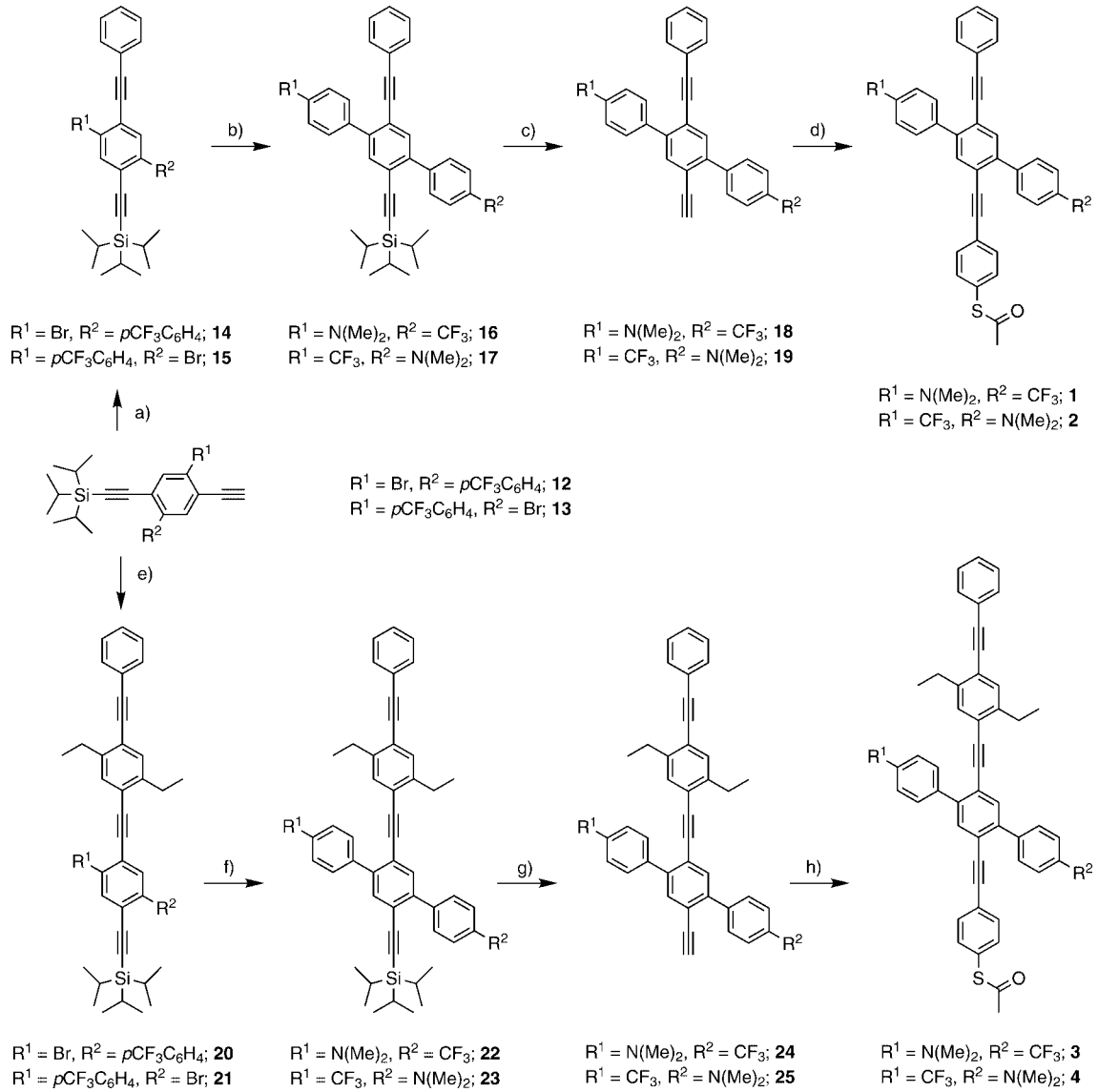
Of particular importance is the structural assignment of both regioisomers **12** and **13** as the further assembly of the target structures is solely based on chemoselectivity and hence, their structures are developed by chemical arguments from the corresponding regioisomer.

As expected, both TIPS-protection groups and both terminal acetylenic protons displayed considerable differences for both regioisomers. The chemical shifts in the ^{1}H NMR spectra for the acetylene proton and for the TIPS protons are 1.17 ppm and 3.17 ppm for one regioisomer and 0.98–0.99 ppm and 3.48 ppm for the other regioisomer. For the chemical shift of these ethynylic groups the functional groups in the corresponding *ortho*-positions are assumed to be the key-players as they are sterically closest and they couple electronically stronger than the groups in the corresponding *meta*-positions. Thus, the very comparable chemical shifts of the TIPS groups with model compounds already synthesized during the assembly of these structures allowed the structural assignment.

The chemical shift of the TIPS protons of the doubly TIPS-protected diacetylene **9** with bromine substituents in

ortho-positions for both acetylenes is with 1.13 and 1.14 very comparable to the TIPS protons at δ = 1.17 ppm of one regioisomer and thus, this regioisomer is expected to be compound **13** with a bromine atom in *ortho*-position of the TIPS acetylene. On the other hand the terphenyl side product **11** has two TIPS-protected acetylenes each in *ortho*-position of a *para*-trifluoromethylphenyl substituent. In similarity to the other regioisomers the signals of his TIPS protons are at δ = 0.98 and 0.99 ppm and thus, the structure of the regioisomer with the TIPS signal at δ = 0.98 and 0.99 ppm is **12** with a *para*-trifluoromethylphenyl substituent in *ortho*-position to the TIPS acetylene. While at this stage of the synthesis the assignment was still questioned to some extend, it was confirmed finally by an x-ray structure of a derivative of **13**.

After identification of both regioisomers **12** and **13**, their functional groups allowed the gradual assembly of the desired target structures **1**–**4**. The synthesis of the target rods **1**–**4** is displayed in Scheme 3. As the limited stability of **12** and **13** was attributed to their free acetylene, this function was first caped with an aromatic system in a Sonogashira coupling reaction. To assemble the shorter target structures **1** and **2**, the corresponding regioisomer **12** and **13** together with 1.5 equiv. of iodobenzene, catalytic amounts of $Pd(PPh_3)_4$ and CuI in a THF/$(i\text{Pr})_2$NH mixture was kept at room temperature overnight. After work up and CC the corresponding phenylacetylene derivatives **14** and **15** were isolated both in 86% yields as colorless oil and as white solid, respectively. Subsequently, the terphenyl push-pull system was completed by substituting the remaining bro-



Scheme 3. Synthesis of target structures **1**–**4**. a) iodobenzene, $Pd(PPh_3)_4$, $(i\text{Pr})_2$NH, CuI, THF, room temp., 16 h, 86% (**14**) and 86% (**15**); b) 4-(dimethylamino)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, DME/H_2O, 80 °C, 16 h, 84% (**16**) and 66% (**17**); c) TBAF, THF, room temp., 97% (**18**) and 94% (**19**); d) *S*-(4-iodophenyl) thioacetate, $Pd(PPh_3)_4$, $(i\text{Pr})_2$NEt, CuI, THF, room temp., 16 h, 80% (**1**) and 83% (**2**); e) 1,4-diethyl-2-iodo-5-(phenylethynyl)benzene, $Pd(PPh_3)_4$, $(i\text{Pr})_2$NH, CuI, THF, room temp., 16 h, 72% (**20**) and 90% (**21**); f) 4-(dimethylamino)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, DME/H_2O, 80 °C, 16 h, 86% (**22**) and 81% (**23**); g) TBAF, THF, room temp., 90% (**24**) and 96% (**25**); h) *S*-(4-iodophenyl) thioacetate, $Pd(PPh_3)_4$, $(i\text{Pr})_2$NEt, CuI, THF, room temp., 16 h, 44% (**3**) and 62% (**4**).

mine of **14** and **15** with commercially available 4-(dimethylamino)phenylboronic acid in a Suzuki cross-coupling reaction. The corresponding bromines **14** and **15** and the boronic acid derivative together with catalytic amounts of $Pd(PPh_3)_4$ and an excess of K_2CO_3 in a DME/water mixture were kept at 80 °C overnight. After work up, the terphenyl push-pull derivatives **16** and **17** were isolated in 84% and 66% yields respectively by CC. While **16** was a brownish oil, compound **17** as a derivative of **13** was a crystalline brownish solid. Single crystals suitable for X-ray analysis were obtained by slow diffusion of ethanol into a solution of **17** in dichloromethane. The solid-state structure of **17** is displayed in Figure 4. Compound **17** crystallizes with two independent molecules in the monoclinic space group $P2_1/n$.[19] These two molecules show an almost coplanar but antiparallel arrangement, such that the trifluoromethyl group of one molecule lies above the dimethylamino group of the other. The distance between the central phenyl rings of these two molecules amounts to 371.4 pm.

