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# Synthesis of Macrocyclic Molecular Rods as Potential Electronic Devices

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The design and synthesis of the macrocycles **1** and **2** as model compounds for the investigation of negative differential conductance phenomena in molecular junctions are reported. The macrocycles **1** and **2** comprise a molecular rod subunit consisting of three ethynyl-linked phenyl rings. While the rotational freedom along the rod axis of both terminal phenyl rings is limited by the macrocyclic frame, the central phenyl ring is revolving. The rod substructure is terminally functionalized with acetyl-protected thiol groups to enable its immobilization between gold contacts. The central phenyl ring is functionalized with one and two nitro groups for **1** and **2**, respectively. The nitro groups are of particular importance as i) both macrocycles are model compounds to investigate a hypothetical intramolecular interaction of the nitro group with the opposite macrocyclic subunits and ii) the nitro group(s) result in limited thermal stability of the compounds due to the intramolecular rearrangement to macrocycles comprising isatogen subunits. These highly functionalized macrocycles have been assembled by acetylene scaffolding strategies in combination with functional group transformation chemistry.



## Introduction

Integration of small assemblies and even single molecules in electronic circuits has become experimentally feasible in the last few years.[1,2] Driven by the vision that molecules as tailor-made nanoscale objects may serve as modular functional units in future electronic devices, these fundamental investigations have attracted large interest.[1–4] While the vision that electronic functions may be engineered by synthetic chemistry was already described by Hans Kuhn in the sixties,[5] the latest rebirth of the concept now called "molecular electronics" is mainly due to the increasing control over nanoscale objects with the development of powerful manipulation and investigation tools.[1–3,6]

Monomolecular films have been investigated as sandwich structures between electrodes,[7] and smaller assemblies down to single molecules have been integrated by scanning probe techniques.[8] More symmetric electrode pairs for the investigation of single molecules have been achieved by mechanically controlled break junctions (MCB),[9,10] electromigration[11] and lithographic techniques.[12] Our systematic variation of the structure of the investigated molecular rod in a MCB enabled fundamental experiments displaying the reflection of the molecules symmetry[10] and the reduced electronic transparency of separated π systems[13] and of rods immobilized in the *meta* position.[14] Recently, even a single molecule diode has been realized.[15] Correlations between molecular structures and electronic signature have also been reported with other experimental setups like e.g. mercury droplet[7b] and crossed-wire junctions.[7d] While comparisons of molecular structures within the same setup often displayed the expected correlations, comparison even of the same structures between different experiments turned out to be more troublesome, pointing at the importance of both, the molecular structure and the close environment (molecular and electronic).

In the field of molecular electronics, special attention has been attracted by an NDR device consisting of a laterally limited self-assembled monolayer (SAM) between two electrodes (Figure 1, A).[16] Systematic variation of the molecular structure of the SAM forming phenylethynyl-based molecular rods indicated that the nitro group at the central unit is crucial to observe the NDR switching.[17] While the electronic property of the device enables the assembly of more complex electronic functions,[18] the origin of the effect is still debated and the topic of numerous theoretical investigations. Many models assumes a change in the torsion angles between adjacent phenyl rings of the phenylethynyl backbone in the SAM as the origin of the conductance changes.[19]

From the point of view of molecular design, a particular interesting explanation has been reported by Stokbro and co-workers.[20] On the basis of density functional theory (DFT) calculations, they suggest an intermolecular interaction between a nitro group and a phenyl ring of a neighboring molecule in the SAM as the origin of the switching

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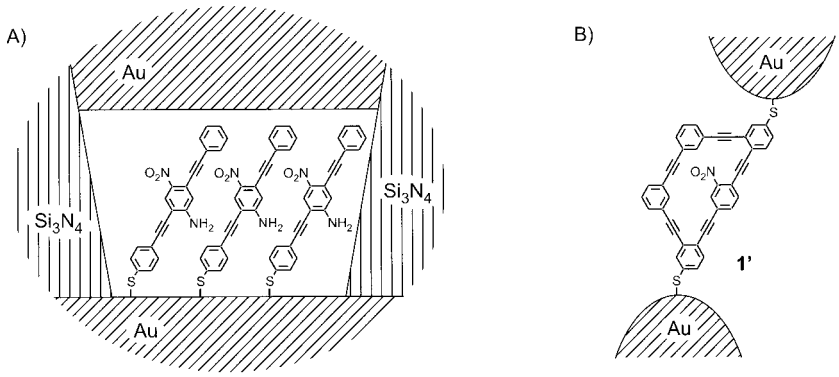



Figure 1. **A**) Schematic representation of the NDR device consisting of a laterally limited self-assembled monolayer of an oligophenyleneethynyl rod between two gold electrodes. The intermolecular interaction between the nitro group and the phenyl ring of the neighboring molecule may play a key role in the observed electronic behavior. **B**) Schematic representation of a single-molecule experiment with the macrocycle **1′** immobilized between two gold electrodes. The macrocyclic structure of **1′** enables the intramolecular proximity of the nitro group and the phenyl subunit.

behavior. An intermolecular origin of the NDR is further supported by the fact that such effects have not been observed in single-molecule experiments on similar structures even at low temperatures.[21]

An appealing approach to integrate an NDR effect in a single molecule would be to combine the nitro-group-functionalized molecular rod and the neighboring phenyl ring in a macrocyclic structure (Figure 1, B). Thereby the intermolecular interaction predicted in the SAM device becomes intramolecular in a single-molecule experiment.

Numerous macrocycles have been assembled in the last few years based on acetylene scaffolding strategies.[22] In particular, because of their unique properties like monodispersity and shape persistence, they are very interesting building blocks in materials chemistry, as host structures[23] and as tailor-made nanoscale objects[22e] for physical experiments.[24] While numerous macrocycles with high degrees of structural symmetry have been synthesized on the basis of modular strategies with repetitive reaction sequences, the synthetic efforts presented here are rather inspired by the step-by-step assembly strategies reported by the groups of Moore[25] and Haley.[26]

Here we present the design, synthesis and characterization of a macrocycle intended for single-molecule investigations between two gold electrodes.

## Molecular Design and Synthetic Strategy

The targeted macrocycles **1** and **2** are displayed in Figure 2. In the following, the design of the macrocyclic structure of **1** is discussed in detail. However, the same arguments are valid for macrocycle **2**, which has an additional nitro group relative to **1**. Generally, macrocycle **1** consists of five ethynyl-linked phenyl rings. It can be divided into three structural units to which we will refer to as *A*, *B* and *C*, as indicated in Figure 2. These units comprise both terminal phenyl rings *A*, the handle-like bridging substructure *B* and the central phenyl ring of the molecular rod *C*.

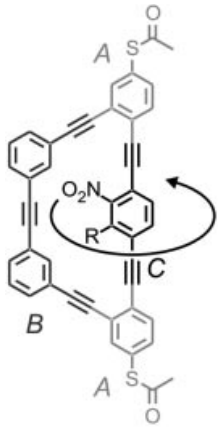



Figure 2. The macrocyclic structures **1** and **2** comprising a revolving central unit *C* harnessed between both terminal units *A* which is planarized by the handle *B*. The central unit *C* is functionalized with nitro groups to enable intramolecular interactions with the phenyl rings of *B*.

The linear molecular rod substructure consists of three ethynyl-linked phenyl rings *A* and *C*. Both terminal phenyl rings *A* are additionally functionalized with acetyl-protected sulfur groups in the *para* position with respect to the linear molecular rod. These acetyl-protected sulfur groups are known to be ideally suited for the immobilization of the macrocycle between both gold electrodes of a MCB.[10,13–15] Furthermore, the *para* positions of these anchor groups guarantee an intense coupling of the molecular rod substructure with the electronic levels of the electrodes,[14] an important requirement for an intense electronic signal upon conformational rearrangement of the molecular rod. Both terminal phenyl rings are further functionalized with the bridging handle *B*. This substructure consists of ethynyl-linked phenyl units; however, the handle is linked to the terminal phenyl rings at the electronically weakly coupled

*meta* position to the sulfur anchor groups. Also the handle substructure itself consists solely of the poorly conjugated *meta*-diethynyl benzene unit. Hence, in an immobilized macrocycle, the current is expected to be dominated by the strongly conjugated molecular rod substructure while only minor contributions should arise from "leaking currents" through the handle. The task of the handle is twofold. First, it locks the rotation of the terminal phenyl rings in a planar conformation. Second, the handle substructure enables the phenyl ring to be in proximity of the nitro group of the central phenyl unit of the molecular rod.The linear molecular rod substructure consists of the central phenyl ring *C*, which is connected on opposite sites by ethynyl linkers to the terminal phenyl units *A*. Both ethynyl linkers in the *para* position of the central phenyl ring *C* provide this central ring the freedom to rotate along the rod's axis. Furthermore, the central phenyl ring *C* is functionalized with one and two nitro groups in the case of **1** and **2**, respectively. The electronic transparency through such phenylethynyl rods has been calculated to depend strongly on the torsion angles between neighboring phenyl units.[19,20] However, in **1** both terminal phenyl rings *A* are locked by the handle *B*. Hence the transport determining torsion angles are given by the relative rotational position of *C* with respect to the plane of the terminal phenyl rings *A*. Furthermore, the proximity of the nitro group of *C* and the phenyl ring of *B* should enable to profit from the proposed voltage-dependent interaction between these two subunits that alters the rotational position of *C* and hence the electronic transparency through the rod substructure.

The concept to harness a phenyl ring by acetylenes in a macrocycle as an intramolecular revolving subunit has already been realized in the turnstile structures of Moore and co-workers.[27] Recently, a comparable turnstile motif provided allosteric binding properties to a macrocyclic host structure.[28]

The synthetic strategies that have been considered for the assembly of the macrocyclic structures **1** and **2** are displayed in Figure 3. In similarity to the design of the macrocycles **1** and **2**, their structures have been divided into retrosynthetic target structures A, B and C. The assembly of these targets to the final macrocyclic structure is based on metal-catalyzed cross-coupling reactions. In particular, the $Pd^0$- and $Cu^I$-catalyzed substitution of leaving groups at the aromatic building blocks by acetylenes, which originates from Sonogashira and co-workers[29] and has been extended to triflates as leaving groups,[30] has been applied.

The choice of the target structure A as the unit that has the leaving groups and of B and C as the acetylene-bearing units is to some extent coincidental. However, it is mainly driven by the straightforward accessibility of the acetylene-functionalized target structures B and C. To increase the range of applicable conditions in these coupling reactions, the terminal sulfur groups have initially been masked by stable *tert*-butyl groups, which are known to be transformable to acetyl protecting groups under rather mild condi-

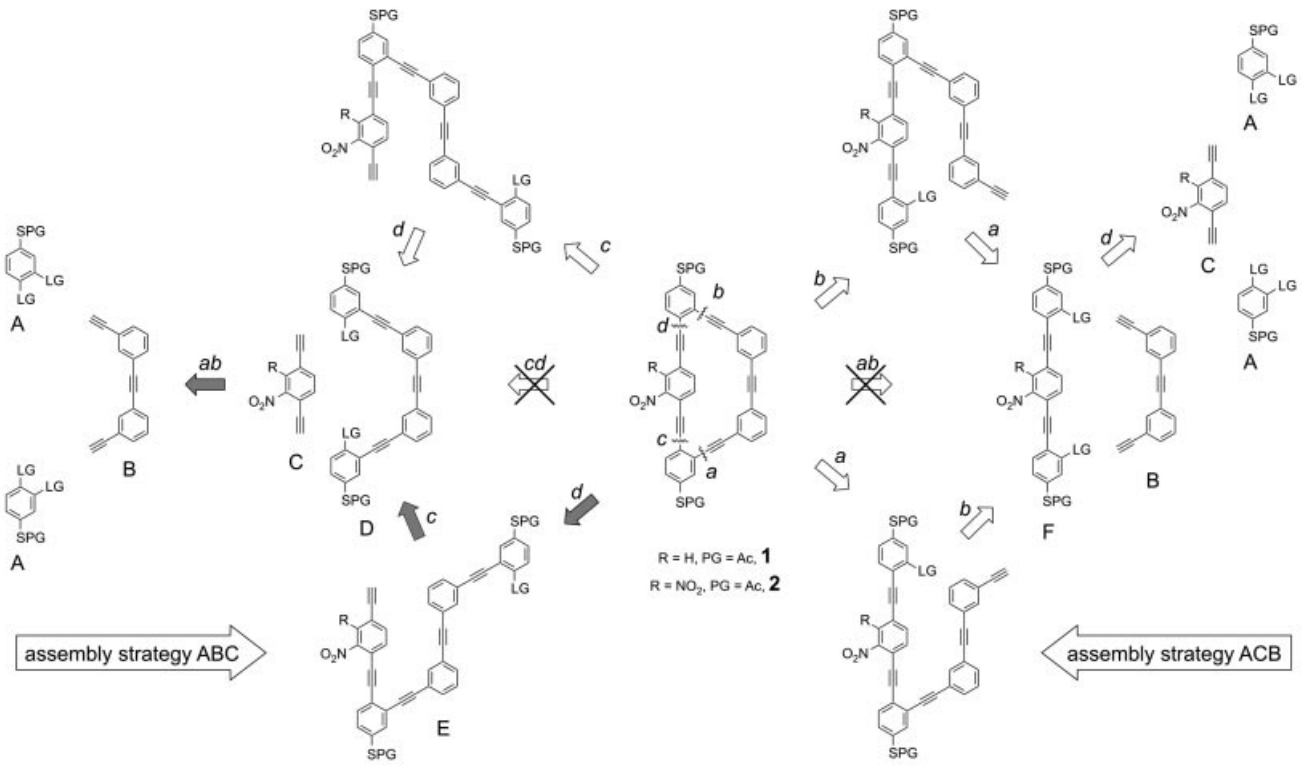



Figure 3. Retrosynthetic strategies to assemble the macrocycles **1** and **2** from the building blocks A, B and C. While not all indicated retrosynthetic options have been investigated to the same extend, the grey retrosynthetic arrows *ab*, *c* and *d* indicate the here successfully followed synthetic path to the macrocyclic structure.

tions.[31,32] To distinguish between both leaving groups of the terminal target structure A, we have masked one of both with a functional group that enabled its transformation into a leaving group after having substituted the first leaving group.

In the further text the different assembly strategies are nominated according to the order of assembled subunits A, B and C. In particular to the approach displayed on the left side of Figure 3 will be referred to as assembly strategy ABC and to the approach displayed on the right side will be referred to as assembly strategy ACB.

The chemistry was mainly developed during the synthesis of macrocycle **1**, while the macrocycle **2** has been assembled in analogy to **1**.

