Donor–Acceptor-Substituted Phenylacetylene Macrocycles with Threefold Symmetry

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Dedicated to Professor Franz Effenberger on the occasion of his 75th birthday

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A stepwise synthesis of the donor–acceptor-substituted macrocycle 5,21,37-tris(diethylamino)-13,29,45-trinitro[2.2.2.2.2.2]metacyclophane-1,9,17,25,33,42-hexayne (**1a**) from 3,5-bis(3-iodo-5-nitrophenylethynyl)-*N*,*N*-diethylaniline (**11**) and 3,5-bis([3-diethylamino-5-ethynylphenyl]ethynyl)nitrobenzene (**12**) failed, mostly due to the low solubility of **1a**. The synthesis of the 5,21,37-tris(*N*,*N*-di-*n*-hexylamino) congener of **1a**, **1b**, was achieved in a one-pot reaction from 1,3-diiodo-5-nitrobenzene (**3**) and 3,5-diethynyl-*N*,*N*-di(*n*-hexyl)aniline (**16**) in 23 % yield. X-ray investigations on **1b** revealed a planar π ring system with an inner diameter of 10 Å. Despite a high absorbance of **1b** at 300 nm, no measurable NLO activity was found.

Introduction

[2.2.2.2.2.2]Metacyclophane-1,9,17,25,33,41-hexaynes have become an increasingly popular topic within the last decade.[1–12] The conformationally rigid and shape-persistent molecules of nanometer scale have attracted much interest because of their potential in materials science, in host–guest systems[13] and as theoretical subjects.[14,15] As in other planar π systems, these combinations of carbon–carbon triple bonds and benzene units are useful building units for such systems, thanks to the reduction in steric hindrance and the rigidity of the building blocks. Furthermore there are several available procedures allowing the connection of a sp carbon to a sp^2 carbon centre.[16–18] In addition, the capability of the acetylene linkage to transmit electronic perturbation within a conjugated system makes them useful components in the construction of molecular wires,[19,20] conjugated dendrimers[21,22] and optical systems.[23–25]

Interest in such macrocycles published in recent years has predominantly been focused on self-association behaviour based on weak interactions[26–29] involving liquid crystals[30] and monolayer surfaces.[7] The large cavities of these phenylacetylene macrocycles (PAMs) should allow the incorporation of metal salts. Moore et al. showed evidence of a PAM doped with silver triflate without destruction of the liquid-crystalline order.[31]

To the best of our knowledge, however, PAMs have not been used for optical or nonlinear optical investigations, although the greatly extended π system of the unsubstituted PAM has a very high absorbance in the short-wavelength range of UV/Vis spectra.[32] The latter property is a necessary requirement for good NLO activities (efficiency transparency problem).[33]

The structures of **1** and **2** each represent an extended octopole, so their syntheses seemed to be a promising target. It is obvious that two-dimensional structures are superior to one-dimensional NLO chromophores in terms of the β_{zzz} values, as shown in our last paper.[23] It is therefore to be expected that, after the introduction of the chromophore groups, the absorbance maximum should not be shifted too far bathochromically, because an absorption over 500 nm is problematic. Another clear advantage of the PAM is the rigidity of the π system. We showed that planarity of the π system corresponds to an increase in β_{zzz} values, so a planar π system with only a limited degree of torsion is advantageous.[23]

Another interesting question is the π stacking with the aromatic units. Studies on other synthesized PAMs have found that PAMs with electron-withdrawing groups have stronger tendencies towards self-association then PAMs with electron-donating groups.[34] The previous work relates to ether and ester groups, so the introduction of other functional groups as in **1** should be interesting as amino and nitro groups should be able to form stronger intermolecular interactions and make the π stacking easier. Studies on these systems should improve understanding of π–π interactions. Experiments with donor–acceptor-substituted PAMs may be compared with already derived theoretical models.[14] PAMs are also interesting as possible candidates for