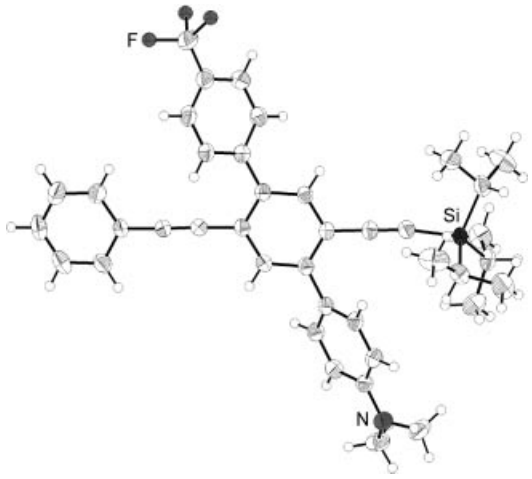


Figure 4. Solid state structure of **17** (ORTEP, thermal ellipsoids set at the 50% probability level).

The solid-state structure of **17** with the *meta* relation at the central ring between the *para*-trifluoromethylphenyl group and the trisisopropylsilylethynyl substituent confirm the above suggested ^{1}H NMR assignment for its precursor **13** and thus, the differentiation between both regioisomers **12** and **13**.

With both ideally substituted terphenyl structures **16** and **17** in hand, the assembly of the desired target structures **1** and **2** was accomplished in two steps. After fluoride promoted desylilation by TBAF in wet THF the free acetylenes **18** and **19** were isolated by CC in yields of 97 and 94%, respectively, both as yellowish solids. To complete the OPE rod, a final Sonogshira coupling between the free acetylenes of **18** and **19** with the known *S*-(4-iodophenyl) thioacetate[20] provided the desired target structures **1** and **2**. For this final reaction step $(i\text{Pr})_2\text{NEt}$ was used instead of $(i\text{Pr})_2\text{NH}$ as for the acetyl-protected thiophenol improved stability features are reported for the tertiary amine as solvent.[21] The acetylene derivatives **18** and **19** and *S*-(4-iodophenyl) thioacetate together with catalytic amounts of $Pd(PPh_3)_4$ and CuI were kept at room temperature overnight in a THF/$(i\text{Pr})_2$NEt mixture. After work up and CC, the desired terminally sulfur-functionalized OPE rods comprising a transversal OP push-pull system **1** and **2** were isolated both as yellow solids in yields of 80 and 83%, respectively.

The assembly of the target structures comprising an elongated OPE rod **3** and **4** was achieved with very similar reaction conditions as described above for the shorter derivatives **1** and **2**. Both regioisomers **20** and **21** were first caped with 1,4-diethyl-2-iodo-5-(phenylethynyl)benzene, which was synthesized following the literature procedure.[22] The reaction proceeded smoothly in $(i\text{Pr})_2$NEt/THF at room temperature to afford the π-extended systems **20** and **21** in 72% and 90% isolated yield, respectively. Subsequently, Suzuki cross-coupling of the commercially available 4-(dimethylamino)phenylboronic acid to the bromide atom of **20** or **21** in a DME/water solvent mixture at 80 °C provided the molecular rods **22** and **23** comprising a terphenyl push-pull system in 86 and 81% isolated yields after CC. The task of both ethyl side chains of the OPE rod was to provide the required solubility and processability of the longer rod target structures **3** and **4** and of their precursors.

Comparable reaction conditions as described for **16** and **17** allowed the efficient removal of the TIPS protection group from **22** and **23** and provided the two acetylenes **24** and **25** in yields of 90 and 96% respectively after CC. Again, a final Sonogashira coupling step of the acetylenes of **24** and **25** with a slight excess of 1.3 to 1.4 equiv. of *S*-(4-iodophenyl) thioacetate in the presence of catalytic amounts of $Pd(PPh_3)_4$ and CuI in a THF/$(i\text{Pr})_2$NEt mixture at room temperature provided the longer terminally sulfur-functionalized OPE rods comprising a transversal OP push-pull system **3** and **4**, both as yellow solids which were isolated by CC in yields of 44 and 62%, respectively.

All new compounds were fully characterized by conventional analytical and spectroscopic techniques like ^{1}H and ^{13}C-NMR spectroscopy and mass spectrometry. However, superimposition of two ^{13}C-NMR signals has been observed for several compounds which display one signal less than expected in the aromatic region of their ^{13}C-NMR spectra. This is the case for compounds **1**, **4**, **7**, **16**, **20**, **21**, **24** and **25**. Furthermore, apart from the too labile intermediates **12** and **13**, the purity of the new synthesized compounds was investigated by elemental analysis.

The cruciform target structures **1**–**4** are soluble in aprotic organic solvents and particularly well soluble in halogenated organic solvents. However, they display limited stability features in particular in chloroform, probably due to traces of acids. These stability restrictions are probably due to an electrophilic cyclization reaction of the cruciforms **1**–**4** to fused aromatic rings in the presence of catalytic amounts of acids. This cyclization reaction has been investigated in details by Swager and co-workers for the cruciform motive consisting of crossed OP and OPE rods and turned out to be efficient with electron-rich terminal substituents

at the OPE substructure.[13] Thus, the cruciform structures **1**–**4** comprising the terminal electron-rich sulfur anchor group at the OPE rod is probably exposed to this unwanted cyclization reaction. Furthermore, by TLC traces of several degradation products emerging from **1**–**4** were observed which may point to several degradation pathways. However, during attempts to crystallize these cruciforms **1**–**4** in acid free solvents in the dark, no degradations of the dissolved molecules were observed over periods of several months.

Of particular interest will be the applied potential dependence of the electronic transport properties of these cruciforms immobilized in nanoscale junctions. The availability of two different length of the longer OPE cross-bars enables to bridge gaps between electrodes of various length. Based on MM+ calculation, the length of the shorter cruciforms **1** and **2** is 1.95 nm between the sulfur atom and the terminal hydrogen atom at the opposite end of the OPE backbone, while the length of the longer cruciform structures **3** and **4** is calculated to be 2.63 nm. Furthermore, for both series of different length both push-pull directions of the transversal OP cross-bar have been synthesized, enabling the investigation of both possible polarization directions of the electrodes. While for the cruciforms **1** and **3** their electron-accepting trifluoromethyl groups of their transversal OP rods point towards the electrode to which the cruciforms are covalently bound, they point towards the opposite electrode for the cruciforms **2** and **4**. We hope to be able to trace more carefully potential switching mechanisms based on this variety of the cruciform structure. First attempts to immobilize these cruciforms between nanoscale-spaced electrodes are currently under investigations.

Conclusions

The synthesis of four new cruciform molecules **1**–**4** consisting of a longer oligophenylene-ethynyl (OPE) cross-bar and a transversal oligophenylene (OP) cross-bar is described. One end of the OPE rod bears an acetyl-protected sulfur as anchor group for metal electrodes. The crossing OP rod is terminally functionalized with an electron-accepting trifluoromethyl group and with an electron-donating dimethylamino group to provide a push-pull system transversal to the rods main axis. Not only two different length of the cruciforms OPE backbone have been synthesized, but also both push-pull directions of the transversal OP rod. The assembly of these cruciforms **1**–**4** is mainly based on metal catalyzed cross-coupling reactions. However, the key step of the synthetic approach is the separation of two regioisomers by column chromatography.

These cruciforms have been designed as prospective electronic potential-dependent switching systems integrated between two electrodes with nanoscale spacing. Limited stability features of these cruciform structures have been observed in the presence of traces of acids.

While these cruciforms are currently immobilized on an electrode surface to investigate their electronic potential-dependent transport properties in electronic circuits, we are improving the stability features of the cruciform substructure by altering the subsituents in proximity of the central phenyl ring.

Experimental Section

General Remarks: All chemicals were used as received from the supplier, solvents were p.a. quality and used without further purification. If necessary the solvents were dried by standard literature procedures, THF with Na/benzophenone[23] and $(i\text{Pr})_2\text{NEt}$, $(i\text{Pr})_2\text{NH}$ over CaH_2. The following instruments were used for the characterization of the synthesized compounds: ^{1}H NMR and ^{13}C-NMR spectra were recorded on a Bruker Ultra Shield 300 MHz, the *J* values are given in Hz. MALDI-TOF spectra was performed on a PerSeptive Biosystems Voyager DE PRO time-of-flight mass spectrometer and EI-MS on a LKB-9000S. Melting points were measured with a Büchi Melting Point B-540 apparatus. TLC was carried out on Merck silica gel 60 F_{254} plates and column chromatography (CC) using Merck silica gel 60 (0.040–0.063 mm). Elemental analyses were performed using the ThermoQuest FlashEA 1112 N/Protein Analyzer.