With suitable building blocks A, B and C in hand, we first focused on forming **1** in two subsequent coupling reactions. While the assembly of suitable functionalized subunits A and B to D turned out to be feasible in good yields (*ab*), the prior assembly of A and C to F was only achieved in very moderate yields of 14% (*ac*). We therefore further investigated the assembly strategy ABC displayed on the left side of Figure 3. However, to harness both terminal subunits of D with C in one step turned out to be troublesome (*cd*). The desired cycle structure was probably formed as the expected signal is observed in the MALDI-ToF mass spectrum of the reaction mixture. However, its formation was accompanied by many side products such that we were not able to isolate the macrocyclic structure. In addition, the yield of the cyclization reaction must be quite low to enable the formation of the numerous side products. An alternative approach is to mask one acetylene of C with a silyl protecting group and to cyclize the macrocycle in two subsequent coupling steps. As indicated in Figure 3 by grey retrosynthetic arrows, this strategy turned out to be successful. The coupling product E of D and C (*c*) has been isolated in its acetylene-protected form and also as free acetylene.

Even though elegant strategies involving the coupling of a monoprotected diacetylene followed by deprotection and subsequent coupling of the second acetylene have been reported by Haley and co-workers,[33,34] we preferred to isolate and characterize these intermediates after the troublesome one-step synthesis (*cd*) described above. Finally, an intramolecular cyclization reaction (*d*) of deprotected E led to the macrocyclic structures.

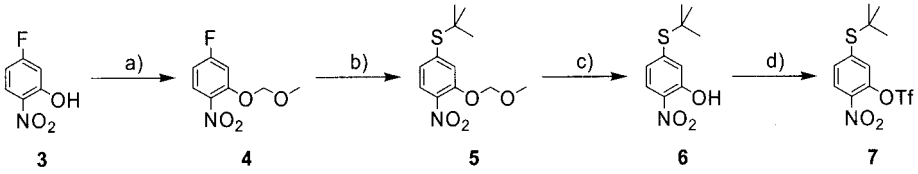
Subsequent protection-group chemistry allowed the conversion of the *tert*-butyl groups at the sulfur into the desired acetyl-protected thiol functions.[31,32]

## Synthesis and Characterization

Depending on the synthetic approach to the macrocycles, differently functionalized building blocks A are required. In the assembly strategy ABC, first two building blocks A are linked to a building block B. Therefore a building block A with an active leaving group in *meta* position and a masked leaving group in *para* position of the *tert*-butyl sulfanyl function is required. In the assembly strategy ACB, two building blocks A are connected to both ends of the central unit C. For such an approach a building block A with an active leaving group in *para* position and a silent (masked) leaving group in *meta* position is required.

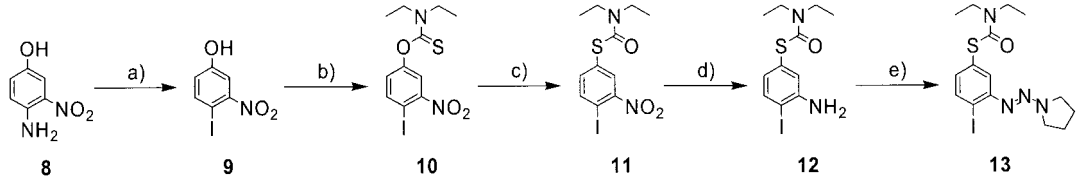
For the assembly strategy ABC, 5-(*tert*-butylsulfanyl)-2-nitrophenyl trifluoromethanesulfonate (**7**, see Scheme 1) is ideally functionalized as building block A. The *tert*-butylsulfanyl group is a masked thiophenol as the *tert*-butyl group can be transferred to an acetyl protecting group quite easily. Furthermore, the *tert*-butylsulfanyl group allows for rather strong nucleophilic (basic) reaction conditions. The nitro group is in place of the second leaving group. In subsequent reaction steps it can be reduced to an amino group and subsequently substituted by e.g. halogens in a Sandmeyer reaction. Furthermore, the nitro group facilitates the aromatic nucleophilic substitution reactions in its *para* and *ortho* positions. The triflate group of **7** allows already the coupling reaction with acetylenes. The synthesis of **7** is displayed in Scheme 1.

Starting with commercially available 5-fluoro-2-nitrophenol (**3**), the phenolic OH was first protected with a methylmethoxy (MOM) group by adding bromomethyl methyl ether to a solution of **3** in tetrahydrofurane (THF) over potassium carbonate ($K_2CO_3$) at 0 °C. The MOM-protected derivative **4** was isolated in 78% yield after column chromatography (CC) as yellow oil. The nitro group in *para* position makes the substitution of the fluorine atom of **4** much easier. Treatment of **4** with the sodium salt of *tert*-butyl thioalcohol in dry dimethylformamide (DMF) at room temperature (room temp.) afforded the *tert*-butylsulfanyl-functionalized derivative **5** in 76% yield after CC. The strong activation of the *para* and *ortho* position by the nitro group is further confirmed by the substitution of the MOM-protected phenol group by the *tert*-butylthiolate nucleophile as main side reaction. The 2,4-bis(*tert*-butylsulfanyl)nitrobenzene was isolated in 10% yield from the reaction mixture. Deprotection of the MOM group of **5** with hydrochloric acid in methanol gave the phenol **6** in 95% as yellow liquid. Treatment of **6** in dichloromethane ($CH_2Cl_2$)




Scheme 1. Synthesis of **7** as potential building block A for the synthetic strategy displayed in Figure 3 on the left side. a) $BrCH_2OCH_3$, $K_2CO_3$, THF, 0 °C to room temp., 78%; b) *t*BuSNa, DMF, room temp., 1 h, 76%; c) HCl, MeOH, 60 °C, 1 h, 95%; d) $Tf_2O$, $Et_3N$, $CH_2Cl_2$, 0 °C, 1 h, 89%.



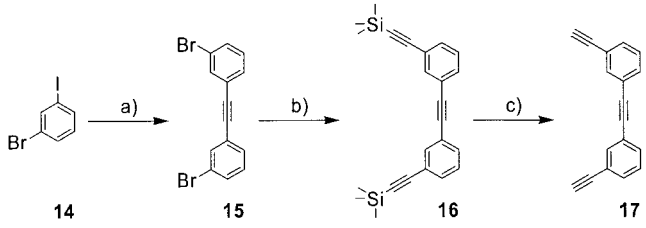

Scheme 2. Synthesis of **13** as potential building block **A** for the synthetic strategy displayed in Figure 3 on the right side. a) 1. HCl, $NaNO_2$, $H_2O$, 0 °C, 1.5 h, 2. KI, $H_2O$, 0 °C to room temp., overnight, 83%; b) 1. KOH, $H_2O$, 0 °C, 30 min, 2. $ClCSNEt_2$, THF, 0 °C to room temp., overnight, 84%; c) 190 °C, 4 h, 86%; d) Sn, $CH_3COOH$, EtOH, 60 °C, 3 h, 91%; e) 1. $BF_3{\cdot}Et_2O$, *t*BuONO, THF, –20 °C to –5 °C, 2 h, 2. pyrrolidine, $Na_2CO_3$, $H_2O$, $CH_3CN$, 0 °C to room temp., 2 h, 49%.

and triethylamine ($Et_3N$) with trifluoromethanesulfonic anhydride ($Tf_2O$) at 0 °C gave the desired building block **7** in 89% after CC as yellow solid.

The assembly strategy ACB requires a protected thiophenol as building block A with a leaving group in the *para* position and a masked leaving group in the *meta* position. *S*-[4-Iodo-3-(pyrrolidin-1-yldiazenyl)phenyl] diethylthiocarbamate (**13**) ideally fulfils these requirements. Its thiophenol function is protected as diethylthiocarbamate, which is stable in basic conditions usually applied in acetylene coupling reactions. Its iodo group in *para* position to the protected thiophenol allows for efficient Sonogashira coupling reactions. Finally, the dialkyltriaza group is a stable precursor of a second iodine as future leaving group in a subsequent coupling step.

The assembly of **13** is displayed in Scheme 2. Starting with commercial 4-amino-3-nitrophenol the amino function was substituted by iodine in a Sandmayer reaction sequence.[35] The amino group was diazotized using HCl/$NaNO_2$ and the diazotate subsequently iodinated with KI to afford 4-iodo-3-nitrophenol (**9**) in 83% yield as red-orange crystalline solid. To introduce the protected thiophenol function, the phenol group of **9** was first protected as *O*-(4-iodo-3-nitrophenyl) diethylthiocarbamate (**10**), which was converted into *S*-(4-iodo-3-nitrophenyl) diethylthiocarbamate (**11**) in a Newman–Kwart rearrangement.[36] Treatment of the potassium salt of **9** with *N*,*N*-diethylthiocarbamoyl chloride in THF at 0 °C gave **10** in 84% yield after crystallization as yellow crystals. Subsequent heating of **10** to 190 °C gave the ester **11** in 86% yield as a yellow crystalline solid after CC and recrystallization from ethanol. Particular caution is needed for the rearrangement reaction. The reaction temperature has to be controlled carefully as explosive decomposition of **10** has been observed applying too high temperatures. Reduction of the nitro group of **11** with tin in acetic acid and ethanol gave the corresponding aniline **12** in 91% yield after crystallization from ethanol. The amino function of **12** was transformed into a dialkyltriaza group by diazotising using $BF_3{\cdot}Et_2O$/*t*BuONO conditions followed by treatment with pyrrolidine[37] in acetonitrile at 0 °C to afford **13** in 49% yield as a pink crystalline solid.

Both synthetic strategies in Figure 3 require diacetylene **17** as the handle-like substructure *B*. Its assembly is straight forward and is based on well-developed acetylene coupling reactions. Most reaction steps have been described in the literature with to a large extent comparable structures.[38] The synthesis of **17** is displayed in Scheme 3.

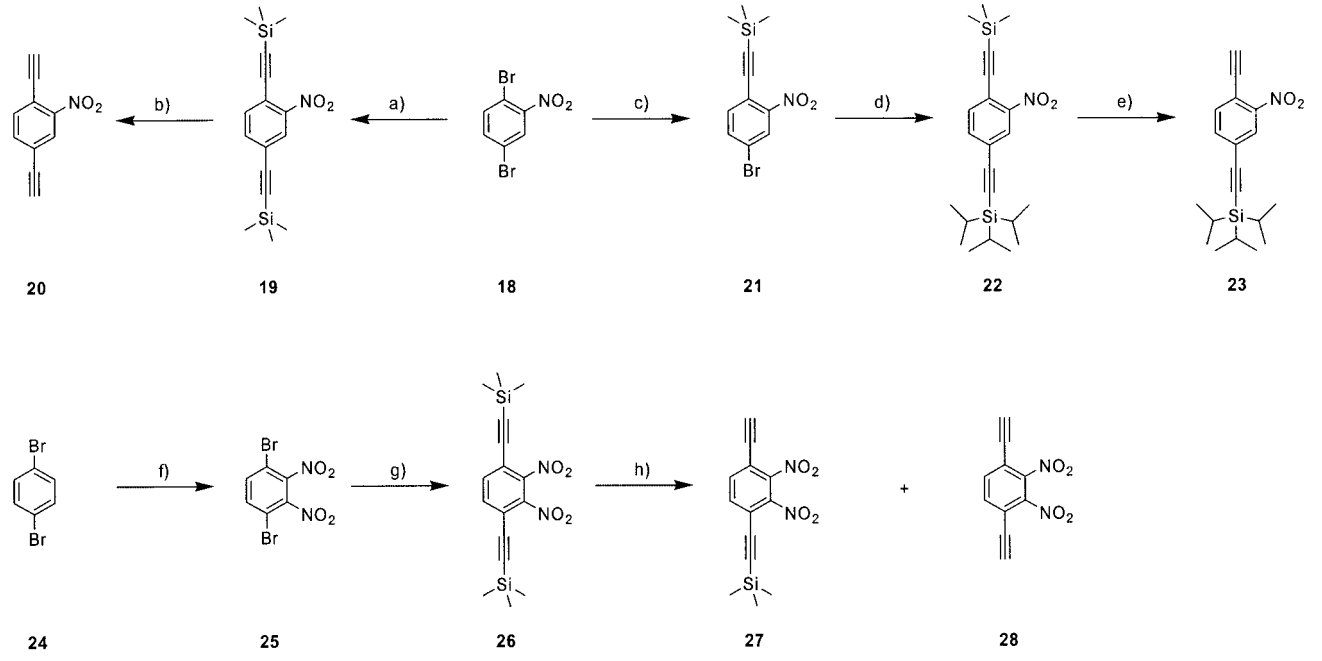



Scheme 3. Synthesis of the diacetylene **17** as handle substructure B. a) $HCCSi(CH_3)_3$, $PdCl_2(PPh_3)_2$, CuI, DBU, THF, $H_2O$, room temp., 16 h, 81%; b) $HCCSi(CH_3)_3$, $PdCl_2(PPh_3)_2$, CuI, $Et_3N$, $PPh_3$, THF, reflux, 4 h, 97%; c) $K_2CO_3$, MeOH, $CH_2Cl_2$, room temp., 98%.

Commercially available 1-bromo-3-iodobenzene (**14**) and trimethylsilyl(TMS)acetylene yielded 3,3′-dibromotolane (**15**), following a literature procedure.[38] Subsequently, both bromines of **15** have been substituted with TMS acetylenes using Sonogashira coupling conditions. The doubly TMS-protected diacetylene **16** has been isolated in 97% yield after CC as a white solid. Both TMS protecting groups have been removed almost quantitatively by treatment with potassium carbonate in a mixture of methanol and dichloromethane. Diacetylene **17** was isolated as a white solid in 98% yield.

In addition, the diacetylenes **20** and **28** are required as building blocks C in both synthetic strategies displayed in Figure 3. As both macrocycles **1** and **2** differ in their central building block C, these diacetylene subunits had to be synthesized separately. Furthermore, for a stepwise closing of the macrocycle, this building block is required in its monoprotected form. While the subunit C of the macrocycle **1** was deliberately synthesized as free diacetylene **20** and as monoprotected diacetylene **23**, the subunit C of the macrocycle **2** was synthesized in its monoprotected form **27**. However, the free acetylene **28** has been isolated as side product. Two different synthetic strategies have been applied for both monoprotected diacetylenes **23** and **27**. While for the synthesis of the monoprotected unit C, **23**, of the macrocycle **1** two acetylenes with different protecting groups have been introduced, the higher symmetry of the C unit of macrocycle **2** enables for a monodeprotection strategy for the




Scheme 4. Synthesis of the free diacetylenes **20** and **28** and their monoprotected derivatives **23** and **27** as central subunits C of the macrocycles **1** and **2** respectively. a) $HCCSi(CH_3)_3$, $PdCl_2(PPh_3)_2$, CuI, $Et_3N$, THF, 61%; b) $K_2CO_3$, MeOH, $CH_2Cl_2$, room temp., 58%; c) $HCCSi(CH_3)_3$, $PdCl_2(PPh_3)_2$, CuI, $HNiPr_2$, THF, room temp., 2 h, 53%; d) $HCCSi[CH(CH_3)_2]_3$, $PdCl_2(PPh_3)_2$, CuI, $HNiPr_2$, THF, room temp., 16 h, 63%; e) $K_2CO_3$, MeOH, $CH_2Cl_2$, room temp., 96%; f) $HNO_3$, $H_2SO_4$, 95 °C, 17%; g) $HCCSi(CH_3)_3$, $Pd(PPh_3)_4$, CuI, $EtNiPr_2$, THF, room temp., 16 h, 63%; h) KF, AcOH, MeOH, $CH_2Cl_2$, room temp., 33%.

monoprotected unit C, **27**. The syntheses of the different subunits C are displayed in Scheme 4.

Starting with commercially available 1,4-dibromo-2-nitrobenzene, the TMS-protected diacetylene **19** was obtained in moderate yields of 61% following a literature procedure.[39] The subsequent removal of both TMS protecting groups of **19** using $K_2CO_3$ in a MeOH/$CH_2Cl_2$ mixture gave 1,4-diethynyl-2-nitrobenzene (**20**) in 58% again following the procedure described in ref.[39].

In analogy to the diacetylene **20**, also the monoprotected diacetylene **23** was assembled starting with 1,4-dibromo-2-nitrobenzene (**19**). First, the bromine in the *ortho* position to the nitro group was substituted with TMS-acetylene using palladium- and copper-catalyzed Sonogashira reaction conditions. The TMS-protected acetylene **21** was isolated in 53% yield after CC. Again Sonogashira reaction conditions have been applied to substitute the remaining bromine of **21** with a tris(isopropylsilyl) (TIPS) acetylene. Diacetylene **22** comprising two different protecting groups has been isolated in 63% yield after CC. Chemoselective deprotection of the TMS group with $K_2CO_3$ in a MeOH/$CH_2Cl_2$ mixture afforded the monoprotected target structure **23** as white solid in 96% yield.

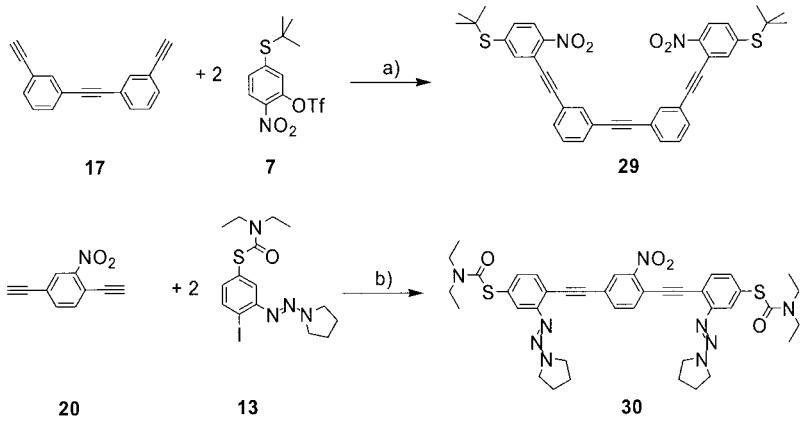
According to a literature procedure,[40] nitration of 1,4-dibromobenzene (**24**) gave the desired 1,4-dibromo-2,3-dinitrobenzene (**25**) in poor yields of 17%. The major product of the nitration reaction is the mono-nitrated 1,4-dibromo-2-nitrobenzene (**18**), which was isolated in 60% yield. Both bromines of **25** were substituted by TMS acetylenes to afford the diprotected diacetylene **26** in 63% yield. For the statistical deprotection of **26**, traces of acetic acid were added to a MeOH/$CH_2Cl_2$ mixture prior to 0.5 equiv. potassium fluoride. The acetic acid slows down the deprotection kinetics probably by providing protons for the protonation of the formed acetylide. The mono-TMS-protected diacetylene **27** was isolated in 33% yield by CC as whitish solid. Besides unreacted starting material, also the fully deprotected diacetylene **28** was isolated in 43% yield as expected side product of the statistical deprotection reaction.

While for the assembly strategy ABC both acetylenes of the diacetylene **17** were further functionalized with a potential building block A, for the assembly strategy ACB both acetylenes of **20** were further functionalized. Both reaction steps are displayed in Scheme 5.

Using palladium- and copper-catalyzed Sonogashira reaction conditions in THF and triethylamine ($Et_3N$) as base at room temp., the diacetylene **17** and the triflate **7** gave the desired oligoethynylphenylene **29** in an excellent yield of 88% after CC. Even though the iodo group is known as powerful leaving group in Sonogashira coupling reactions,[29] the coupling of diacetylene **20** with iodophenyl **13** turned out to be less efficient. The best result of this coupling reaction was achieved with similar reaction conditions as applied for **17** and **7**. However, the functionalized molecular rod **30** was isolated as yellow oil in only 14% yield after CC.

The attractivity of the assembly strategy ACB decreased considerably as all attempts to improve the yield of **30** failed. We therefore focused our synthetic endeavour on the more promising assembly strategy ABC.




Scheme 5. First assembly steps of the strategy ABC (top) and of the strategy ACB (bottom). While the synthesis of **29** represents the assembly of two units A with the subunit B, the synthesis of **30** represents the merging of two units A with a subunit C. a) $PdCl_2(PPh_3)_2$, CuI, $Et_3N$, THF, room temp., 4 h, 88%; b) $PdCl_2(PPh_3)_2$, CuI, $Et_3N$, THF, room temp., 16 h, 14%.

To introduce the central subunit C, both nitro groups of **29** have to be transformed to leaving groups suitable for acetylene coupling reactions. We intended to reduce the nitro groups to amines which can be converted to halide leaving groups in a Sandmeyer reaction.

Treatment of the dinitro compound **29** in THF with concentrated hydrochloric acid (HCl) and tin afforded the diamine **31** as white solid in 95% yield after CC. Diazotizing of **31** in dry THF with $BF_3{\cdot}Et_2O$/*t*BuONO gave the diazonium salt as a yellow precipitate from cold THF/hexane.[41] Treatment of the precipitate with potassium iodide and iodine in a mixture of acetonitrile ($CH_3CN$), and water ($H_2O$) afforded the desired diiodo compound **32** together with the monoiodinated derivative. Compound **32** was isolated in 38% yield as white solid by recrystallization from ethyl acetate (Scheme 6).

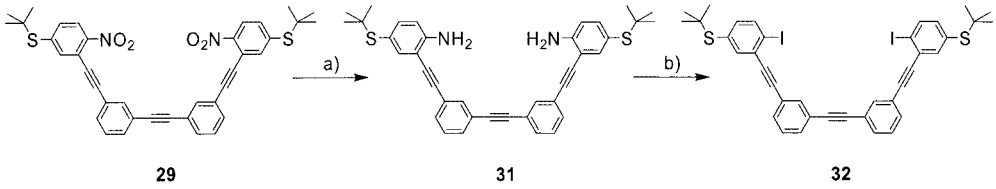
Compound **32** comprises two terminal subunits A linked by the subunit B. Furthermore, both iodines are excellent leaving groups to introduce the subunit C with a Sonogashira coupling protocol.

The reaction of **32** with the free diacetylene subunits C, **20** or **28**, may afford the desired macrocyclic precursors **36** or **39** in a one-pot cyclization reaction. Indeed, for **36** as precursor of the macrocycle **1** this macrocyclization step has been investigated to some extend. However, the control of the reaction of both bifunctional subunits **32** and **20** turned out to be troublesome.

For the one-pot macrocyclization reaction between **32** and **20** high-dilution conditions in THF using $Pd(dba)_2{\cdot}CHCl_3$ as source of $Pd^0$ have been investigated. As ligand for the active $Pd^0$ species triphenylphosphane was added, together with CuI as cocatalyst and diisopropylethylamine as base. The course of the macrocyclization reaction was monitored by thin layer chromatography and MALDI-TOF-MS. Within a few hours numerous new compounds with very comparable polarities were formed. Investigation of the crude reaction mixture by MALDI-TOF-MS displayed among numerous other signals also the one expected for the desired product (*m*/*z* 722) and the one of the open iodo precursor (*m*/*z* 849). However, the large number of side products with comparable polarities considerably reduced the attractivity of the one-pot macrocyclization reaction as route to the desired precursor **36**.

Alternatively, the macrocycle **36** may also be assembled stepwise by using the monoprotected diacetylene subunits **23** and **27**. However, the challenge of such a subsequent two-step ring-closing strategy is to minimize the substitution of both iodines of **32** by the acetylene. To favor the formation of the monosubstituted product over the disubstituted one, pseudo-high dilution conditions have been applied.

An excess of 2 equiv. of the diiodo derivative **32** in a degassed THF/$(i\text{Pr})_2$NEt mixture have been charged with $Pd(PPh_3)_4$ and CuI as catalysts. The acetylene **23** has been added dropwise over a period of 10 h at room temp. After completed addition, the reaction mixture was kept at room temp. for another 16 h. From the crude reaction mixture the desired monosubstituted derivative **33** has been isolated in 64% yield as yellow solid by CC, while the doubly substituted compound **34** has been isolated in 30% yield. For the




Scheme 6. Transformation of both nitro groups of **29** into iodines of **32** via amines of **31**. a) Sn/HCl, THF, room temp., 1 h, 95%; b) 1) $BF_3{\cdot}Et_2O$, *t*BuONO, THF, 2) KI/$I_2$ in $H_2O$, $CH_3CN/CH_2Cl_2$, 38%.

synthesis of the dinitro derivative **37**, toluene has been used as solvent instead of THF. Furthermore, the excess of **32** was reduced to 1.5 equiv.. Otherwise comparable reaction conditions afforded **37** in only 23% yield after column chromatography. The doubly acetylene-substituted side product was not isolated from the numerous by-products of the reaction mixture.

Deprotection of the TIPS-protected acetylene **33** with tetrabutylammonium fluoride (TBAF) in THF with traces of acetic acid afforded the free acetylene **35** in 93% yield after CC. The TMS-protected acetylene of the dinitro derivative **37** was deprotected with potassium fluoride (KF) in a $MeOH/CH_2Cl_2$ mixture to afford the acetylene **38** in 98% yield after CC. Usually potassium carbonate is used instead of KF for the deprotection of TMS-protected acetylenes. However, these conditions applied to **37** results in the substitution of one of both hydrogen atoms in the aromatic ring system activated with two nitro groups by methoxide nucleophiles and are therefore not suitable for the deprotection of the dinitro derivative **37**.

The key step of the synthesis is an intramolecular ring-closing Sonogashira reaction as macrocyclization of the precursors **35** and **38**. High-dilution ($10^{-4}$ M) reaction conditions have been applied to favor the intramolecular reaction over intermolecular ones. The courses of the cyclization reactions were monitored by MALDI-TOF-MS analysis. The most successful macrocyclization has been obtained with a $2.4 \cdot 10^{-4}$ M solution of **35** in dry and degassed toluene. Diisopropylethylamine [$(i\text{Pr})_2\text{NEt}$] was added as base, followed by tetrakis(triphenylphosphane)palladium(0) [$Pd(PPh_3)_4$] and copper(I) iodide (CuI) as catalysts. The reaction mixture was stirred for 20 h at room temp. The desired macrocycle **36** was isolated by CC in a fair yield of 30% as yellow solid. The macrocyclization turned out to be very sensitive to the reaction solvent. The use of THF instead of toluene, but otherwise similar reaction conditions as those described above, reduced the yield of the targeted macrocycle **37** to 17%. The ring-closing reaction to the dinitro macrocycle **39** was even more troublesome. A $3.8 \cdot 10^{-4}$ M solution of the precursor **38** in dry and degassed toluene charged with $(i\text{Pr})_2\text{NEt}$, $Pd(PPh_3)_4$ and CuI was stirred at room temp. for 6 h. Only 11% of the desired macrocycle **39** were isolated by CC as yellow solid. However, numerous side reactions during Sonogashira reactions with nitro-group-containing aromatic units have been reported. In particular, the proximity of the acetylene in *ortho* position of the nitro group is known to tend to the formation of a bicyclic nitrogen radical heterostructure called isatogen.[42] According to the literature, successful coupling protocols for these nitro-group-containing compounds are characterized by lower temperatures, shorter reaction times and low concentrations of base to reduce side reactions.[43] In particular, compounds with two nitro groups in the aromatic ring are reported to be very sensitive to any base.[44] The considerably lower yield of the ring-closing reaction for the macrocycle **39** comprising two nitro groups each with an acetylene in *ortho* position compared with **36** is therefore not surprising.

The structures of **36** and **39** are both confirmed by $^1H$ and $^{13}C$ NMR spectroscopy and mass spectrometry (MALDI-TOF-MS). In particular, the disappearance of the singlets of the acetylene protons ($\delta$ = 3.27 ppm for **35** and $\delta$ = 3.57 ppm for **38**) documented successful cyclizations. Furthermore, a substantial reduction of signals in the $^1H$ and $^{13}C$ NMR spectra of **39** compared to the precursor **38** pointed to its increased symmetry. The MALDI-TOF mass spectra of **36** and **39** displayed with *m*/*z* 721.66 and *m*/*z* 766.51 exclusively the signals expected for both [$M^+$] ions. While the target compound **36** and its synthetic precursors are further characterized by elemental analysis, this additional purity information was not available for **39** and its intermediates due to the small-scale synthesis of the dinitro target structure **39**.

In addition, the side product **34** with two silyl-protected acetylenes is an ideal precursor for an extended macrocyclic structure. In an oxidative coupling both acetylenes may close the macrocycle with an additional acetylenic $C_2$ unit compared to the macrocycles **36** and **39**.