2,5-Diethyl-1,4-diiodobenzene: Synthesis according to a literature procedure[22] (42.7 g, 65%). M.p. 70–72 °C (ref.[22] 68–69 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.18 (t, $^3J_{H,H}$ = 7.5 Hz, 9 H, CH_3), 2.64 (q, $^3J_{H,H}$ = 7.5 Hz, 4 H, CH_2), 7.62 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.6, 33.3, 100.5, 138.8, 146.0 ppm. MS (EI): *m*/*z* (%) = 386.0 (100) [M^+], 370.9 (37.5) [M^+ – CH_3], 259.0 (9.4) [M^+ – I], 132.1 (8.0) [M^+ – 2I], 117.1 (23.8) [M^+ – 2I, – CH_3].

1,4-Diethyl-2-iodo-5-(phenylethynyl)benzene: Synthesis according to a literature procedure[22] (5.7 g, 76%, colorless oil). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.24 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.31 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 2.72 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.83 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 7.27–7.40 (m, 4 H), 7.50–7.59 (m, 2 H), 7.72 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.6, 14.8, 27.0, 33.6, 87.7, 93.8, 101.0, 122.8, 123.4, 128.5, 128.5, 131.6, 131.7, 138.9, 143.9, 145.4 ppm. MS (EI): *m*/*z* (%) = 360.0 (100) [M^+], 345.0 (10.4) [M^+ – CH_3], 233.2 (9.1) [M^+ – I], 218.1 (14) [M^+ – I, – CH_3].

1,4-Dibromo-2,5-diiodobenzene (5): Compound **5** was synthesized according to a literature procedure[17] (25.1 g, 52%). M.p. 164–166 °C (ref.[17] 163–165 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.06 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 101.8, 129.6, 142.7 ppm. MS (EI): *m*/*z* (%) = 489.5 (49), 487.6 (100), 485.6 (51) [M^+], 362.7 (9), 360.7 (19), 358.7 (9) [M^+ – I], 235.8 (7), 233.8 (15), 231.8 (8) [M^+ – 2I], 154.9 (10), 152.9 (11) [M^+ – 2I, – Br].

2,5-Dibromo-4-iodo-4′-(trifluoromethyl)biphenyl (6): To a mixture of **5** (8.5464 g, 17.5 mmol) in degassed DME (200 mL), 4-(trifluoromethyl)phenylboronic acid (2.2158 g, 11.7 mmol), $Pd(PPh_3)_4$ (0.6759 g, 0.58 mmol), K_2CO_3 (16.1928 g, 117 mmol) and degassed water (50 mL) were added. The reaction mixture was heated to 75 °C and kept at 75 °C for 16 h under a nitrogen atmosphere. DME was removed by rotary evaporation and the residue was extracted with CH_2Cl_2. The solvent was removed and the residue was absorbed on silica gel. Purification by column chromatography (CC) (silica gel, hexane) afforded **6** as a white solid (2.81 g, 48%). M.p. 91–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.49 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.55 (s, 1 H), 7.69 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 8.17 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 101.4, 121.4, 122.3, 124.1 (q, $^1J_{C,F}$ = 270.7 Hz), 125.4 (q, $^3J_{C,F}$ = 3.9 Hz), 129.2, 129.6, 129.8, 130.6 (q, $^2J_{C,F}$ = 32.5 Hz), 134.2, 142.5 (q, $^4J_{C,F}$

= 1.3 Hz), 142.7, 143.6 ppm. MS (EI): *m/z* (%) = 507.6 (45), 505.6 (100), 503.6 (47) [M^+], 299.9 (24), 297.9 (24) [M^+ – Br, – I], 219.0 (15) [M^+ – 2Br, – I].

2′,5′-Dibromo-4-dimethylamino-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (7): Similar reaction conditions as described above for **6** have been applied for the synthesis of **7**. A solution of **6** (2.78 g, 5.50 mmol), 4-(dimethylamino)phenylboronic acid (1.36 g, 8.2 mmol), $Pd(PPh_3)_4$ (0.3172 g, 0.27 mmol), K_2CO_3 (2.2747 g, 16.5 mmol) in degassed DME/H_2O (90/30 mL) was heated to 75 °C and kept at 75 °C for 16 h under a nitrogen atmosphere. After similar work-up as described above for **6**, the residue was purified by CC (silica gel, hexane:CH_2Cl_2 = 2:1) and gave **7** as beige solid (402 mg, 15%). M.p. 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.04 (s, 6 H, CH_3), 6.81 (broad d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.37 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.56 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.60 (s, 1 H), 7.66 (s, 1 H), 7.72 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 40.6, 111.8, 121.0, 121.9, 124.3 (q, $^1J_{C,F}$ = 273.0 Hz), 125.3 (q, $^3J_{C,F}$ = 3.8 Hz), 129.9, 130.2 (q, $^2J_{C,F}$ = 32.5 Hz), 130.3, 135.2, 135.5, 140.5, 143.2 (q, $^4J_{C,F}$ = 1.5 Hz), 144.0, 150.3 ppm. $C_{21}H_{16}Br_2F_3N$ (499.16): calcd. C 50.53, H 3.23, N 2.81; found C 50.89, H 3.43, N 2.69. MS (MALDI-TOF): calcd. for $C_{21}H_{16}Br_2F_3N$ 498.9577; found: 499.4195.

4-Dimethylamino-4′′-trifluoromethyl-2′,5′-bis[2-(triisopropylsilyl)-ethynyl][1,1′:4′,1′′]terphenyl (8): To a solution of **7** (289.5 mg, 0.58 mmol), $Pd(PPh_3)_2Cl_2$ (20.3 mg, 0.029 mmol), CuI (11 mg, 0.058 mmol), (iPr)$_2$NH (10 mL) in dry and degassed THF (200 mL) (triisopropylsilyl)acetylene (0.34 mL, 1.52 mmol) was added. The reaction mixture was kept at room temperature for 16 h under a nitrogen atmosphere. After removal of the solvent by rotary evaporation the crude product was purified by CC (silica gel, hexane:CH_2Cl_2 = 1:1) to provide **8** (399.1 mg, 98%) as a white solid. M.p. 166–169 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.04 (apparent s, 21 H, TIPS), 1.10 (apparent s, 21 H, TIPS), 3.03 (s, 6 H, NCH_3), 6.82 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.60 (s, 1 H), 7.63 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.67 (s, 1 H), 7.71 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.77 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.4, 11.5, 18.6, 18.8, 40.7, 96.1, 96.4, 105.7, 106.4, 112.3, 122.0, 122.1, 124.5 (q, $^1J_{C,F}$ = 270.5 Hz), 125.1 (q, $^3J_{C,F}$ = 3.7 Hz), 127.4, 129.7 (q, $^2J_{C,F}$ = 32.2 Hz), 129.9, 130.1, 134.3, 134.5, 140.5, 143.6 (q, $^4J_{C,F}$ = 1.5 Hz), 143.8, 150.4 ppm. $C_{43}H_{58}F_3NSi_2$ (702.09): calcd. C 73.56, H 8.33, N 1.99; found C 73.70, H 8.21, N 2.09. MS (MALDI-TOF): calcd. for $C_{43}H_{58}F_3NSi_2$ 701.4054; found 701.2474.

1,4-Dibromo-2,5-bis[2-(triisopropylsilyl)ethynyl]benzene (9): Compound **9** was synthesized according to a literature procedure[18] (4.63 g, 77%). M.p. 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.13 (s, 6 H, CH), 1.14 (s, 36 H, CH_3), 7.67 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.4, 18.8, 99.9, 103.4, 123.9, 126.8, 136.7 ppm. MS (EI): *m/z* (%) = 598.2 (3.2), 596.2 (5.8), 594.2 (2.6) [M^+], 555.1 (58), 553.1 (100), 551.1 (48) [M^+ – C_3H_7].