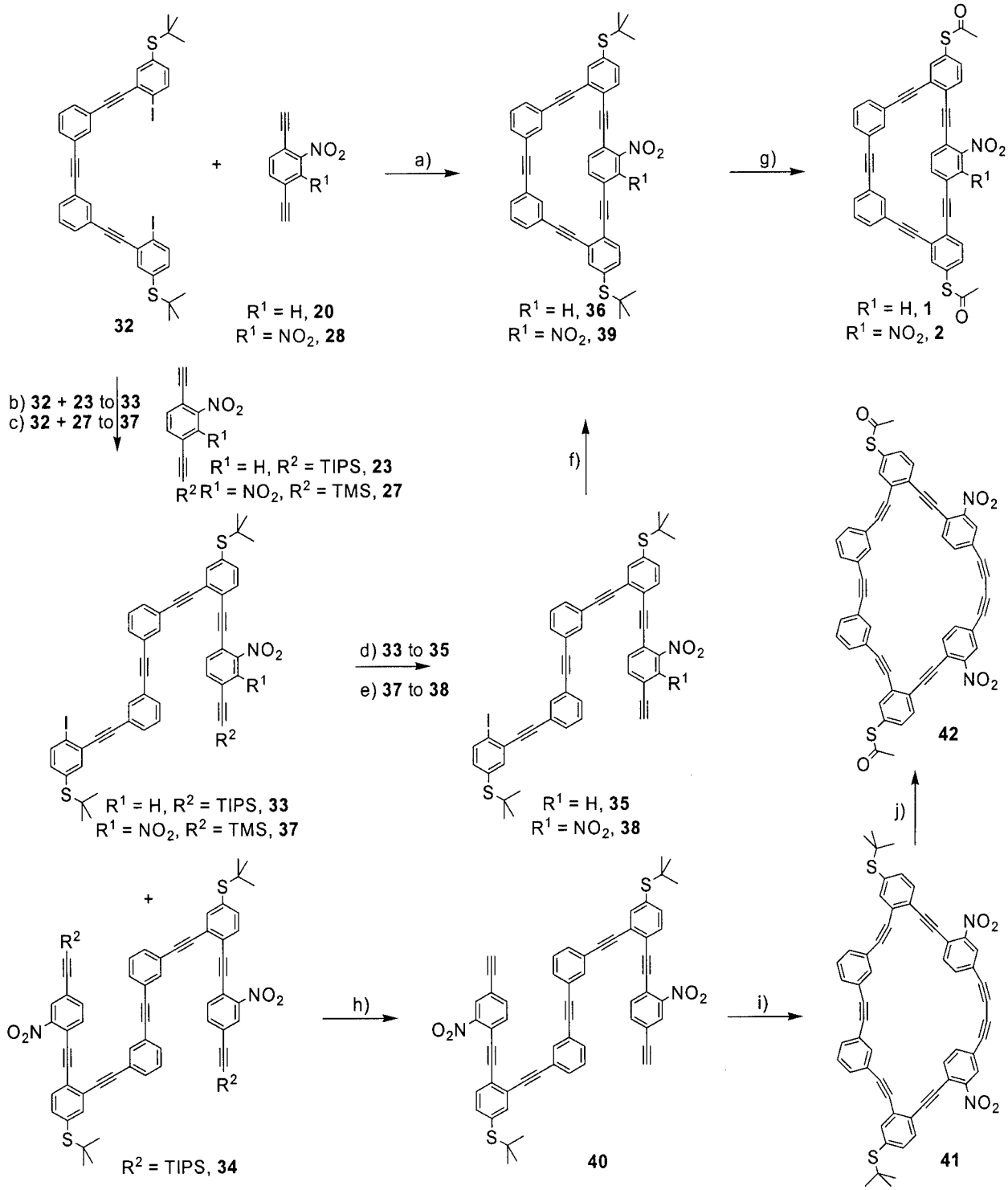
Therefore, both silyl-functionalized acetylenes of **34** have been deprotected with TBAF in THF to afford the diacetylene **40** in 88% yield after CC. A $4 \times 10^{-5}$ M solution of the diacetylene **40** in acetonitrile was treated with 1 equiv. of copper(II) acetate at 80 °C for 6 h. To dissolve **40** in acetonitrile, a minor amount of $CH_2Cl_2$ was used, which probably evaporated during the course of the reaction. The macrocycle **41** was isolated in 36% yield after CC. Again the formation of **41** is confirmed by its $^1H$- and $^{13}C$ NMR spectra. In particular the disappearance of the acetylene proton singlet at $\delta$ = 3.29 ppm pointed to the successful diacetylene formation. Furthermore, only a signal at *m*/*z* 890.49, which corresponds to [$M^+$] of **41** is observed in the MALDI-TOF mass spectra and corroborates the macrocyclic structure.

All three macrocyclic structures **36**, **39** and **41** are functionalized with two terminal sulfur atoms which are protected with *tert*-butyl groups. To immobilize these rods on metal surfaces these sulfur groups have to be deprotected. However, these terminal thiophenol substructures tend to the formation of disulfides in the presence of oxygen, yielding in insoluble polymers of these bifunctional molecular rods. Ideally suited to store these compounds as monomer and for the in-situ deprotection followed by subsequent immobilization on metal surfaces are acetyl protecting groups. The last step of the synthesis is hence the transprotection of S-*tert*-butyl groups into *S*-acetyl groups.[31,32]

First attempts were based on a protocol that we have developed ourselves.[31] However, treatment of the macrocycle **36** in acetyl chloride with traces of bromine did not result in the desired macrocycle **1** with acetyl-protected terminal sulfur groups. Most likely the poor solubility of **36** in acetyl chloride prevents the desired transprotection reaction. Fortunately, a variation of the protocol reported from Stuhr–Hansen[32] was more successful. Compound **36** was dissolved in $CH_2Cl_2$ with toluene as cosolvent, the later is reported to be crucial for the successful transprotection reaction. Treatment with acetyl chloride and boron tribro-

mide ($BBr_3$) afforded the desired acetyl-protected macrocycle **1** as yellow solid in 49% yield after CC. A similar protocol applied to the dinitro precursor **39** gave the acetyl-protected dinitro macrocycle **2** in 53% yield after CC. Interestingly, the enlarged macrocycle **41** is considerably more soluble than **36** and **39**. The increased solubility is probably due to a less planar structure of the macrocycle compared to **36** and **39**. The additional ethynyl unit in **41** results in




Scheme 7. Macrocyclization reactions. a) $Pd(dba)_2{\cdot}CHCl_3$, $PPh_3$, CuI, $(iPr)_2NEt$, THF; b) $Pd(PPh_3)_4$, CuI, $(iPr)_2NEt$, THF, room temp., 24 h, (**33**–64%, **34**–30%); c) $Pd(PPh_3)_4$, CuI, $(iPr)_2NEt$, toluene, room temp., 24 h, 23%; d) TBAF, AcOH, THF, room temp., 93%; e) KF, MeOH/$CH_2Cl_2$, room temp., 98%; f) $Pd(PPh_3)_4$, CuI, toluene, $(iPr)_2NEt$, room temp., (**36**–30%, **39**–11%); g) $BBr_3$, AcCl, $CH_2Cl_2$/toluene, room temp., (**1** 49%, **2** 53%); h) TBAF, AcOH, THF, room temp., 88%; i) $Cu(OAc)_2$, $CH_3CN/CH_2Cl_2$, 80 °C, 6 h, 36%; j) $Br_2$, AcCl/AcOH/$CH_2Cl_2$, 37%.

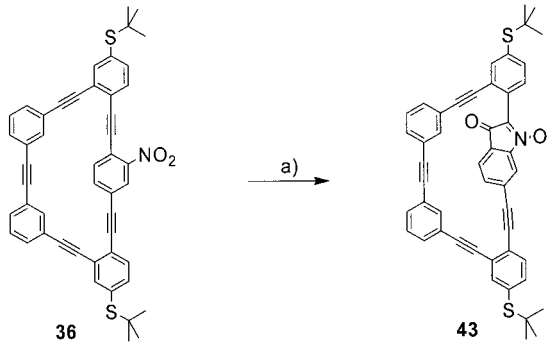
  

an increased ring tension, which does no longer allow a planar arrangement of the macrocycle and thus, formation of poorly soluble stacks is less favorable for the uneven macrocycle **41** (Scheme 7).

As consequence of the increased solubility of **41**, the bromine-catalyzed transprotection protocol[31] was applied successfully. Treatment of **41** in $CH_2Cl_2$/AcCl/AcOH with bromine gave the enlarged macrocycle **42** with terminal acetyl-protected sulfur groups in 37% yield after CC.

X-ray structures of the macrocycles are of particular interest as they provide further insight into structural features in general, but also into the interaction between the central revolving unit *C* and the handle subunit *B*. Therefore considerable endeavours were focused on the crystallization of the target structures **1** and **2**. However, the very poor solubility of the acetyl-protected macrocycles **1** and **2** did not allow for the growth of single crystals of these compounds. We therefore focused our crystallization investigations on the slightly more soluble macrocycles **36** and **39**. To increase the solubility of **36**, a small sample in toluene was gently heated with the heatgun. Upon heating, a color change from yellow to orange was observed. The orange decomposition product displayed an increased solubility more suitable for the growth of single crystals. To further investigate the origin of this temperature-induced color change we expanded the crystallization investigations on these "decomposed" macrocycles as well. A solution of the "decomposed" orange macrocycle in $CH_2Cl_2$ overlaid with methanol yielded in single crystals suitable for X-ray analysis. Figure 4 displays the X-ray structure of the orange decomposition product.

As displayed in Scheme 8, an intramolecular rearrangement reaction between the nitro group and the acetylene unit in proximity yields in the heterobicyclic isatogen derivative **43**. The formation of isatogens and thus the delicate thermal stability features of *ortho* ethynyl- and nitro-functionalized benzene structures have been reported.[42] However, there was some hope that the increase of ring tension upon formation of the isatogen substructure might provide these macrocyclic isatogen precursors with superior stability features. Generally, the macrocycle **36** displayed rather delicate stability features in solution. Most crystallization samples of **36** in various solvents turned orange within several weeks. TLC investigations of the crystallization samples monitored the formation of the isatogen **43** in solution at room temperature.




Scheme 8. Formation of the macrocycle comprising an isatogen subunit **43**. a) toluene, reflux.

The fact that the already poor yields of the macrocyclization reactions of nitro group containing precursors **35** and **38** was further reduced by increasing reaction temperature is easily rationalized considering the efficient formation of macrocyclic isatogen derivatives.

The macrocycle **43** crystallizes in the triclinic space group $P\bar{1}$ with half a $CH_2Cl_2$ molecule per formula unit.[45] This solvent molecule is disordered around the inversion center. The C–C bond length of the acetylene groups are on average 119.7 pm, the acetylene bridge angles range between 174.4(3)° [C(47)–C(48)–C(9)] and 179.0(3)° [C(19)–

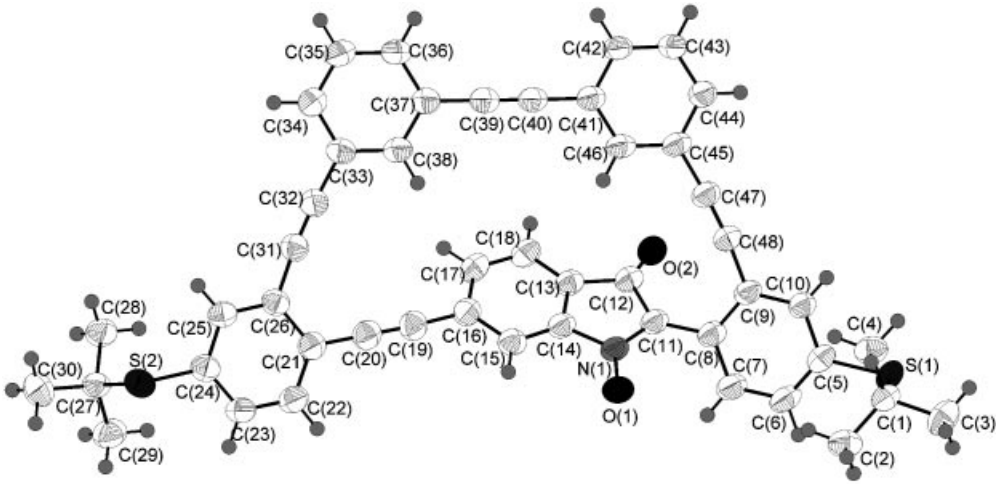



Figure 4. X-ray structure of the macrocyclic isatogen derivative **43**. Selected bond lengths [pm] and bond angles [°]: S(1)–C(1) 186.4(3), S(1)–C(5) 177.7(3), S(2)–C(24) 177.6(3), S(2)–C(27) 185.7(3), O(1)–N(1) 127.2(3), O(2)–C(12) 121.8(3), N(1)–C(11) 132.8(4), N(1)–C(14) 146.3(3), C(8)–C(11) 146.2(4), C(11)–C(12) 149.8(3), C(12)–C(13) 149.0(4), C(19)–C(20) 119.9(4), C(31)–C(32) 119.4(4), C(39)–C(40) 119.3(4), C(47)–C(48) 120.3(4); C(1)–S(1)–C(5) 102.76(2), C(24)–S(2)–C(27) 103.61(3).

C(20)–C(21)], which essentially shows a linear arrangement. The intramolecular sulfur–sulfur distance was determined to 1.85(3) nm.

## Conclusions

The synthesis of several macrocycles consisting of ethynyl-linked phenyl units based on acetylene scaffolding strategies is described. These macrocycles have been designed as model compounds to investigate the nature of switching mechanisms on a single-molecule level. They are functionalized by either *tert*-butyl- or acetyl-protected sulfanyl groups and with one or two nitro groups. These nitro groups were not only troublesome during the synthesis; they considerably reduce the stability features of the final macrocycles. Degradation of the *ortho*-nitro phenylethynyl substructure by intramolecular rearrangement to the heterocyclic isatogen substructure has been observed either upon heating or upon keeping these macrocycles for several weeks in solution. With respect to the intended investigation of switching properties of these structures, their tendency for intramolecular rearrangement reactions has to be considered also as potential origin of alterations in electronic transparency along the structure.

While the transport characteristics of these macrocycles are currently investigated in electronic circuits, we are applying the concept of a revolving turnstile as subunit of a macrocycle for molecular switches based on redox-switchable intramolecular interactions and for molecules comprising well-defined and tuneable spectroscopic transport characteristics.

## Experimental Section

**General Remarks:** All chemicals for synthesis were purchased and used without further purification. Toluene and THF have been dried by distillation over sodium/benzophenone. Dry DMF and dry $CH_3CN$ have been used as delivered from Aldrich. $CH_2Cl_2$ has been dried by distillation over $CaH_2$. Characterizations were performed with the following instruments: $^1H$ NMR and $^{13}C$ NMR spectra were recorded with a Bruker Ultra Shield 300 MHz or 500 MHz, the *J* values are given in Hz. MALDI-TOF spectra was performed with 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.