4-Bromo-4′-trifluoromethyl-2,5-bis[2-(triisopropylsilyl)ethynyl]biphenyl (10) and 2′,5′-Bis[2-(triisopropylsilyl)ethynyl]-4,4′′-bis(trifluoromethyl)[1,1′:4′,1′′]terphenyl (11): Similar reaction conditions as described above for **6** have been applied for the synthesis of **10** and **11**. A solution of 1,4-dibromo-2,5-bis(triisopropylsilylethynyl)-benzene (**9**) (8.374 g, 14.0 mmol), 4-(trifluoromethyl)phenylboronic acid (2.6658 g, 14.0 mmol), $Pd(PPh_3)_4$ (0.8089 g, 0.7 mmol), K_2CO_3 (7.7398 g, 56 mmol) in degassed DME/H_2O (200/50 mL) was heated to 80 °C and kept for 14 h at 80 °C under a nitrogen atmosphere. After evaporation of the organic solvent, extraction with CH_2Cl_2 and again evaporation of the solvents the remaining residue was fractioned by CC (silica gel, hexane) to afford **10** (4.2622 g, 46%) as a white solid and the side product **11** (3.257 g, 32%) as a white solid.

10: M.p. 89–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.97 (s, 3 H, CH), 0.98 (s, 18 H, CH_3), 1.15 (s, 3 H, CH), 1.16 (s, 18 H, CH_3), 7.46 (s, 1 H), 7.64 (s, 4 H), 7.81 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.3, 11.4, 18.6, 18.8, 98.5, 99.0, 103.9, 104.3, 123.3, 124.3 (q, $^1J_{C,F}$ = 272.4 Hz), 124.8, 125.2 (q, $^3J_{C,F}$ = 3.9 Hz), 125.9, 129.7, 130.1 (q, $^2J_{C,F}$ = 32.4 Hz), 134.0, 136.8, 141.9, 142.7 (q, $^4J_{C,F}$ = 1.7 Hz) ppm. $C_{35}H_{48}BrF_3Si_2$ (661.83): calcd. C 63.52, H 7.31; found C 63.75, H 7.65. MS (EI): *m/z* (%) = 662.3 (6) [M^+], 660.3 (5) [M^+], 619.2 (100) [M^+ – C_3H_7], 617.3 (87) [M^+ – C_3H_7].

11: M.p. 215–218 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.98 (s, 6 H, CH), 0.99 (s, 36 H, CH_3), 7.59 (s, 2 H), 7.68 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.72 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.3, 18.6, 97.6, 105.0, 122.4, 124.4 (q, $^3J_{C,F}$ = 270.4 Hz), 125.2 (q, $^3J_{C,F}$ = 3.7 Hz), 129.8, 130.0 (q, $^3J_{C,F}$ = 32.7 Hz), 134.2, 142.4, 143.1 (q, $^4J_{C,F}$ = 1.6 Hz) ppm. MS (EI): *m/z* (%) = 726.3 (6) [M^+], 683.3 (100) [M^+ – C_3H_7].

[2-(4-Bromo-6-ethynyl-4′-(trifluoromethyl)biphenyl-3-yl)ethynyl]triisopropylsilane (12) and [2-(4-Bromo-5-ethynyl-4′-(trifluoromethyl)-biphenyl-2-yl)ethynyl]triisopropylsilane (13): To a solution of **10** (1.7949 g, 2.71 mmol) in degassed THF (200 mL) with some drops of acetic acid a solution of TBAF (2 mL, 1 M TBAF in THF) was added. The reaction mixture was stirred at room temperature for 16 h. After filtration through silica gel (hexane) all solvents were removed. The residue was separated by CC (silica gel, hexane) to afford **12** (397 mg, 29%) and **13** (288 mg, 21%) both as brown oils.

12: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.98 (s, 3 H, CH), 0.99 (s, 18 H, CH_3), 3.48 (s, 1 H), 7.49 (s, 1 H), 7.60–7.70 (m, 4 H), 7.82 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.3, 18.6, 81.5, 83.8, 98.9, 103.7, 122.5, 124.1, 124.3 (q, $^1J_{C,F}$ = 272.4 Hz), 124.6, 125.3 (q, $^3J_{C,F}$ = 3.7 Hz), 129.7, 129.8 (q, $^2J_{C,F}$ = 32.6 Hz), 134.3, 137.0, 142.0, 142.5 (q, $^4J_{C,F}$ = 1.6 Hz) ppm. MS (EI): *m/z* (%) = 506.0 (11), 504.0 (10) [M^+], 462.8 (100), 460.8 (84) [M^+ – C_3H_7].

13: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.17 (apparent s, 21 H, TIPS), 3.17 (s, 1 H), 7.49 (s, 1 H), 7.64–7.74 (m, 4 H), 7.85 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.4, 18.8, 81.0, 83.4, 99.4, 104.1, 121.6, 124.3 (q, $^3J_{C,F}$ = 3.7 Hz), 124.9, 125.3 (q, $^1J_{C,F}$ = 273.2 Hz), 126.6, 129.6, 130.3 (q, $^2J_{C,F}$ = 32.2 Hz), 134.3, 137.3, 141.8, 142.2 (q, $^4J_{C,F}$ = 1.6 Hz) ppm. MS (EI): *m/z* (%) = (%) 506.0 (3.2), 504.0 (3.0) [M^+], 462.9 (100), 460.9 (95) [M^+ – C_3H_7].

[2-(4-Bromo-5-(2-phenylethynyl)-4′-(trifluoromethyl)biphenyl-2-yl)-ethynyl]triisopropylsilane (14): A similar reaction protocol as described above for **8** has been applied for the synthesis of **14**. A solution of iodobenzene (0.593 mmol, 0.07 mL), **12** (200 mg, 0.396 mmol), $Pd(PPh_3)_4$ (22.9 mg, 0.022 mmol), CuI (7.5 mg, 0.039 mmol) and (iPr)$_2$NH (3 mL) in degassed THF (50 mL) was stirred for 16 h at room temperature. The solvents were removed and the residue was purified by CC (silica gel, hexane) to get **14** as an colorless oil (197.6 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.99 (s, 3 H, CH), 1.00 (s, 18 H, CH_3), 7.35–7.41 (m, 3 H), 7.53 (s, 1 H), 7.56–7.61 (m, 2 H), 7.66 (s, 4 H), 7.85 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.3, 18.6, 87.8, 96.2, 98.5, 104.0, 122.7, 123.3, 124.3 (q, $^1J_{C,F}$ = 270 Hz), 124.6, 125.2 (q, $^3J_{C,F}$ = 3.7 Hz), 125.8, 128.6, 129.1, 129.7, 130.1 (q, $^2J_{C,F}$ = 32.5 Hz), 131.9, 133.4, 136.9, 142.0, 142.6 (q, $^4J_{C,F}$ = 1.1 Hz) ppm. $C_{32}H_{32}BrF_3Si$ (581.58): calcd. C 66.09, H 5.55; found C 66.13, H

5.78. MS (MALDI-TOF): calcd. for $C_{32}H_{32}BrF_3Si$ 582.1388; found 580.3855.

[2-(4-Bromo-6-(2-phenylethynyl)-4′-(trifluoromethyl)biphenyl-3-yl)-ethynyl]triisopropylsilane (15): A similar reaction protocol as described above for **8** has been applied for the synthesis of **15**. A solution of iodobenzene (0.445 mmol, 0.05 mL), **13** (150 mg, 0.297 mmol), $Pd(PPh_3)_4$ (17.2 mg, 0.015 mmol), CuI (5.7 mg, 0.03 mmol) and $(i\text{Pr})_2NH$ (3 mL) in degassed THF (50 mL) was stirred for 16 h at room temperature. The solvents were removed and the residue was purified by CC (silica gel, hexane) to afford **15** as a white solid (151.2 mg, 86%). M.p. 112–114 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.21 (apparent s, 21 H, TIPS), 7.28–7.39 (m, 5 H), 7.56 (s, 1 H), 7.76 (s, 4 H), 7.91 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.5, 18.8, 87.3, 95.6, 99.0, 104.4, 123.0, 124.2 (q, $^1J_{C,F}$ = 271.3 Hz), 125.0, 125.2 (q, $^3J_{C,F}$ = 3.6 Hz), 125.7, 126.1, 128.6, 129.0, 129.7, 130.2 (q, $^2J_{C,F}$ = 32.6 Hz), 131.6, 134.2, 136.3, 141.2, 142.6 (q, $^4J_{C,F}$ = 1.5 Hz) ppm. $C_{32}H_{32}BrF_3Si$ (581.58): calcd. C 66.09, H 5.55; found C 66.17, H 5.64. MS (MALDI-TOF): calcd. for $C_{32}H_{32}BrF_3Si$ 582.1388; found 580.4558.