**4-Fluoro-2-(methoxymethoxy)-1-nitrobenzene (4):** To a mixture of 5-fluoro-2-nitrophenol (27.499 g, 0.175 mol) and potassium carbonate (48.38 g, 0.35 mol) in dry THF (250 mL) was added dropwise bromomethyl methyl ether (43.3 mL, 0.525 mol) at 0 °C. Then it was stirred overnight (18 h) at room temperature. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. The combined organic fractions were washed with sodium hydroxide to remove remaining starting material. After removing of the solvents the residue was purified by flash chromatography on silica gel (hexane/EtOAc, 9:1) to afford 4-fluoro-2-methoxymethoxy-1-nitrobenzene (**4**) as a yellowish liquid (78% yield, 27.457 g). $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 3.56 (s, 3 H, $CH_3$), 5.31 (s, 2 H, $OCH_2$), 6.79 (ddd, $^3J_{F,H}$ = 9.0 Hz, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H), 7.06 (dd, $^3J_{F,H}$ = 10.1 Hz, $^4J_{H,H}$ = 2.6 Hz, 1 H), 7.91 (dd, $^4J_{F,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.0 Hz, 1 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 57.0 ($CH_3$), 95.9 ($OCH_2$), 105.3 (d, $^2J_{F,C}$ = 27.0 Hz), 108.9 (d, $^2J_{F,C}$ = 23.8 Hz), 127.7 (d, $^3J_{F,C}$ = 11.3 Hz), 152.8 (d, $^3J_{F,C}$ = 11.5 Hz), 165.5 (d, $^1J_{F,C}$ = 255.8 Hz) ppm. $C_8H_8FNO_2$ (201.15): calcd. C 47.77, H 4.01, N 6.96; found C 47.69, H 3.93, N 6.91. MS (EI): *m*/*z* (%) = = 201.1 (30) [$M^+$], 170.0 (100) [$M^+ - OCH_3$], 140.1 (50) [$M^+ - C_2H_5O_2$].

**4-(*tert*-Butylsulfanyl)-2-(methoxymethoxy)-1-nitrobenzene (5):** To a solution of **4** (14.0 g, 0.07 mol) in dry DMF (50 mL) was added *t*BuSNa (1.1 equiv., 8.587 g) in several portions. The reaction mixtuire was stirred for 1 h at room temperature. The reaction mixture was poured into satd. solution of NaCl and the organic products were extracted with $Et_2O$. After removal of the solvents in vacuo, flash chromatography on silica gel (hexane/EtOAc, 9:1) afforded **5** as a yellowish liquid (14.435 g, 76%). $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.34 (s, 9 H, $CH_3$), 3.51 (s, 3 H, $CH_3$), 5.31 (s, 2 H, $OCH_2$), 7.21 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.48 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.75 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.2 ($CH_3$), 47.6 (SC), 56.8 ($OCH_3$), 95.4 ($OCH_2$), 124.9, 125.0, 129.3, 140.3, 141.0, 149.8 ppm. $C_{12}H_{17}NO_4S$ (271.33): calcd. C 53.12, H 6.32, N 5.16; found C 53.01, H 6.19, N 4.99. MS (EI): *m*/*z* (%) = 271.0 (25) [$M^+$], 215.0 (40) [$M^+ - C_4H_8$], 57.2 (100) [$C_4H_9^+$].

**5-(*tert*-Butylsulfanyl)-2-nitrophenol (6):** The MOM-protected phenol **5** (14.031 g, 0.0517 mol) was dissolved in methanol (200 mL) and concentrated HCl (15 mL) was added. After heating for 1 h to 60 °C, the reaction mixture was poured into cold water. After extraction with $Et_2O$ the combined organic phases were dried with $MgSO_4$. Flash chromatography (silica gel, hexane/EtOAc, 9:1) afforded **6** as a yellow liquid (11.1654 g, 95%). $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.40 (s, 9 H, $CH_3$), 7.05 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.9 Hz, 1 H), 7.29 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.01 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 10.65 (s, 1 H, OH) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.3 ($CH_3$), 48.1 (SC), 124.7, 125.1, 126.5, 132.8, 147.0, 154.5 ppm. $C_{10}H_{13}NO_3S$ (227.28): calcd. C 52.85, H 5.77, N 6.16; found C 52.45, H 5.71, N 6.07. MS (EI): *m*/*z* (%) = 227.1 (15) [$M^+$], 171.0 (20) [$M^+ - C_4H_8$], 57.2 (100) [$C_4H_9^+$].

**5-(*tert*-Butylsulfanyl)-2-nitrophenyl Trifluoromethanesulfonate (7):** To a solution of the phenol **6** (16.0 g, 70.4 mmol) in dry $CH_2Cl_2$, was added $Et_3N$ (2 equiv., 140.8 mmol, 19.5 mL), and the reaction mixture was cooled to 0 °C. After the dropwise addition of trifluoromethanesulfonic anhydride (1.1 equiv., 13 mL), the reaction was stirred for 1 h at 0 °C. The reaction mixture was concentrated and filtered through a silica plug. Flash chromatography on silica gel (hexane/$Et_2O$, 9:1) afforded **7** as a yellow solid (22.5148 g, 89%). M.p. 38–40 °C. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.39 (s, 9 H, $CH_3$), 7.56 (d, $^4J_{H,H}$ = 1.7 Hz, 1 H), 7.66 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.12 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.1 ($CH_3$), 48.8 (SC), 118.7 (q, $^1J_{F,C}$ = 320 Hz), 126.4, 130.55, 130.57, 135.8, 140.9, 144.5 ppm. $C_{11}H_{12}F_3NO_5S_2$ (359.34): calcd. C 36.77, H 3.37, N 3.90; found C 37.06, H 3.02, N 4.03. MS (EI): *m*/*z* (%) = 359.1 (5) [$M^+$], 57.2 (100) [$C_4H_9^+$].

**4-Iodo-3-nitrophenol (9):**[35] A solution of $NaNO_2$ (187 g, 2.71 mol) in $H_2O$ (280 mL) was added dropwise to a mechanically stirred suspension of 4-amino-3-nitrophenol (**8**) (209 g, 1.36 mol) in concentrated HCl (500 mL) and $H_2O$ (85 mL) over 1 h at 0 °C . Subsequently, a solution of KI (450 g, 2.71 mol) in $H_2O$ (350 mL) was

added dropwise over 1.5 h at 0 °C. The speed at which both reagents were added was chosen such that stirring was maintained in spite of precipitation. After stirring the reaction mixture overnight at room temperature, the precipitate was collected by filtration, washed with water and dried under vacuum. CC of the crude product ($SiO_2$, hexane/$Et_2O$, 4:1) afforded **9** as red-orange crystalline solid (299 g, 83%). M.p. 155–156 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 5.34 (br. s, 1 H, OH), 6.82 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 3 Hz, 1 H, 6-H), 7.40 (d, $^4J_{H,H}$ = 3.0 Hz, 1 H, 2-H), 7.85 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 5-H), ppm. $^{13}$C NMR (75 MHz, $CD_3CN$, 25 °C): $\delta$ = 73.4, 113.4, 122.3, 143.0, 154.9 (br. s), 158.8 ppm. $C_6H_4INO_3$ (265.01): calcd. C 27.19, H 1.52, N 5.29; found C 27.43, H 1.56, N 5.24. MS (EI): *m*/*z* (%) = 264.9 (100) [$M^+$], 218.9 (26) [$M^+ - NO_2$].

***O*-(4-Iodo-3-nitrophenyl) Diethylthiocarbamate (10):** A solution of KOH (51.1 g, 0.911 mol) in $H_2O$ (155 mL) was added dropwise to a stirred solution of 4-iodo-3-nitrophenol (**9**) (221 g, 0.834 mol) in THF (1500 mL) over 25 min at 0 °C. Subsequently, a solution of *N*,*N*-diethylthiocarbamoyl chloride (152 g, 1 mol) in THF (400 mL) was added dropwise over 15 min at 0 °C. The reaction mixture was stirred at room temperature for 16 h. The solid precipitate was removed by filtration. The water phase of the filtrate was extracted by $CH_2Cl_2$ (2×250 mL) and combined with the organic phase of the filtrate. Removing of the solvents resulted in an oil. Crystalization from ethanol afforded **10** as yellow crystals (265 g, 84%). M.p. 75.5–76.5 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 8.02 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, 5-H), 7.65 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, 2-H), 7.05 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.7 Hz, 1 H, 6-H), 3.87 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2$), 3.68 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2$), 1.32 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_3$), 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 11.7, 14.0 ($CH_3$), 44.7, 48.8 ($CH_2$), 82.4, 121.0, 128.9, 142.1, 152.8, 154.0, 185.2 ppm. $C_{11}H_{13}IN_2O_3S$ (380.20): calcd. C 34.75, H 3.45, N 7.37; found; C 34.73, H 3.19, N 7.27. MS (MALDI-TOF): found *m*/*z* 380.5582, 379.9686 calculated for $C_{11}H_{13}IN_2O_3S$.

***S*-(4-Iodo-3-nitrophenyl) Diethylthiocarbamate (11):** Ester **10** (235 g, 0.618 mol) was melted and heated at 190 °C for 4 h under argon. (**CAUTION**: Upon heating to temperatures higher than 190 °C, the melt decomposes with violent explosion!) After cooling to room temperature, the crude product was purified by CC ($SiO_2$, $CH_2Cl_2$). Crystallization from EtOH afforded **11** as yellow crystals (201 g, 86%). M.p. 81–81.5 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.17 (br. s, 3 H, $CH_3$), 1.28 (br. s, 3 H, $CH_3$), 3.42 (q, $^3J_{H,H}$ = 7.2 Hz, 4 H, $CH_2$), 7.37 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 2.1 Hz, 1 H, 6-H), 8.00 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, 2-H), 8.02 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 13.2, 14.0 ($CH_3$), 42.8, 87.3 ($CH_2$), 131.7, 131.9, 140.1, 142.1, 152.8, 163.3 (C=O) ppm. $C_{11}H_{13}IN_2O_3S$ (380.20): calcd. C 34.75, H 3.45, N 7.37; found C 34.75, H 3.07, N 7.04. MS (MALDI-TOF): found *m*/*z* 380.5272, 379.9686 calculated for $C_{11}H_{13}IN_2O_3S$.

***S*-(3-Amino-4-iodophenyl) Diethylthiocarbamate (12):** Tin powder (205 g, 1.73 mol) was slowly added in portions to a solution of **11** (219 g, 0.576 mol) in EtOH (900 mL) and AcOH (260 mL, 4.55 mol) at 60 °C. The reaction mixture was refluxed for 3 h and subsequently filtered through sea sand. The filtrate was evaporated and the crude was distributed between 10% KOH (2 L) and $CHCl_3$. The aqueous layer was extracted by $CHCl_3$ (3×2 L) and the combined organic layers dried with $MgSO_4$. Evaporation of the solvents and crystallization from EtOH afforded **12** as beige crystalline solid (183 g, 91%). M.p. 109.5–110 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.16 (br. s, 3 H, $CH_3$), 1.25 (br. s, 3 H, $CH_3$), 3.41 (q, $^3J_{H,H}$ = 7.2 Hz, 4 H, $CH_2$), 6.63 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 2.1 Hz, 1 H, 6-H), 6.94 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, 2-H), 7.63 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 13.2, 13.8 (br. s, $CH_3$), 42.5, 85.6 ($CH_2$), 121.5, 126.6, 129.8, 139.2, 147.3, 165.4 (C=O) ppm. $C_{11}H_{15}IN_2OS$ (350.22): calcd. C 37.72, H 4.32, N 8.00; found C 37.85, H 4.17, N 7.95. MS (MALDI-TOF): found *m*/*z* 350.7293, 349.9944 calculated for $C_{11}H_{15}IN_2OS$.

***S*-[4-Iodo-3-(pyrrolidin-1-ylazo)phenyl] Diethylthiocarbamate (13):** A solution of **12** (187 g, 0.534 mol) in dry THF (600 mL) was added over 30 min to a stirred solution of $BF_3{\cdot}Et_2O$ (268 mL, 2.13 mol) in THF under argon at –20 °C. Subsequently, a solution of *t*BuONO (240 mL, 1.86 mol) in dry THF (600 mL) was added over 45 min. The reaction mixture was warmed to –5 °C, during another 40 min the diazonium salt precipitated. The precipitation was completed by pouring the reaction mixture into cold EtOH (2 L). The precipitation was collected on a fritted disc funnel, washed with cold $Et_2O$ (2×500 mL) and dissolved in $CH_3CN$ (500 mL). Pyrrolidine (132 mL, 1.60 mol) and an aqueous solution of $Na_2CO_3$ (170 g, 1.60 mol) were slowly added at 0 °C, and the mixture was stirred for 2 h at room temperature. The crude product was precipitated by pouring the reaction mixture into $H_2O$ (2 L). The precipitate was collected by filtration and washed with water. A first portion was isolated by crystallization from EtOH. Evaporation of the mother liquid and subsequent CC ($SiO_2$, hexane/$Et_2O$, 1:1) afforded another portion. Combination of both portions gave the ester **13** as a pink crystalline solid (113 g, 49%). M.p. 106.5–107 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.21 (br. s, 6 H, $CH_3$), 2.02 (br. s, 4 H, $CH_2$-$\beta$-$N_3$), 3.41 (q, $^3J_{H,H}$ = 7.2 Hz, 4 H, $CH_2$), 3.72 (br. s, 2 H, $CH_2$–$N_3$), 3.92 (br. s, 2 H, $CH_2$–$N_3$), 6.97 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.1 Hz, 1 H, 6-H), 7.49 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, 2-H), 7.83 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, 5-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 13.2, 13.8 (br. s, $CH_3$), 23.6, 24.1 (br. s, $CH_2$-$\beta$-$N_3$), 42.4 ($CH_2$–N), 47.3 ($CH_2$–$N_3$), 51.1, 97.9, 124.3, 129.6, 133.3, 139.3, 150.8, 165.3 (C=O) ppm. $C_{15}H_{21}IN_4OS$ (432.32): calcd. C 41.67, H 4.90, N 12.96; found; C 41.94, H 4.94, N 13.14. MS (MALDI-TOF): calcd. for $C_{15}H_{21}IN_4OS$ 432.0475; found 432.6874.

**3,3′-Dibromotolane (15):** Compound **15** was synthesized according to a literature procedure.[38] Yield 81% (white solid). M.p. 105–107 °C (ref.[38] 102 °C). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.23 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.42–7.52 (m, 4 H), 7.68 (t, $^4J_{H,H}$ = 1.6 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 89.2 (C≡C), 122.4, 124.9, 130.0, 130.3, 131.9, 134.5 ppm. MS (EI): *m*/*z* (%) = 336.0 (100) [$M^+$], 176.0 (75) [$M^+ - 2$ Br].

**3,3′-Bis(trimethylsilylethynyl)tolane (16):** The dibromotolane **15** (8.70 g, 26.0 mmol) was dissolved in degassed dry THF (250 mL). Subsequently trimethylsilylacetylene (3.5 equiv., 91.0 mmol, 12.8 mL), $Pd(PPh_3)_2Cl_2$ (0.9124 g, 1.3 mmol), CuI (0.4951 g, 2.6 mmol) and $Et_3N$ (40 mL) were added under nitrogen. After refluxing for 4 h, all solvents were removed, the residue dissolved in $CH_2Cl_2$ and absorbed on silica gel. CC (silica gel, hexane) gave **16** as a white solid (9.3473 g, 97%). M.p. 112–113 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.26 (s, 18 H, $CH_3$), 7.29 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H), 7.43 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H), 7.64 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.06 ($CH_3$), 89.2 (C≡C), 95.2 (C≡C), 104.2 (C≡C), 123.4, 123.7, 128.5, 131.6, 131.9, 135.2 ppm. $C_{24}H_{26}Si_2$ (370.63): calcd. C 77.77, H 7.07; found C 77.44, H 7.11. MS (MALDI-TOF): calcd. for $C_{24}H_{26}Si_2$ 370.1568; found 370.0192.

**3,3′-Bis(ethynyl)tolane (17):** $K_2CO_3$ (6 equiv., 145.8 mmol, 20.15 g) was added to a solution of **16** (9.01 g, 24.3 mmol) in degassed $CH_2Cl_2$/MeOH (200 mL, 1:1). After stirring for 1 h under $N_2$,

water was added. Extraction with $CH_2Cl_2$ and filtration through a silica plug gave **11** (5.498 g, 98%) as a white solid. M.p. 109–110 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 3.11 (s, 2 H, ≡CH), 7.31 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.48 (m, 4 H), 7.66 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 78.0 (C≡C), 82.8 (C≡C), 89.1 (C≡C), 122.7, 123.4, 128.6, 132.0, 132.2, 135.3 ppm. $C_{18}H_{10}$ (226.27): calcd. C 95.55, H 4.45; found C 95.72, H 4.47. MS (EI): *m*/*z* (%) = 226.1 (100) [M$^+$], 224.0 (35) [M$^+$–2H].

**2-Nitro-1,4-bis(trimethylsilanylethynyl)benzene (19):** Synthesized according to ref.[39]. Yield 61%. M.p. 78.5–79.5 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.26 (s, 9 H, $SiCH_3$), 0.27 (s, 9 H, $SiCH_3$), 7.56–7.58 (m, 2 H), 8.06–8.08 (m, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = –0.3, –0.2, 99.2, 99.7, 102.0, 105.9, 118.0, 124.3, 127.9, 135.0, 135.6, 150.3 ppm. MS (EI): *m*/*z* (%) = 315.1 (28) [M$^+$], 300.1 (100) [M$^+$–$CH_3$].

**1,4-Diethynyl-2-nitrobenzene (20):** Synthesized according to ref.[39]. Yield 58%. M.p. 123–125 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 3.31 (s, 1 H, ≡CH), 3.61 (s, 1 H, ≡CH), 7.63–7.67 (m, 2 H), 8.13–8.15 (m, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 78.3, 80.8, 81.9, 87.1, 117.6, 123.9, 128.2, 135.6, 136.0, 150.2 ppm. MS (EI): *m*/*z* (%) = 171.0 (100) [M$^+$], 125.0 (31) [M$^+$–$NO_2$].

**(4-Bromo-2-nitrophenylethynyl)trimethylsilane (21):** 1,4-Dibromo-2-nitrobenzene (18.157 g, 64.6 mmol) was dissolved in dry and degassed THF (250 mL). $Pd(PPh_3)_2Cl_2$ (2.2671 g, 3.2 mmol), CuI (1.2302 g, 6.46 mmol), *i*$Pr_2$NH (6 mL) and trimethylsilylacetylene (6.980 g, 71.0 mmol) were added. After stirring for 2 h at room temperature under $N_2$, the solvents were removed and the residue adsorbed on silica gel. CC (silica gel, hexane/ethyl acetate, 9:1) afforded **13** (10.2101 g, 53%) as yellow liquid. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.27 (s, 9 H, $CH_3$), 7.51 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.67 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.1 Hz, 1 H), 8.16 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = –0.3 ($CH_3$), 98.5 (C≡C), 105.5 (C≡C), 117.5, 122.3, 127.7, 135.9, 136.2, 150.5 ppm. $C_{11}H_{12}BrNO_2Si$ (298.21): calcd. C 44.30, H 4.06, N 4.70; found C 44.39, H 3.98, N 4.65. MS (EI): *m*/*z* (%) = 297.0 (25) [M$^+$], 282.0 (100) [M$^+$–$CH_3$].

**2-Nitro-4-[(triisopropylsilanyl)ethynyl]-1-(trimethylsilanylethynyl)-benzene (22):** Triisopropylsilylacetylene (2.7521 g, 15.0 mmol) was added to a solution of **21** (3.00 g, 10.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.3509 g, 0.5 mmol), CuI (0.190 g, 1.0 mmol) and $(i\text{Pr})_2$NH (4 mL) in degassed THF (150 mL). The reaction mixture was stirred for 16 h at room temperature. The solvents were removed and the residue was absorbed on silica gel and purified by CC (hexane/ethyl acetate, 9:1) to afford **22** (2.5179 g, 63%) as a brownish liquid. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.28 (s, 9 H, $CH_3$), 1.12 (apparent s, 21 H, CH, $CH_3$), 7.52–7.62 (m, 2 H), 8.06 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = –0.06 ($SiCH_3$), 11.6 ($SiCH_3$), 19.0 ($CH_3$), 96.7 (C≡C), 99.4 (C≡C), 104.2 (C≡C), 106.0 (C≡C), 118.1, 124.8, 128.1, 135.2, 135.9, 150.3 ppm; $C_{22}H_{33}NO_2Si_2$ (399.67): calcd. C 66.11, H 8.32, N 3.50; found C 66.03, H 8.11, N 3.39. MS (EI): *m*/*z* (%) = 399.1 (6) [M$^+$], 356.1 (100) [M$^+$–$C_3H_7$].

**(4-Ethynyl-3-nitrophenylethynyl)triisopropylsilane (23):** $K_2CO_3$ (3 equiv., 0.017 mol, 2.3841 g) was added to a solution of **22** (2.30 g, 5.75 mmol) in degassed $CH_2Cl_2$/MeOH (1:1, 100 mL),. The reaction mixture was stirred for 30 min at room temperature. Extraction with $CH_2Cl_2$ and filtration through a silica plug afforded **23** (1.8077 g, 96%) as a whitish solid. M.p. 42–43 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.13 (apparent s, 21 H, CH, $CH_3$), 3.61 (s, 1 H, ≡CH), 7.60–7.64 (m, 2 H), 8.11 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 11.6 (SiCH), 19.0 ($CH_3$), 78.3 (C≡C), 86.6 (C≡C), 96.7 (C≡C), 103.6 (C≡C), 116.7, 125.1, 127.7, 135.2, 135.7, 150.4 ppm. $C_{19}H_{25}NO_2Si$ (327.49): calcd. C 69.68, H 7.69, N 4.28; found C 70.02, H 7.91, N 4.40. MS (MALDI-TOF): calcd. for $C_{19}H_{25}NO_2Si$ 327.1649; found 327.7591.

**1,4-Dibromo-2,3-dinitrobenzene (25):** Synthesized according to ref.[40]. The desired product was separated by CC (silica, ether/hexane, 1:1) to provide **25** as a yellowish solid (17% yield). M.p. 162–163 °C (ref.[44] 159–160 °C). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.75 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 114.5, 137.0, 144.6 ppm. $C_6H_2BrN_2O_4$ (325.90): calcd. C 22.11, H 0.62, N 8.60; found C 22.13, H 0.63, N 8.84. MS (EI): *m*/*z* (%) = 325.8 (100) [M$^+$].

**2,3-Dinitro-1,4-bis(trimethylsilanylethynyl)benzene (26):** Trimethylsilylacetylene (5.38 mL, 0.0381 mol) was added to a solution of 1,4-dibromo-2,3-dinitrobenzene **25** (4.1422 g, 0.0127 mol), $Pd(PPh_3)_4$ (0.3669 g, 0.32 mmol), CuI (0.1209 g, 0.64 mmol) and $(i\text{Pr})_2$NEt (3 mL) in degassed THF (100 mL). After stirring for 18 h at room temperature, the solvents were removed and the residue was absorbed on silica gel. Purification by CC (silica, hexane/dichloromethan: 2:1) afforded **26** (2.8963 g, 63%) as a whitish solid. M.p. 98–100 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.26 (s, 18 H, $CH_3$), 7.66 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = –0.5 ($CH_3$), 95.8 (C≡C), 108.4 (C≡C), 118.4, 135.4 ppm. $C_{16}H_{20}N_2O_4Si_2$ (360.51): calcd. C 53.31, H 5.59, N 7.77; found C 53.67, H 5.58, N 7.51. MS (EI): *m*/*z* (%) = 360.1 (20) [M$^+$], 345.1 (100) [M$^+$–$CH_3$].

**(4-Ethynyl-2,3-dinitrophenylethynyl)trimethylsilane (27) and 1,4-Diethynyl-2,3-dinitrobenzene (28):** A solution of **26** (7.02 g, 0.0195 mol) in degassed $CH_2Cl_2$/MeOH (500 mL, 1:1) and acetic acid (0.5 mL) was treated with portions of potassium fluoride (0.5 equiv., 9.75 mmol, 0.5665 g). After stirring for 30 min at room temperature, the reaction mixture was extracted with $CH_2Cl_2$. Purification by CC (silica, hexane/$CH_2Cl_2$, 1:1) afforded (4-ethynyl-2,3-dinitrophenylethynyl)trimethylsilane as a whitish solid (1.8554 g, 33%) and 1,4-diethynyl-2,3-dinitrobenzene as beige solid (1.8192 g, 43%).

**(4-(Ethynyl-2,3-dinitrophenylethynyl)trimethylsilane (27):** M.p. 86–87 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.25 (s, 9 H, $CH_3$), 3.59 (s, 1 H, ≡CH), 7.67 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 7.70 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = –06 ($CH_3$), 75.4 (C≡C), 88.5 (C≡C), 95.5 (C≡C), 108.9 (C≡C), 117.2, 119.1, 135.7, 135.9, 145.1, 145.4 ppm. $C_{13}H_{12}N_2O_4Si$ (288.33): calcd. C 54.15, H 4.19, N 9.72; found C 54.06, H 4.54, N 9.38. MS (EI): *m*/*z* (%) = 288.0 (20) [M$^+$], 273.1 (100) [M$^+$–$CH_3$].

**1,4-Diethynyl-2,3-dinitrobenzene (28):** M.p. 170–173 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 3.61 (s, 2 H, ≡CH), 7.74 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 75.3 (C≡C), 88.9 (C≡C), 118.2, 136.1, 144.0 ppm. MS (EI): *m*/*z* (%) = 216.0 (100) [M$^+$], 127.0 (96), 99.0 (48), 98 (47), 86 (50).

**3,3′-Bis[(5′′-*tert*-butylsulfanyl-2′′-nitrophenyl)ethynyl]tolane (29):** A mixture of **17** (6.8 g, 0.03 mol), **7** (27.0 g, 0.075 mol), $Pd(PPh_3)_4$ (1.7175 g, 1.49 mmol), CuI (0.2856 g, 1.50 mmol) and triethylamine (50 mL) in dry, degassed THF (300 mL) was stirred for 4 h at room temperature. All solvents were removed and the residue was adsorbed on silica gel. CC (silica, $CH_2Cl_2$/hexane: 1:1) afforded **29** as yellow solid (17.0227 g, 88%). M.p.162–164 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.38 (s, 18 H, $CH_3$), 7.39 (t, 2 H, $^3J_{H,H}$ = 7.9 Hz), 7.53–7.62 (m, 6 H), 7.79 (s, 2 H), 7.86 (d, 2 H, $^4J_{H,H}$ = 1.9 Hz), 8.04 (d, 2 H, $^3J_{H,H}$ = 8.6 Hz) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.3 ($CH_3$), 47.9 (SC), 85.2 (C≡C), 89.3 (C≡C), 96.7 (C≡C), 118.7, 122.8, 123.6, 124.8, 128.8, 132.1, 132.6, 135.3, 136.5, 140.6, 142.0, 149.2 ppm. $C_{38}H_{32}N_2O_4S_2$ (644.80): calcd. C 70.78, H 5.00, N 4.34; found C 70.98, H 5.21, N

4.29. MS (MALDI-TOF): calcd. for $C_{38}H_{32}N_2O_4S_2$ 644.1798; found 644.6097.

**1,4-Bis{2′-[4′′-(diethylcarbamoylsulfanyl)-2′′-(pyrrolidin-1′′′-ylazo)-phenyl]ethynyl}-2-nitrobenzene (30):** A solution of 1,4-diethynyl-2-nitrobenzene (**20**) (0.058 g, 0.268 mmol), **13** (0.232 g, 2 equiv., 0.536 mmol), $Pd(PPh_3)_2Cl_2$ (9.4 mg, 0.0134 mmol), CuI (5.1 mg, 0.0268 mmol) and $Et_3N$ (0.7 mL) in degassed THF (10 mL) was stirred for 16 h at room temperature under nitrogen. All solvents were removed, the residue was dissolved in $CH_2Cl_2$ and absorbed on silica gel. Purification by CC (silica, toluene/ethyl acetate, 8:2) afforded **30** as a yellow oil (0.03 g, 14%). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.22 (br. s, 12 H, $CH_3$), 2.06 (br. s, 8 H, $CH_2$), 3.43 (q, $^3J_{H,H}$ = 7.2 Hz, 8 H, $CH_2$), 3.72 (br. s, 4 H, $CH_2$), 3.92 (br. s, 4 H, $CH_2$), 7.22–7.28 (m, 2 H), 7.51 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 7.57 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.62–7.68 (m, 4 H), 8.18 (br. s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 13.2 (br. s, $CH_3$), 13.8 (br. s, $CH_3$), 23.8 (br. s, $CH_2$), 24.2 (br. s, $CH_2$), 42.5 ($CH_3$), 47.2 (br. s, $CH_2$), 51.4 (br. s, $CH_2$), 90.1, 92.4, 94.8, 98.0, 117.5, 117.6, 118.6, 124.0, 124.5, 127.7, 130.9, 131.2, 131.4, 131.6, 133.0, 133.7, 134.9, 135.1, 147.5, 149.2, 153.0, 153.2, 165.25, 165.29 ppm. MS (MALDI-TOF): calcd. for $C_{40}H_{45}N_9O_4S_2$ 779.3931; found 779.2193.