4-Dimethylamino-2′-(2-phenylethynyl)-4′′-trifluoromethyl-5′-[2-(triisopropylsilanyl)ethynyl][1,1′:4′,1′′]terphenyl (16): A similar synthetic protocol as described for the synthesis of **6** has been applied for the synthesis of **16**. A solution of **14** (228 mg, 0.392 mmol), 4-(dimethylamino)phenylboronic acid (91 mg, 0.549 mmol), $Pd(PPh_3)_4$ (22.6 mg, 0.019 mmol), K_2CO_3 (217 mg, 1.57 mmol) in degassed DME/H_2O (30/10 mL) was heated to 70 °C and kept at 70 °C for 16 h under a nitrogen atmosphere. After work-up, the residue was purified by CC (silica gel, hexane:CH_2Cl_2 = 2:1) to afford **16** as brownish oil (206 mg, 84%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.07 (apparent s, 21 H, TIPS), 3.07 (s, 6 H, NCH_3), 6.89 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.28–7.32 (m, 4 H), 7.42–7.49 (m, 2 H), 7.64–7.75 (m, 6 H), 7.79 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.3, 18.6, 40.6, 89.6, 93.9, 96.4, 105.7, 112.0, 121.5, 122.1, 123.5, 124.5 (q, $^1J_{C,F}$ = 270 Hz), 125.0 (q, $^3J_{C,F}$ = 3.8 Hz), 127.1, 128.4, 129.8, 129.9 (q, $^2J_{C,F}$ = 32.6 Hz), 130.2, 131.6, 133.8, 134.4, 140.5, 143.2, 143.5 (q, $^4J_{C,F}$ = 1.2 Hz), 150.4 ppm. $C_{40}H_{42}F_3NSi$ (621.85): calcd. C 77.26, H 6.81, N 2.25; found C 77.32, H 6.73, N 1.98. MS (MALDI-TOF): calcd. for $C_{40}H_{42}F_3NSi$ 621.3033; found 620.6691.

4-Dimethylamino-5′-(2-phenylethynyl)-4′′-trifluoromethyl-2′-[2-(triisopropylsilanyl)ethynyl][1,1′:4′,1′′]terphenyl (17): A similar synthetic protocol as described for the synthesis of **6** has been applied for the synthesis of **17**. A solution of **15** (140 mg, 0.241 mmol), 4-(dimethylamino)phenylboronic acid (47.7 mg, 0.289 mmol), $Pd(PPh_3)_4$ (13.9 mg, 0.012 mmol), K_2CO_3 (133.2 mg, 0.964 mmol) in degassed DME/H_2O (30/10 mL) was heated to 80 °C and kept at 80 °C for 16 h under a nitrogen atmosphere. After evaporation of the organic solvent, extraction with CH_2Cl_2, drying over $MgSO_4$ followed by evaporation of the solvents the remaining residue was fractioned by CC (silica gel, hexane:CH_2Cl_2 = 2:1) to afford **17** as brownish solid (98.5 mg, 66%). M.p. 93–96 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.04 (apparent s, 21 H, TIPS), 3.02 (s, 6 H, NCH_3), 6.82 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.30 (s, 5 H), 7.57–7.65 (m, 3 H), 7.67 (s, 1 H), 7.73 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.81 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.5, 18.8, 40.7, 88.9, 94.1, 96.1, 106.5, 112.3, 121.7, 121.9, 123.1, 124.40 (q, $^1J_{C,F}$ = 272.0 Hz), 125.0 (q, $^3J_{C,F}$ = 3.6 Hz), 127.2, 128.5, 128.6, 129.7 (q, $^2J_{C,F}$ = 32.0 Hz), 129.8, 130.1, 131.5, 133.7, 134.8, 139.7, 143.4 (q, $^4J_{C,F}$ = 1.5 Hz), 143.7, 150.3 ppm. $C_{40}H_{42}F_3NSi$ (621.85): calcd. C 77.26, H 6.81, N 2.25; found C 77.47, H 6.64, N 2.10. MS (MALDI-TOF): calcd. for $C_{40}H_{42}F_3NSi$ 621.3033; found 620.6773.

4-Dimethylamino-5′-ethynyl-2′-(2-phenylethynyl)-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (18): To a solution of **18** (181 mg, 0.29 mmol) in degassed THF (30 mL) a solution of TBAF (0.1 mL, 1 M TBAF in THF) was added. The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvents the residue was purified by CC (silica gel, hexane:CH_2Cl_2 = 2:1) to provide **18** as yellowish solid (131 mg, 97%). M.p. 64–66 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.06 (s, 6 H, NCH_3), 3.18 (s, 1 H), 6.86 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.31–7.37 (m, 3 H), 7.43–7.49 (m, 2 H), 7.65–7.82 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 40.6, 82.0, 82.7, 89.5, 94.1, 111.9, 120.4, 122.1, 123.4, 124.4 (q, $^1J_{C,F}$ = 270.6 Hz), 125.1 (q, $^3J_{C,F}$ = 3.7 Hz), 126.8, 128.4, 128.5, 129.7, 129.7 (q, $^2J_{C,F}$ = 32.5 Hz), 130.2, 131.6, 134.2, 134.7, 140.3, 143.0 (q, $^4J_{C,F}$ = 1.5 Hz), 143.2, 150.4 ppm. $C_{31}H_{22}F_3N$ (465.51): calcd. C 79.98, H 4.76, N 3.01; found C 80.17, H 4.89, N 2.89. MS (MALDI-TOF): calcd. for $C_{31}H_{22}F_3N$ 465.1699; found 464.8913.

4-Dimethylamino-2′-ethynyl-5′-(2-phenylethynyl)-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (19): To a solution of **17** (81 mg, 0.13 mmol) in degassed THF (20 mL) a solution of TBAF (0.5 mL, 1 M TBAF in THF) was added. The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvents the residue was purified by CC (silica gel, hexane:CH_2Cl_2 = 2:1) to afford **19** as yellowish solid (57 mg, 94%). M.p. 189–192 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.05 (s, 6 H, NCH_3), 3.22 (s, 1 H), 6.83 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.34 (s, 5 H), 7.61 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.67 (s, 1 H), 7.71 (s, 1 H), 7.75 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.83 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 40.5, 81.8, 83.3, 88.7, 94.3, 111.9, 120.4, 122.3, 123.0, 124.4 (q, $^1J_{C,F}$ = 272.0 Hz), 125.1 (q, $^3J_{C,F}$ = 3.9 Hz), 126.6, 128.5, 128.7, 129.6, 129.6 (q, $^2J_{C,F}$ = 32.2 Hz), 130.1, 131.5, 133.9, 135.0, 139.7, 143.2 (q, $^4J_{C,F}$ = 1.7 Hz), 144.0, 150.3 ppm. $C_{31}H_{22}F_3N$ (465.51): calcd. C 79.98, H 4.76, N 3.01; found C 79.66, H 4.80, N 2.97. MS (MALDI-TOF): calcd. for $C_{31}H_{22}F_3N$ 465.1699; found 464.6519.

5′-[2-(4-Acetylsulfanylphenyl)ethynyl]-4-dimethylamino-2′-(2-phenylethynyl)-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (1): For the synthesis of **1** a similar Sonogashira coupling protocol as described for **8** has been applied. A solution of *S*-(4-iodophenyl) thioacetate (101 mg, 0.36 mmol), **18** (130 mg, 0.28 mmol), $Pd(PPh_3)_4$ (16.2 mg, 0.014 mmol), CuI (5.3 mg, 0.028 mmol) and $(i\text{Pr})_2NEt$ (2 mL) in degassed THF (50 mL) was stirred for 16 h at room temperature. After removing of the solvents the residue was absorbed on silica gel to charge a column. CC (silica gel, hexane:CH_2Cl_2 = 1:1) afforded **1** (137.5 g, 80%) as yellow solid. M.p. 187–189 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 H, CH_3), 3.05 (s, 6 H, NCH_3), 6.86 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.30–7.48 (m, 9 H), 7.67–7.78 (m, 6 H), 7.83 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 30.4, 40.7, 89.6, 90.6, 93.3, 94.1, 112.0, 121.3, 121.8, 123.4, 124.3, 124.4 (q, $^1J_{C,F}$ = 270.3 Hz), 125.0 (q, $^3J_{C,F}$ = 3.6 Hz), 126.9, 128.4, 128.5, 129.7 (q, $^2J_{C,F}$ = 32.5 Hz), 129.8, 130.2, 131.6, 132.0, 133.8, 134.1, 134.3, 139.8, 143.2 (q, $^4J_{C,F}$ = 1.6 Hz), 143.3, 150.3, 193.5 ppm. $C_{39}H_{28}F_3NOS$ (615.71): calcd. C 76.08, H 4.58, N 2.27; found C 76.35, H 4.69, N 2.18. MS (MALDI-TOF): calcd. for $C_{39}H_{28}F_3NOS$ 615.1838; found 614.6310.