**3,3′-Bis[(2′′-amino-5′′-*tert*-butylsulfanylphenyl)ethynyl]tolane (31):** To a solution of compound **29** (16.0 g, 0.024 mol) in THF (200 mL) was added concentrated HCl (10 mL) followed by portions of tin powder (6 equiv., 0.144 mol, 17.091 g). The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was poured into water. After neutralization with a NaOH solution the organic phase was extracted with $CH_2Cl_2$. Filtration through a short column with $CH_2Cl_2$ afforded **31** as a white solid (13.3343 g, 95%). M.p. 208–210 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.27 (s, 18 H, $CH_3$), 4.42 (br. s, 4 H, $NH_2$), 6.68 (d, 2 H, $^3J_{H,H}$ = 8.4 Hz), 7.29 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.1 Hz, 2 H), 7.36 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.50 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H), 7.54 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H), 7.71 (s, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.1 ($CH_3$), 45.9 (SC), 86.3 (C≡C), 89.5 (C≡C), 94.5 (C≡C), 108.1, 114.6, 120.6, 123.8, 123.9, 129.0, 131.68, 131.73, 134.8, 139.8, 141.5, 148.8 ppm. $C_{38}H_{36}N_2S_2$ (584.84): calcd. C 78.04, H 6.20, N 4.79; found C 77.86, H 6.24, N 4.58. MS (MALDI-TOF): calcd. for $C_{38}H_{36}N_2S_2$ 584.2314; found 583.6667.

**3,3′-Bis[(5′′-*tert*-butylsulfanyl-2′′-iodophenyl)ethynyl]tolane (32):** To a solution of **32** (13.012 g, 0.022 mol) in dry THF (250 mL) was added $BF_3{\cdot}Et_2O$ (14 equiv., 0.31 mol) over 30 min at –20 °C until the starting compound disappeared (monitored by TLC). *tert*-BuONO (4 equiv., 0.088 mol) in THF (20 mL) was added over 15 min. The reaction mixture was warmed to –5 °C over 30 min. After this time the yellow solid started to precipitate. Cold hexane (100 mL) was added to effect precipitation of the yellow diazonium salt. The salt was filtered and washed with cold hexane. The diazonium salt was dissolved in cold acetonitrile (100 mL) and a solution of KI (6 equiv.) and $I_2$ (3 equiv.) in water/acetonitrile was added. During this addition a brown solid was precipitated and $CH_2Cl_2$ (50 mL) was added in order to dissolve it. The reaction mixture was stirred for 16 h at room temperature. Then it was extracted with $CH_2Cl_2$ and washed with a solution of $Na_2S_2O_3$ in order to remove unreacted iodine. The solvent was removed and the residue was absorbed on silica gel. Purification by CC (silica, hexane/$CH_2Cl_2$, 1:1) afforded a mixture of the desired tolane **32** and the monoiodinated derivative. Recrystallization from ethyl acetate afforded **32** as a whitish powder (6.76 g, 38%). M.p. 169.5–170.5 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.31 (s, 18 H, $CH_3$), 7.17 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.2 Hz, 2 H), 7.38 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.54 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H), 7.58 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.68 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H), 7.79 (s, 2 H), 7.83 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.1 ($CH_3$), 46.6 (SC), 89.3 (C≡C), 91.9 (C≡C), 92.7 (C≡C), 102.2, 123.3, 123.6, 128.8, 130.1, 131.7, 132.0, 133.3, 134.8, 138.5, 139.0, 140.9 ppm. $C_{38}H_{32}I_2S_2$ (806.60): calcd. C 56.58, H 4.00; found C 56.93, H 4.01. MS (EI): *m*/*z* (%) = 806.8 (10) [$M^+$], 749.7 (10) [$M^+ - C_4H_9$], 694.1 (100) [$M^+ - C_8H_{17}$].

**3-{[5′′-*tert*-Butylsulfanyl-3′′-(2′′′-nitro-4′′′-triisopropylsilylethynylphenyl)ethynyl]phenylethynyl}-3′-(5′′′′-*tert*-butylsulfanyl-2′′′′-iodophenylethynyl)tolane (33) and 3,3′-Bis{[5′′-*tert*-butylsulfanyl-2′′-(2′′′-nitro-4′′′-triisopropylsilylethynylphenyl)ethynyl]phenylethynyl}-tolane (34):** $Pd(PPh_3)_4$ (0.3721 g, 0.322 mmol) and CuI (0.1206 g, 0.633 mmol) were added o a solution of **32** (2 equiv., 6.44 mmol, 5.2094 g) in degassed THF (500 mL), ($i$Pr)$_2$NEt (4 mL). A solution of **20** (1.0549 g, 3.22 mmol) in degassed THF (100 mL) was added dropwise over 10 h at room temperature. The reaction mixture was stirred for 16 h room temperature. The solvents were removed and the residue adsorbed on silica gel. Purification by CC (silica, hexane/$CH_2Cl_2$, 2:1) afforded the monosubstituted desired product **33** (2.0735 g, 64%) and the doubly substituted derivative **34** (1.166 g, 30%).

**Compound 33:** M.p. 74.5–76.5 °C (yellow solid). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.11 (s, 3 H, SiCH), 1.12 (s, 18 H, $CH_3$), 1.31 (s, 9 H, $CH_3$), 1.34 (s, 9 H, $CH_3$), 7.17 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.2 Hz, 1 H), 7.37 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H), 7.48–7.64 (m, 7 H), 7.65–7.70 (m, 2 H), 7.75–7.81 (m, 3 H), 7.83 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 8.17 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 11.4 (SiCH), 18.8 ($CH_3$), 31.1 ($SCCH_3$), 31.2 ($SCCH_3$), 46.6 (SC), 47.2 (SC), 88.1 (C≡C), 89.29 (C≡C), 89.33 (C≡C), 90.0 (C≡C), 91.9 (C≡C), 92.7 (C≡C), 93.6 (C≡C), 96.8 (C≡C), 97.1 (C≡C), 102.2 (C≡C), 104.1, 118.0, 123.3, 123.4, 123.55, 123.56, 124.7, 124.9, 126.1, 128.2, 128.7, 128.8, 130.1, 131.66, 131.74, 131.9, 132.0, 132.6, 133.29, 133.31, 134.7, 134.8, 135.0, 135.9, 137.1, 138.4, 138.9, 140.5, 140.9, 149.3 ppm. $C_{57}H_{56}INO_2S_2Si$ (1006.18): calcd. C 68.04, H 5.61, N 1.39; found C 68.22, H 5.77, N 1.46. MS (MALDI-TOF): calcd. for $C_{57}H_{56}INO_2S_2Si$ 1005.2561; found 1005.4937.

**Compound 34:** M.p. 155–157 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.11 (s, 6 H, SiCH), 1.12 (s, 36 H, $CH_3$), 1.34 [s, 18 H, $SC(CH_3)$], 7.37 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.49–7.64 (m, 10 H), 7.68 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.75 (d, $^4J_{H,H}$ = 1.7 Hz, 2 H), 7.77–7.79 (m, 2 H), 8.16 (d, $^4J_{H,H}$ = 1.6 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 11.3, 18.8, 31.2, 47.2, 88.1, 89.3, 90.0, 93.6, 96.8, 97.1, 104.0, 118.0, 123.4, 123.6, 124.7, 124.9, 126.1, 128.2, 128.8, 131.7, 131.9, 132.6, 134.8, 134.98, 134.99, 135.9, 137.1, 140.5, 149.3 ppm. $C_{76}H_{80}N_2O_4S_2Si_2$ (1204.76): calcd. C 75.70, H 6.69, N 2.32; found C 76.02, H 6.71, N 2.46. MS (MALDI-TOF): calcd. for $C_{76}H_{80}N_2O_4S_2Si_2$ 1204.5093; found 1204.2429.

**3-{[5′′-*tert*-butylsulfanyl-3′′-(4′′′-Ethynyl-2′′′-nitrophenyl)-ethynyl]phenylethynyl}-3′-(5′′′′-*tert*-butylsulfanyl-2′′′′-iodophenylethynyl)tolane (35):** To a solution of **33** (2.80 g, 2.78 mmol) in degassed THF (200 mL) was added glacial acetic acid (3 drops), followed by 16 mL of a 1 M TBAF/THF solution. After stirring for 30 min at room temperature, the solvents were removed and the residue adsorbed on silica gel. Purification by CC (silica, hexane/$CH_2Cl_2$, 1:1) afforded **35** (2.202 g, 93%) as a yellow solid. M.p. 80.0–81.5 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.31 (s, 9 H, $CH_3$), 1.34 (s, 9 H, $CH_3$), 3.27 (s, 1 H, ≡CH), 7.17 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.1 Hz, 1 H), 7.38 (td, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 3.0 Hz, 2 H), 7.49–7.61 (m, 6 H), 7.65 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.68 (d, $^3J_{H,H}$ = 2.1 Hz, 1 H), 7.72 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H),

7.75 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.77 (t, $^4J_{H,H}$ = 1.5 Hz, 2 H), 7.84 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 8.21 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.1 ($CH_3$), 31.2 ($CH_3$), 46.6 (SC), 47.2 (SC), 81.0 (C≡C), 81.8 (C≡C), 88.2 (C≡C), 89.28 (C≡C), 89.31 (C≡C), 89.8 (C≡C), 91.9 (C≡C), 92.7 (C≡C), 93.7 (C≡C), 97.5 (C≡C), 102.2, 118.8, 123.31, 123.38, 123.41, 123.6, 124.9, 126.2, 128.5, 128.79, 128.81, 130.1, 131.7, 132.1, 132.6, 132.9, 133.32, 133.34, 134.8, 135.01, 135.05, 135.1, 136.1, 137.09, 137.11, 138.5, 139.0, 140.4, 140.9, 149.2 ppm. $C_{48}H_{36}INO_2S_2$ (849.84): calcd. C 67.84, H 4.27, N 1.65; found C 67.95, H 4.59, N 1.61. MS (MALDI-TOF): calcd. for $C_{48}H_{36}INO_2S_2$ 849.1227; found 849.3932.

**3,22-Bis(*tert*-butylsulfanyl)-28-nitro-5,6,12,13,19,20,25,26,31,32-decadehydro-27,30-etheno-7,11:14,18-dimethenodibenzo[*a*,*k*]cyclooctacosane (36):** $Pd(PPh_3)_4$ (1 equiv., 1.6694 g) and CuI (1 equiv., 0.2742 g) were added under nitrogen to a solution of **35** (1.2277 g, 1.44 mmol) in dry and degassed toluene (6 L), ($i$Pr)$_2$NEt (20 mL). The reaction mixture was stirred for 20 h at room temperature. All solvents were removed and the residue was dissolved in $CH_2Cl_2$. Absorption on silica gel and subsequent CC (silica, hexane/$CH_2Cl_2$, 1:2 to 1:1) afforded the macrocycle **36** as a yellow solid (0.3116 g, 30%). No m.p., compound decomposes above 345 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.35 (s, 18 H, $CH_3$), 7.39 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.48–7.58 (m, 7 H), 7.63 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 7.68–7.77 (m, 4 H), 7.97 (s, 2 H), 8.37 (s, 1 H) ppm. $^{13}$C NMR (75 MHz, [D$_8$]THF, 25 °C): $\delta$ = 29.0 ($CH_3$), 44.8 (SC), 44.9 (SC), 86.5 (C≡C), 87.3 (C≡C), 87.4 (C≡C), 88.1 (C≡C), 90.1 (C≡C), 90.5 (C≡C), 91.9 (C≡C), 92.0 (C≡C), 92.1 (C≡C), 95.1 (C≡C), 116.4, 121.9, 122.0, 122.1, 122.8, 123.4, 123.6, 124.4, 124.5, 126.2, 127.28, 127.34, 129.74, 129.72, 130.0, 130.1, 130.4, 130.8, 133.1, 133.2, 133.4, 133.8, 134.0, 135.3, 138.1, 148.6 ppm. $C_{48}H_{35}NO_2S_2$ (721.93): calcd. C 79.86, H 4.89, N 1.94; found C 79.63, H 4.66, N 2.05. MS (MALDI-TOF): calcd. for $C_{48}H_{35}NO_2S_2$ 721.2104; found 721.6479.

**3,22-Bis(acetylsulfanyl)-28-nitro-5,6,12,13,19,20,25,26,31,32-decadehydro-27,30-etheno-7,11:14,18-dimethenodibenzo[*a*,*k*]cyclooctacosane (1):** To a solution of **36** (20.1 mg, 0.0278 mmol) in degassed and dry $CH_2Cl_2$ (25 mL), toluene (1 mL) and acetyl chloride (5 mL) was added dropwise a solution of $BBr_3$ in $CH_2Cl_2$ (0.5 mL) at room temperature. After the addition of $BBr_3$, the reaction mixture was stirred for 15 min and subsequently pored on ice water. The organic compounds were extracted with $CH_2Cl_2$. Evaporation of the solvent, absorption of the residue on silica gel and subsequent purification by CC (silica, hexane/$CH_2Cl_2$, 1:2) afforded the target compound **1** as a yellow solid (9.5 mg, 49%). M.p. 296–298 °C. $^1$H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): $\delta$ = 2.47 (s, 6 H, $CH_3$), 7.37–7.44 (m, 4 H), 7.54–7.59 (m, 4 H), 7.66 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.67–7.72 (m, 4 H), 7.74 (s, 1 H), 7.95–8.00 (m, 2 H), 8.38 (br. s, 1 H) ppm. $^{13}$C NMR (126 MHz, $C_2D_2Cl_4$, 25 °C): $\delta$ = 30.3 ($CH_3$), 87.8 (C≡C), 88.98 (C≡C), 89.03 (C≡C), 89.7 (C≡C), 91.9 (C≡C), 94.0 (C≡C), 94.1 (C≡C), 97.0 (C≡C), 100.3 (C≡C), 117.9, 122.8, 122.9, 123.0, 123.1, 124.1, 125.2, 125.4, 126.3, 126.4, 127.9, 128.69, 128.73, 129.7, 131.30, 131.33, 131.7, 131.8, 132.4, 132.9, 133.66, 133.67, 134.5, 134.7, 134.9, 135.1, 136.9, 149.2, 192.6 (C=O), 192.7 (C=O) ppm. $C_{44}H_{23}NO_4S_2$ (693.79): calcd. C 76.17, H 3.34, N 2.02; found C 75.98, H 3.31, N 2.16. MS (MALDI-TOF): calcd. for $C_{44}H_{23}NO_4S_2$ 693.1063; found 693.2740.