2′-[2-(4-Acetylsulfanylphenyl)ethynyl]-4-dimethylamino-5′-(2-phenylethynyl)-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (2): For the synthesis of **2** a similar Sonogashira coupling protocol as described for **8** has been applied. A solution of *S*-(4-iodophenyl) thioacetate (46.6 mg, 0.168 mmol), **19** (50 mg, 0.107 mmol), $Pd(PPh_3)_4$ (7.5 mg, 0.0065 mmol), CuI (2.5 mg, 0.013 mmol) and $(i\text{Pr})_2NEt$ (2 mL) in

degassed THF (25 mL) was stirred for 16 h at room temperature. After removing of the solvents the residue was absorbed on silica gel to charge a column. CC (silica gel, hexane:CH_2Cl_2 = 1:1) afforded **2** (54.7 mg, 83%) as yellow solid. M.p. 214–215 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 H, CH_3), 3.05 (s, 6 H, NCH_3), 6.86 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.32 (s, 5 H), 7.36 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.44 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.64–7.77 (m, 6 H), 7.84 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 30.4, 40.7, 88.9, 91.4, 93.1, 94.3, 112.0, 121.1, 122.0, 123.0, 124.4 (q, $^1J_{C,F}$ = 272.0 Hz), 124.7, 125.1 (q, $^3J_{C,F}$ = 3.9 Hz), 126.9, 128.1, 128.5, 128.7, 129.75 (q, $^2J_{C,F}$ = 32.7 Hz), 129.8, 130.2, 131.5, 132.2, 133.8, 134.1, 134.3, 139.8, 143.3, 143.5, 150.3, 193.7 ppm. $C_{39}H_{28}F_3NOS$ (615.71): calcd. C 76.08, H 4.58, N 2.27; found C 75.98, H 4.48, N 2.14. MS (MALDI-TOF): calcd. for $C_{39}H_{28}F_3NOS$ 615.1838; found 614.5119.

Biphenyl Derivative 20: For the synthesis of **20** a similar Sonogashira coupling protocol as described for **8** has been applied. A solution of 2,5-diethyl-4-iodotolane (0.591 mmol, 212.8 mg), **12** (248.9 mg, 0.492 mmol), $Pd(PPh_3)_4$ (28.4 mg, 0.0246 mmol), CuI (9.4 mg, 0.0494 mmol) and $(i\text{Pr})_2$NH (5 mL) in degassed THF (50 mL) was stirred for 16 h at room temperature. After evaporation of the solvents, the residue was purified by CC (silica gel, hexane) to get **20** as colorless oil that solidifies into white solid upon standing (261.4 mg, 72%). M.p. 106–108 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.11 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 1.22 (apparent s, 21 H, TIPS), 1.32 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 2.52 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.86 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 7.19 (s, 1 H), 7.34–7.42 (m, 4 H), 7.53–7.59 (m, 3 H), 7.71–7.78 (m, 4 H), 7.93 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.5, 14.6, 14.7, 18.8, 26.9, 27.2, 88.2, 91.7, 94.6, 94.8, 99.1, 104.4, 121.6, 123.35, 123.40, 123.42, 124.3 (q, $^1J_{C,F}$ = 271.8 Hz), 125.0, 125.3 (q, $^3J_{C,F}$ = 3.6 Hz), 125.7, 128.5, 129.7, 130.2 (q, $^2J_{C,F}$ = 32.7 Hz), 131.58, 131.64, 131.8, 134.2, 136.3, 141.2, 142.9 (q, $^4J_{C,F}$ = 1.1 Hz), 143.53, 143.54 ppm. $C_{44}H_{44}BrF_3Si$ (737.80): calcd. C 71.63, H 6.01; found C 71.97, H 6.22. MS (MALDI-TOF): calcd. for $C_{44}H_{44}BrF_3Si$ 738.2332; found 736.4347.

Biphenyl Derivative 21: For the synthesis of **21** a similar Sonogashira coupling protocol as described for **8** has been applied. A solution of 2,5-diethyl-4-iodotolane (0.805 mmol, 289.9 mg), **13** (312.9 mg, 0.619 mmol), $Pd(PPh_3)_4$ (35.8 mg, 0.031 mmol), CuI (11.8 mg, 0.062 mmol) and $(i\text{Pr})_2$NH (3 mL) in degassed THF (50 mL) was stirred for 16 h at room temperature. After evaporation of the solvents, the residue was purified by CC (silica gel, hexane) to afford **21** as yellowish solid (410.3 mg, 90%). M.p. 126–128 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.06 (apparent s, 21 H, TIPS), 1.37 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, CH_3), 2.86–3.04 (m, 4 H, CH_2), 7.35–7.42 (m, 3 H), 7.48 (d, $^3J_{H,H}$ = 6.3 Hz, 2 H), 7.54–7.62 (m, 3 H), 7.71 (s, 4 H), 7.91 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.3, 14.8, 15.2, 18.6, 27.4, 27.4, 88.3, 92.2, 94.7, 95.1, 98.5, 104.0, 121.8, 123.2, 123.5, 124.30 (q, $^1J_{C,F}$ = 271.9 Hz), 124.31, 125.2 (q, $^3J_{C,F}$ = 3.7 Hz), 126.0, 128.51, 128.52, 129.7, 130.1 (q, $^2J_{C,F}$ = 32.3 Hz), 131.6, 131.8, 132.0, 133.5, 137.0, 142.0, 142.6, 143.6, 144.1 ppm. $C_{44}H_{44}BrF_3Si$ (737.80): calcd. C 71.63, H 6.01; found C 71.89, H 6.19. MS (MALDI-TOF): calcd. for $C_{44}H_{44}BrF_3Si$ 738.2332; found 736.4537.

2′-[2-(2,5-Diethyl-4-(2-phenylethynyl)phenyl)ethynyl]-4-dimethylamino-4′′-trifluoromethyl-5′-[2-(triisopropylsilanyl)ethynyl]-[1,1′:4′,1′′]terphenyl (22): For the synthesis of **22** a similar Suzuki coupling protocol as described for **6** has been applied. A solution of **20** (230.9 mg, 0.313 mmol), 4-(dimethylamino)phenylboronic acid (72.3 mg, 0.438 mmol), $Pd(PPh_3)_4$ (18.1 mg, 0.0157 mmol) and K_2CO_3 (172.9 mg, 1.25 mmol) in degassed DME/H_2O (30/10 mL) was heated to 80 °C and kept at 80 °C for 16 h under a nitrogen atmosphere. After evaporation of the organic solvent, extraction with CH_2Cl_2, drying over $MgSO_4$ followed by evaporation of the solvents the remaining residue was charged on a column. CC (silica gel, hexane:CH_2Cl_2 = 1:1) afforded **22** as brown oil that solidifies upon standing (210.7 mg, 86%). M.p. 94–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.05–1.17 (m, 24 H), 1.33 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 2.57 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.87 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 3.05 (s, 6 H, NCH_3), 6.84 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.23 (s, 1 H), 7.34–7.43 (m, 4 H), 7.55–7.60 (m, 2 H), 7.65 (s, 1 H), 7.68 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.75 (s, 1 H), 7.78 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.83 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.5, 14.6, 14.7, 18.8, 26.9, 27.2, 40.7, 88.3, 93.2, 93.4, 94.5, 96.2, 106.5, 112.3, 121.9, 122.1, 122.3, 122.9, 123.5, 124.5 (q, $^1J_{C,F}$ = 271.9 Hz), 125.2 (q, $^3J_{C,F}$ = 3.7 Hz), 127.3, 128.4, 128.5, 129.8 (q, $^2J_{C,F}$ = 32.3 Hz), 129.9, 130.2, 131.58, 131.64, 131.8, 133.7, 134.8, 139.8, 143.4, 143.5, 143.8 (q, $^4J_{C,F}$ = 1.1 Hz), 143.9, 150.4 ppm. $C_{52}H_{54}F_3NSi$ (778.07): calcd. C 80.27, H 7.00, N 1.80; found C 80.77, H 6.89, N 1.78. MS (MALDI-TOF): calcd. for $C_{52}H_{54}F_3NSi$ 777.3972; found 776.6136.