**3-{[5′′-*tert*-Butylsulfanyl-3′′-(2′′′,3′′′-dinitro-4′′′-trimethylsilylethynylphenyl)ethynyl]phenylethynyl}-3′-(5′′′′-*tert*-butylsulfanyl-2′′′′-iodophenylethynyl)tolane (37):** A similar protocol as described for **33** has been applied: **32** (1.5 equiv., 6.63 mmol, 5.3589 g), degassed toluene (1000 mL), ($i$Pr)$_2$NEt (4 mL), $Pd(PPh_3)_4$ (0.4210 g, 0.36 mmol), CuI (0.0686 g, 0.36 mmol) and (4-ethynyl-2,3-dinitrophenylethynyl)trimethylsilane **27** (1.2739 g, 4.42 mmol) in degassed toluene (200 mL). CC (silica, hexane/$CH_2Cl_2$, 7:3) provided **37** as a yellow solid (0.966 g, 23%). M.p. 76–78 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.25 (s, 9 H, $SiCH_3$), 1.31 (s, 9 H, $CH_3$), 1.34 (s, 9 H, $CH_3$), 7.17 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.2 Hz, 1 H), 7.39 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.48–7.61 (m, 6 H), 7.65 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.68 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 7.73 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.74–7.79 (m, 3 H), 7.83 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = –0.5 ($SiCH_3$), 31.06 ($CH_3$), 31.19 ($CH_3$), 46.6 (SC), 47.3 (SC), 86.4 (C≡C), 87.7 (C≡C), 89.2 (C≡C), 89.4 (C≡C), 91.9 (C≡C), 92.7 (C≡C), 94.0 (C≡C), 95.8 (C≡C), 98.8 (C≡C), 102.2 (C≡C), 108.5, 118.3, 118.6, 123.1, 123.2, 123.46, 123.54, 126.3, 128.78, 128.83, 130.0, 131.7, 132.0, 132.7, 133.3, 134.7, 135.0, 135.3, 135.6, 136.0, 136.9, 138.4, 138.9, 140.4, 140.9, 144.3, 145.7 ppm. MS (MALDI-TOF): calcd. for $C_{51}H_{43}IN_2O_4S_2Si$ 966.1473; found 966.2072.

**3-{[5′′-*tert*-Butylsulfanyl-3′′-(4′′′-ethynyl-2′′′,3′′′-dinitrophenyl)ethynyl]phenylethynyl}-3′-(5′′′′-*tert*-butylsulfanyl-2′′′′-iodophenylethynyl)tolane (38):** A similar protocol as described for **35** has been applied: Used were **37** (0.950 g, 0.98 mmol), KF (1.2 equiv., 1.18 mmol, 0.0685 g) and degassed MeOH/$CH_2Cl_2$ (150 mL) for 1 h. The residue was purified by CC (silica, hexane/$CH_2Cl_2$, 1:1) to provide **38** (0.8612 g, 98%) as a yellow solid. M.p. 95–97 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.30 (s, 9 H, $CH_3$), 1.33 (s, 9 H, $CH_3$), 3.57 (s, 1 H, ≡CH), 7.15 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.2 Hz, 1 H), 7.36 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H), 7.44–7.59 (m, 6 H), 7.65 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.67 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 7.71–7.77 (m, 4 H), 7.81 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.0 ($CH_3$), 31.1 ($CH_3$), 46.5 (SC), 47.3 (SC), 75.3 (C≡C), 86.2 (C≡C), 87.6 (C≡C), 88.7 (C≡C), 89.2 (C≡C), 89.4 (C≡C), 91.9 (C≡C), 92.6 (C≡C), 94.0 (C≡C), 99.2 (C≡C), 102.2, 117.1, 119.2, 123.0, 123.1, 123.2, 123.3, 123.4, 126.2, 128.7, 128.8, 129.9, 131.6 (broad), 131.96, 131.98, 132.7, 133.2, 134.5, 134.9, 135.5, 136.0, 136.1, 136.8, 138.4, 138.8, 140.3, 140.7, 143.9, 145.7 ppm. $C_{48}H_{35}IN_2O_4S_2$ (894.84): calcd. C 64.43, H 3.94, N 3.13; found C 64.43, H 4.18, N 3.33. MS (MALDI-TOF): calcd. for $C_{48}H_{35}IN_2O_4S_2$ 894.1078; found 894.3807.

**3,22-Bis(*tert*-butylsulfanyl)-28,29-dinitro-5,6,12,13,19,20,25,26,31,32-decadehydro-27,30-etheno-7,11:14,18-dimethenodibenzo-[*a*,*k*]cyclooctacosane (39):** A similar protocol as described for **36** has been applied: Used were compound **38** (0.8601 g, 0.96 mmol), $Pd(PPh_3)_4$ (0.7513 g, 0.65 mmol), CuI (0.183 g, 0.96 mmol), ($i$Pr)$_2$NEt (5 mL) in degassed toluene (2.5 L) for 6 h at room temperature. The course of the reaction was monitored by TLC. After disappearance of the starting material **38**, the, solvents were removed and the residue was adsorbed on silica gel. Purification by CC (silica, hexane/$CH_2Cl_2$, 2:1 to 1:1) provided the macrocycle **39** (0.0836 g, 11%) as a yellow solid. No m.p., compound decomposes above 350 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.35 (s, 18 H, $CH_3$), 7.40 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.49–7.59 (m, 8 H), 7.66–7.70 (m, 2 H), 7.73–7.76 (m, 2 H), 8.03 (s, 2 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.2 ($CH_3$), 47.4 (SC), 86.5 (C≡C), 88.2 (C≡C), 89.3 (C≡C), 94.0 (C≡C), 99.1 (C≡C), 118.7, 123.3, 123.5, 123.8, 126.2, 129.2, 131.7, 132.1, 132.8, 134.8, 135.2, 136.2, 137.1, 140.1, 145.2 ppm. MS (MALDI-TOF): calcd. for $C_{48}H_{34}N_2O_4S_2$ 766.1955; found 766.5106.

**3,22-Bis(acetylsulfanyl)-28,29-dinitro-5,6,12,13,19,20,25,26,31,32-decadehydro-27,30-etheno-7,11:14,18-dimethenodibenzo[*a*,*k*]cyclooctacosane (2):** A similar protocol as described for **1** has been applied: Used were **39** (20.0 mg, 0.0261 mmol), degassed $CH_2Cl_2$ (25 mL), toluene (1 mL), acetyl chloride (5 mL) and a solution of

boron tribromide (0.5 mL of 1 M solution in $CH_2Cl_2$). CC (silica, hexane/$CH_2Cl_2$, 1:2) afforded target structure **2** (10.2 mg, 53%) as a yellow solid. M.p. > 410 °C. $^1$H NMR (300 MHz, $C_2D_2Cl_4$/$CDCl_3$, 25 °C): $\delta$ = 2.47 (s, 6 H, $CH_3$), 7.36–7.44 (m, 4 H), 7.51–7.58 (m, 4 H), 7.62 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.67 (br. s, 4 H), 8.03 (s, 2 H) ppm. $^{13}$C NMR (126 MHz, $C_2D_2Cl_4$, 25 °C): $\delta$ = 29.2, 85.7, 87.1, 88.7, 94.1, 98.3, 118.0, 122.3, 122.6, 123.6, 126.2, 128.5, 130.3, 131.1, 131.6, 132.7, 133.4, 134.4, 134.8, 136.6, 144.3, 192.3 ppm. MS (MALDI-TOF): calcd. for $C_{44}H_{22}N_2O_6S_2$ 738.0914; found 738.3336.

**3,3′-Bis{[5′′-*tert*-butylsulfanyl-2′′-(4′′′-ethynyl-2′′′-nitrophenyl)-ethynylphenyl]ethynyl}tolane (40):** A similar deprotection protocol has been applied as for the preparation of **35**. Compound **40** was obtained as a pale yellow solid (0.681 g, yield 88%). M.p. 204–206 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.36 (s, 18 H, $CH_3$), 3.29 (s, 2 H, ≡CH), 7.38 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.49–7.58 (m, 8 H), 7.61 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.64 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.6 Hz, 2 H), 7.72 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.75–78 (m, 4 H), 8.19 (d, $^4J_{H,H}$ = 1.5 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.2, 47.2, 81.0, 81.8, 88.2, 89.3, 89.9, 93.7, 97.5, 118.8, 123.39, 123.44, 123.6, 124.9, 126.2, 128.4, 128.8, 131.91, 131.95, 132.6, 135.0, 135.1, 135.2, 136.1, 137.1, 140.4, 149.2 ppm. $C_{58}H_{40}N_2O_4S_2$ (893.08): calcd. C 78.00, H 4.51, N 3.14; found C 77.90, H 4.53, N 3.14. MS (MALDI-TOF): calcd. for $C_{58}H_{40}N_2O_4S_2$ 892.2424; found 892.4198.

**2,23-Bis(*tert*-butylsulfanyl)-8,17-dinitro-5,6,11,12,13,14,19,20,25,26,32,33,39,40-tetradecadehydro-7,10:15,18-dietheno-27,31:34,38-dimethenodibenzo[*a*,*o*]cyclododotriacontane (41):** To the open-chain precursor **40** (61.3 mg, 0.069 mmol) in acetonitrile (1500 mL) and dichloromethane (20 mL) was added $Cu(OAc)_2$ (66.7 mg, 3.34 mmol), and the mixture was heated to 80 °C for 6 h. After removal of the solvents the residue was absorbed on silica gel. Purification by CC (silica, hexane/$CH_2Cl_2$, 1:1) afforded the macrocycle **41** (22.0 mg, 36%). No m.p., compound decomposes above 350 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.35 (s, 18 H, $CH_3$), 7.28–7.32 (m, 4 H), 7.49 (dd, 2 H, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.5 Hz), 7.51–7.57 (m, 6 H), 7.63 (br. s, 2 H), 7.74–7.79 (m, 4 H), 8.13 (d, 2 H, $^4J_{H,H}$ = 1.6 Hz) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.2, 47.3, 80.3, 87.3, 88.5, 89.5, 92.2, 93.5, 100.3, 120.2, 122.8, 123.5, 123.7, 125.0, 125.5, 127.8, 128.9, 130.8, 132.5, 132.7, 133.0, 135.4, 136.8, 137.3, 138.7, 140.2, 147.9 ppm. MS (MALDI-TOF): calcd. for $C_{58}H_{38}N_2O_4S_2$ 890.2268; found 890.4945.

**2,23-Bis(acetylsulfanyl)-8,17-dinitro-5,6,11,12,13,14,19,20,25,26,32,33,39,40-tetradecadehydro-7,10:15,18-dietheno-27,31:34,38-dimethenodibenzo[*a*,*o*]cyclodotriacontane (42):** To a well-stirred solution of starting compound **41** (51.3 mg, 0.058 mmol) in $CH_2Cl_2$/AcCl (15 mL/20 mL) was added a solution of bromine (4.7 mg, 0.029 mmol, 0.3 mL of a 0.0976 mol/dm$^3$) in AcCl/AcOH (1:1) over 30 min at room temperature. The course of the reaction is monitored by TLC. After completion of the reaction, all solvents were removed by evaporation and the crude residues were purified by CC (silica, hexane/$CH_2Cl_2$, 2:1) to afford the macrocycle **42** (18.2 mg, 37%) as a yellow solid. No m.p., compound decomposes above 190 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 2.47 (s, 6 H, $CH_3$), 7.28–7.31 (m, 4 H), 7.44 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.5 Hz, 2 H), 7.47 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.5 Hz, 2 H), 7.49–7.54 (m, 2 H), 7.59–7.66 (m, 6 H), 7.76 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 8.13 (d, $^4J_{H,H}$ = 1.5 Hz, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 30.4 ($CH_3$), 80.1 (C≡C), 87.1 (C≡C), 87.9 (C≡C) 89.3 (C≡C), 92.1 (C≡C), 93.9 (C≡C), 99.6 (C≡C), 119.8, 122.9, 123.2, 123.6, 125.6, 125.7, 128.3, 128.8, 130.0, 131.2, 132.5, 132.6, 132.8, 134.2, 136.7, 137.3, 138.4, 147.8, 192.6 ppm. MS (MALDI-TOF): calcd. for $C_{54}H_{26}N_2O_6S_2$ 862.1227; found 862.5415.

**3,22-Bis(*tert*-butylsulfanyl)-30,33-carbonyl-5,6,12,13,19,20,25,26-octadehydro-7,11:14,18:27,31-trimethenodibenzo[*a*,*k*]azacyclononacos-32-ene 32-Oxide (43):** The macrocycle **36** was heated for short time in order to dissolve it in toluene. During heating the yellow solution became orange. The solvent was removed and the residue was dissolved in dichloromethane and methanol was added. From this solution an appropriated crystal (orange crystal) was obtained for performing of X-ray. No m.p., compound decomposes above 380 °C. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.35 (s, 9 H, $CH_3$), 1.38 (s, 9 H, $CH_3$), 7.13 (t, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.28–7.56 (m, 8 H), 7.61–7.69 (m, 3 H), 7.73–7.78 (m, 2 H), 7.84 (br. s, 1 H), 7.95 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.98 (br. s, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 31.2 ($CH_3$), 31.3 ($CH_3$), 47.2 (SC), 47.3 (SC), 88.4 (C≡C), 89.0 (C≡C), 89.2 (C≡C), 89.3 (C≡C), 93.2 (C≡C), 92.9 (C≡C), 94.2 (C≡C), 95.6 (C≡C), 116.9, 122.2, 122.4, 123.1, 123.2, 123.4, 123.5, 124.0, 125.3, 126.5, 127.2, 128.9, 129.0, 130.2, 130.5, 130.7, 131.0, 131.2, 131.5, 131.7, 134.9, 135.6, 135.9, 136.0, 136.3, 136.5, 137.2, 139.8, 140.4, 148.2, 183.8 (C=O) ppm. MS (MALDI-TOF): calcd. for $C_{48}H_{35}NO_2S_2$ 721.2104; found 721.4700.

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[45] **1**· 1/2 $CH_2Cl_2$ ($C_{48}H_{35}NO_2S_2$ · 1/2 $CH_2Cl_2$): $a$ = 1203.5(2), $b$ = 1298.7(3), $c$ = 1327.9(3) pm, $\alpha$ = 82.84(3), $\beta$ = 78.30(3), $\gamma$ = 80.03(3)°, $V$ = 1993.0(7)·$10^6$ $pm^3$; triclinic $P\bar{1}$, $Z$ = 2, $\rho_{calcd.}$ = 1.272 $gcm^{-1}$, $\mu$(Mo-$K_\alpha$) = 0,241 $mm^{-1}$, STOE IPDS2, Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å, $T$ = 200 K, $2\theta_{max}$ = 52°; 14182 reflections measured, 7242 independent reflections ($R_{int}$ = 0.0422), 5917 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 $F^2$, 490 parameters (S, O, C refined anisotropically, H atoms were calculated at ideal positions, the solvent molecule was refined isotropically with split positions); $R_1$ = 0.0635; $wR_2$ = 0.1917 (all data); Gof: 1.062; maximum peak 0.635 e·$Å^{-3}$. CCDC-285116 contains the 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.

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