5′-[2-(2,5-Diethyl-4-(2-phenylethynyl)phenyl)ethynyl]-4-dimethylamino-4′′-trifluoromethyl-2′-[2-(triisopropylsilanyl)ethynyl][1,1′:4′,-1′′]terphenyl (23): For the synthesis of **23** a similar Suzuki coupling protocol as described for **6** has been applied. A solution of **21** (410 mg, 0.556 mmol), 4-(dimethylamino)phenylboronic acid (128.4 mg, 0.778 mmol), $Pd(PPh_3)_4$ (32.1 mg, 0.028 mmol) and K_2CO_3 (307 mg, 2.22 mmol) in degassed DME/H_2O (30/10 mL) was heated to 80 °C and kept at 80 °C for 16 h under a nitrogen atmosphere. After evaporation of the organic solvent, extraction with CH_2Cl_2, drying over $MgSO_4$ followed by evaporation of the solvents the remaining residue was charged on a column. CC (silica gel, hexane:CH_2Cl_2 = 1:1) afforded **23** as yellow solid (350 mg, 81%). M.p. 187–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.03 (s, 3 H, CH), 1.4 (s, 18 H, CH_3), 1.20 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.32 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 2.69 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.86 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 3.06 (s, 6 H), 6.87 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 7.32 (s, 1 H), 7.33–7.42 (m, 4 H), 7.53–7.59 (m, 2 H), 7.62–7.74 (m, 6 H), 7.79 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 11.4, 14.7, 14.8, 18.6, 27.0, 27.2, 40.7, 88.4, 92.9, 94.1, 94.4, 96.6, 105.7, 112.1, 121.99, 122.04, 122.7, 123.5, 124.5 (q, $^1J_{C,F}$ = 271.8 Hz), 125.1 (q, $^3J_{C,F}$ = 3.7 Hz), 127.4, 128.4, 128.5, 129.6 (q, $^2J_{C,F}$ = 32.2 Hz), 129.8, 130.2, 131.5, 131.6, 131.9, 133.7, 134.5, 140.6, 143.33, 143.35, 143.5, 150.4 ppm. $C_{52}H_{54}F_3NSi$ (778.07): calcd. C 80.27, H 7.00, N 1.80; found C 79.90, H 6.93, N 1.99. MS (MALDI-TOF): calcd. for $C_{52}H_{54}F_3NSi$ 777.3972; found 776.6738.

2′-[2-(2,5-Diethyl-4-(2-phenylethynyl)phenyl)ethynyl]-4-dimethylamino-5′-ethynyl-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (24): To a solution of **22** (210.7 mg, 0.271 mmol) in degassed THF (50 mL) a solution of TBAF (0.3 mL, 1 M TBAF in THF) was added. The reaction mixture was stirred at room temperature for 30 min. After evaporation of the solvents, the residue was purified by CC (silica gel, hexane:CH_2Cl_2 = 1:1) to provide **24** as whitish solid (152.4 mg, 90%). M.p. 160–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.14 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 1.33 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 2.58 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 2.87 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 3.06 (s, 6 H, NCH_3), 3.25 (s, 1 H), 6.86 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.24 (s, 1 H), 7.33–7.45 (m, 4 H), 7.54–7.69 (m, 5 H), 7.73–7.83 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.6, 14.7, 26.9, 27.2, 40.5, 81.8, 83.3, 88.7, 93.1, 93.3, 94.5, 111.9, 120.3, 122.1, 122.6, 123.0, 123.5, 124.4 (q, $^1J_{C,F}$ = 271.0 Hz), 125.1 (q, $^3J_{C,F}$ = 3.6 Hz), 126.6, 128.4, 128, 5, 129.81, 129.82 (q, $^2J_{C,F}$ = 32.3 Hz), 130.1, 131.58, 131.63, 131.8, 133.9, 134.9, 139.8, 143.47,

143.49, 144.1, 150.3 ppm. $C_{43}H_{34}F_3N$ (621.73): calcd. C 83.07, H 5.51, N 2.25; found C 83.37, H 5.32, N 2.01. MS (MALDI-TOF): calcd. for $C_{43}H_{34}F_3N$ 621.2638; found 620.6378.

5′-[2-(2,5-Diethyl-4-(2-phenylethynyl)phenyl)ethynyl]-4-dimethylamino-2′-ethynyl-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (25): To a solution of **23** (310 mg, 0.398 mmol) in degassed THF (50 mL) a solution of TBAF (0.5 mL, 1 M TBAF in THF) was added. The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvents the residue was purified by CC (silica gel, hexane:CH_2Cl_2 = 1:1) to get **25** as yellowish solid (238.9 mg, 96%). M.p. 170–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.20 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.35 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 2.70 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.86 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 3.06 (s, 6 H, NCH_3), 3.18 (s, 1 H), 6.86 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 7.32 (s, 1 H), 7.34–7.42 (m, 4 H), 7.52–7.59 (m, 2 H), 7.61–7.68 (m, 3 H), 7.70–7.77 (m, 3 H), 7.80 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.7, 14.8, 27.0, 27.2, 40.6, 82.1, 82.6, 88.3, 93.1, 93.9, 94.4, 112.1, 120.4, 122.6, 122.8, 123.5, 124.4 (q, $^1J_{C,F}$ = 271.9 Hz), 125.2 (q, $^3J_{C,F}$ = 3.6 Hz), 127.1, 128.4, 128.5, 129.7, 129.8 (q, $^2J_{C,F}$ = 32.0 Hz), 130.2, 131.5, 131.6, 131.9, 134.1, 134.8, 140.5, 143.0, 143.3, 143.4, 143.5, 150.4 ppm. $C_{43}H_{34}F_3N$ (621.73): calcd. C 83.07, H 5.51, N 2.25; found C 82.70, H 5.57, N 2.34. MS (MALDI-TOF): calcd. for $C_{43}H_{34}F_3N$ 621.2638; found 621.6614.

5′-[2-(4-Acetylsulfanylphenyl)ethynyl]-2′-[2-(2,5-diethyl-4-(2-phenylethynyl)phenyl)ethynyl]-4-dimethylamino-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (3): For the synthesis of **3** a similar Sonogashira coupling protocol as described for **8** has been applied. A solution of *S*-(4-iodophenyl) thioacetate (84.3 mg, 0.303 mmol), **24** (145 mg, 0.23 mmol), $Pd(PPh_3)_4$ (13.3 mg, 0.0115 mmol), CuI (4.4 mg, 0.0231 mmol) and $(i\text{Pr})_2$NEt (2 mL) in degassed THF (25 mL) was stirred for 16 h at room temperature. By evaporation of the solvents the residue was absorbed on silica gel to charge a column. CC (silica gel, hexane:CH_2Cl_2 = 1:1) afforded **3** (77.5 mg, 44%) as yellow solid. M.p. 210–212 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.11 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.30 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 2.55 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.84 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 3.07 (s, 6 H, NCH_3), 6.87 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.21 (s, 1 H), 7.30–7.41 (m, 6 H), 7.46 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.51–7.58 (m, 2 H), 7.65–7.78 (m, 6 H), 7.81 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.6, 14.7, 26.9, 27.2, 30.4, 40.6, 88.3, 91.4, 93.2, 93.3, 93.4, 94.5, 112.0, 121.1, 122.2, 122.4, 123.0, 123.5, 124.4 (q, $^1J_{C,F}$ = 271.9 Hz), 124.7, 125.2 (q, $^3J_{C,F}$ = 3.9 Hz), 126.9, 128.2, 128.4, 128.5, 129.80 (q, $^2J_{C,F}$ = 32.2 Hz), 129.83, 130.2, 131.57, 131.63, 131.8, 132.1, 133.8, 134.1, 134.3, 135.1, 139.9, 143.46, 143.49, 143.6, 150.4, 193.7 ppm. $C_{51}H_{40}F_3NOS$ (771.93): calcd. C 79.35, H 5.22, N 1.81; found C 79.66, H 5.66, N 1.93. MS (MALDI-TOF): calcd. for $C_{51}H_{40}F_3NOS$ 771.2777; found 770.5919.

2′-[2-(4-Acetylsulfanylphenyl)ethynyl]-5′-[2-(2,5-diethyl-4-(2-phenylethynyl)phenyl)ethynyl]-4-dimethylamino-4′′-trifluoromethyl[1,1′:4′,1′′]terphenyl (4): For the synthesis of **4** a similar Sonogashira coupling protocol as described for **8** has been applied. A solution of *S*-(4-iodophenyl) thioacetate (144.1 mg, 0.518 mmol), **25** (230 mg, 0.37 mmol), $Pd(PPh_3)_4$ (21.4 mg, 0.0185 mmol), CuI (7.1 mg, 0.0373 mmol) and $(i\text{Pr})_2$NEt (2 mL) in degassed THF (100 mL) was stirred for 16 h at room temperature. By evaporation of the solvents the residue was absorbed on silica gel to charge a column. CC (silica gel, hexane:CH_2Cl_2 = 1:1) afforded **4** (177 mg, 62%) as yellow solid. M.p. 179–182 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.22 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 1.33 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.72 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.87 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 3.06 (s, 6 H, NCH_3), 6.86 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 7.33 (s, 1 H), 7.34–7.42 (m, 8 H), 7.55–7.60 (m, 2 H), 7.68 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 7.71 (s, 1 H), 7.74–7.81 (m, 3 H), 7.84 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.7, 14.8, 27.0, 27.2, 30.4, 40.6, 88.3, 90.6, 93.1, 93.3, 94.2, 94.4, 112.0, 121.2, 122.2, 122.6, 122.7, 123.5, 124.3, 124.4 (q, $^1J_{C,F}$ = 272.1 Hz), 125.1 (q, $^3J_{C,F}$ = 3.9 Hz), 127.1, 128.4, 128.5, 129.77, 129.76 (q, $^2J_{C,F}$ = 32.3 Hz), 130.1, 131.5, 131.6, 131.8, 132.0, 133.9, 134.1, 134.3, 140.0, 143.28, 143.32, 143.4, 143.5, 150.3, 193.7 ppm. $C_{51}H_{40}F_3NOS$ (771.93): calcd. C 79.35, H 5.22, N 1.81; found C 78.99, H 4.91, N 1.99. MS (MALDI-TOF): calcd. for $C_{51}H_{40}F_3NOS$ 771.2777; found 770.6451.

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[1] Reviews on molecular electronics: a) A. Nitzan, M. A. Ratner, *Science* **2003**, *300*, 1384–1389; b) G. Maruccio, R. Cingolani, R. Rinaldi, *J. Mater. Chem.* **2004**, *14*, 542–554; c) R. A. Wassel, C. B. Gorman, *Angew. Chem. Int. Ed.* **2004**, *43*, 5120–5123; d) D. K. James, J. M. Tour, *Chem. Mater.* **2004**, *16*, 4423–4435.

[2] a) Z. K. Keane, J. W. Ciszek, J. M. Tour, D. Natelson, *Nano Lett.* **2006**, *6*, 1518–1521; b) R. Beckman, K. Beverly, A. Boukai, Y. Bunimovich, J. W. Choi, E. DeIonno, J. Green, E. Johnston-Halperin, Y. Luo, B. Sheriff, J. F. Stoddart, J. R. Heath, *J. Chem. Soc., Faraday Trans.* **2006**, *131*, 9–21; c) D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402.

[3] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, *286*, 1550–1552.

[4] Examples are: a) M. Galperin, M. A. Ratner, A. Nitzan, *Nano Lett.* **2005**, *5*, 125–130; b) F. Zahid, M. Paulsson, E. Polizzi, A. W. Ghosh, L. Siddiqui, S. Datta, *J. Chem. Phys.* **2005**, *123*, 064707; c) H. Dalgleish, G. Kirczenow, *Phys. Rev. B* **2006**, *73*, 245431; d) I. Cacelli, A. Ferretti, M. Girlanda, M. Macucci, *Chem. Phys.* **2006**, *320*, 84–94; e) R.-R. Fan, R. Y. Lai, J. Cornil, Y. Karzazi, J.-L. Bredas, L. Cai, L. Cheng, Y. Yao, D. W. Price, S. M. Shawn, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2004**, *126*, 2568–2573; f) Y. Karzazi, J. Cornil, J. L. Bredas, *Nanotechnology* **2003**, *14*, 165–171; g) J. Taylor, M. Brandbyge, K. Stokbro, *Phys. Rev. B* **2003**, *68*, 121101; h) J. M. Seminario, A. G. Zacarias, P. A. Derosa, *J. Chem. Phys.* **2002**, *116*, 1671–1683; i) E. G. Emberly, G. Kirczenow, *Phys. Rev. B* **2001**, *64*, 125318/1–125318/5; j) J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.* **2000**, *122*, 3015–3020.

[5] A. Błaszczyk, M. Chadim, C. von Hänisch, M. Mayor, *Eur. J. Org. Chem.* **2006**, 3809–3825.

[6] a) J. Chen, W. Wang, M. A. Reed, A. M. Rawlett, D. W. Price, J. M. Tour, *Appl. Phys. Lett.* **2000**, *77*, 1224–1226; b) J. M. Tour, A. M. R. M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C.-W. Zhou, J. Chen, W. Wang, I. Campbell, *Chem. Eur. J.* **2001**, *7*, 5118–5134; c) J. Chen, W. Wang, J. Klemic, M. A. Reed, B. W. Axelrod, D. M. Kaschak, A. M. Rawlett, D. W. Price, S. M. Dirk, J. M. Tour, D. S. Grubisha, D. W. Bennett, *Ann. N. Y. Acad. Sci.* **2002**, *960*, 69–99.

[7] a) P. A. Lewis, C. E. Inman, Y. Yao, J. M. Tour, J. E. Hutchison, P. S. Weiss, *J. Am. Chem. Soc.* **2004**, *126*, 12214–12215; b) P. A. Lewis, C. E. Inman, F. Maya, J. M. Tour, J. E. Hutchison, P. S. Weiss, *J. Am. Chem. Soc.* **2005**, *127*, 17421–17426.

[8] J. E. Klare, G. S. Tulevski, K. Sugo, A. de Picciotto, K. A. White, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 6030–6031.

[9] a) H. Kang, P. Zhu, Y. Yang, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 15974–15975; b) H. Kang, G. Evmenenko, P. Dutta, K. Clays, K. Song, T. J. Marks, *J. Am. Chem. Soc.* **2006**, *128*, 6194–6205.
[10] J. N. Wilson, M. Josowicz, Y. Wang, U. H. F. Bunz, *Chem. Commun.* **2003**, 2962–2963.
[11] J. N. Wilson, U. H. F. Bunz, *J. Am. Chem. Soc.* **2005**, *127*, 4124–4125.
[12] W. W. Gerhardt, A. J. Zucchero, J. N. Wilson, C. R. South, U. H. F. Bunz, M. Weck, *Chem. Commun.* **2006**, 2141–2143.
[13] a) M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578–4593; b) M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Org. Chem.* **1998**, *63*, 1676–1686.
[14] M. B. Goldfinger, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *116*, 7895–7896.
[15] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467–4470.
[16] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513–515.
[17] H. Hart, K. Harada, C. F. Du, *J. Org. Chem.* **1985**, *50*, 3104–3110.
[18] J. D. Tovar, T. M. Swager, *J. Organomet. Chem.* **2002**, *653*, 215–222.
[19] **17** ($C_{40}H_{42}F_3NSi$): a = 1616.0(3), b = 2022.0(4), c = 2230.2(5) pm, α = 90, β = 108.86(3), γ = 90°, V = 6896(2)·10^6 pm^3; monoclinic $P2_1/n$, Z = 8, $\rho_{calcd.}$ = 1.2198 g cm^{-1}, μ(Mo-K_α) = 0.113 mm^{-1}, STOE IPDS2, Mo-K_α radiation, λ = 0.71073 Å, T = 160 K, $2\theta_{max}$ = 52°; 22059 reflections measured, 10381 independent reflections (R_{int} = 0.0975), 7697 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined, by full-matrix least square techniques against F^2, 830 parameters (Si, N, C refined anisotropically, the CF_3 groups are disorderd and were refined with split positions, H atoms were calculated at ideal positions). R_1 = 0.0725 wR_2 = 0.2122 (all data); Gof: 1.020; maximum peak 0.506 e·Å^{-3}. CCDC-634158 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[20] D. T. Gryko, C. Clausen, K. M. Roth, N. Dontha, D. F. Bocian, W. G. Kuhr, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 7345–7355.
[21] R. P. Hsung, J. R. Babcock, C. E. D. Chidsey, L. R. Sita, *Tetrahedron Lett.* **1995**, *36*, 4525–4528.
[22] D. V. Kosynkin, J. M. Tour, *Org. Lett.* **2001**, *3*, 993–996.
[23] H. G. O. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fischer, F. Gentz, K. Gewald, R. Gluch, W. D. Habicher, R. Mayer, P. Metz, K. Müller, D. Pavel, H. Schmidt, K. Schollberg, K. Schwetlick, E. Seiler, G. Zeppenfeld in *Organikum*, Wiley-VCH, Weinheim, **2001**, chapter F, p. 741–762.

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