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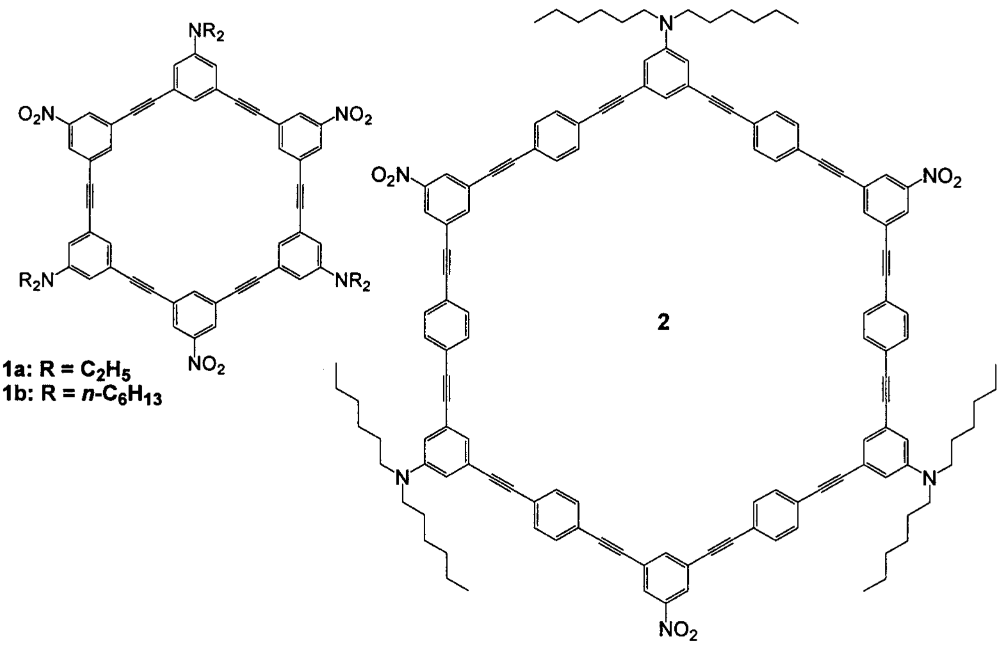
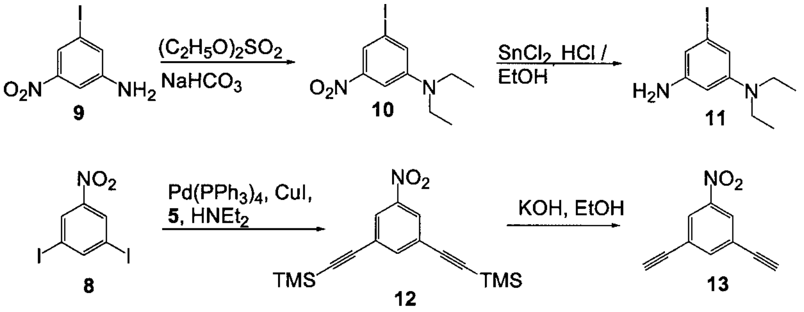


1a: R = C_2H_5
1b: R = n-C_6H_{13}

2



Scheme 3.

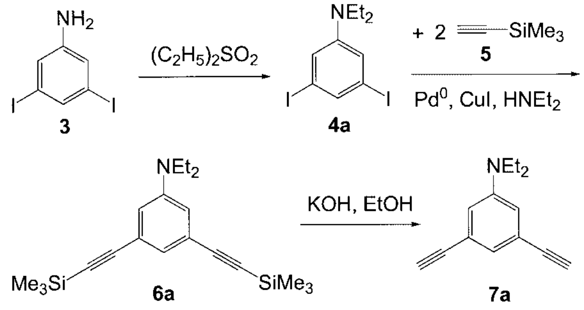
the formation of tubular structures in the solid state,[7] and it would also be very desirable to insert some host molecules and compare the differences in their NLO behaviour.

Synthesis

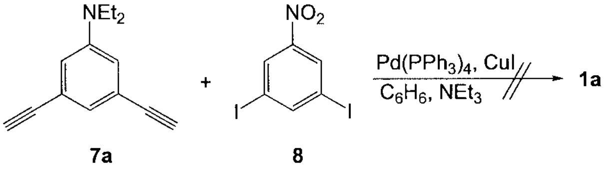
Our first approach involved a one-pot synthesis, the starting materials being 3,5-bis(ethynyl)-*N*,*N*-diethylaniline (**7a**) and 1,3-diiodo-5-nitrobenzene (**8**).[35] Compound **7a** was readily available from 3,5-diiodoaniline (**3**)[36] by the sequence shown in Scheme 1.

An attempted one-pot synthesis[30] with **7a** and **8** under high-dilution conditions with use of $Pd(PPh_3)_4$/CuI and diethylamine (Scheme 2) was unsuccessful, as we were unable to detect any **1a** in the mass spectrum of the raw material.

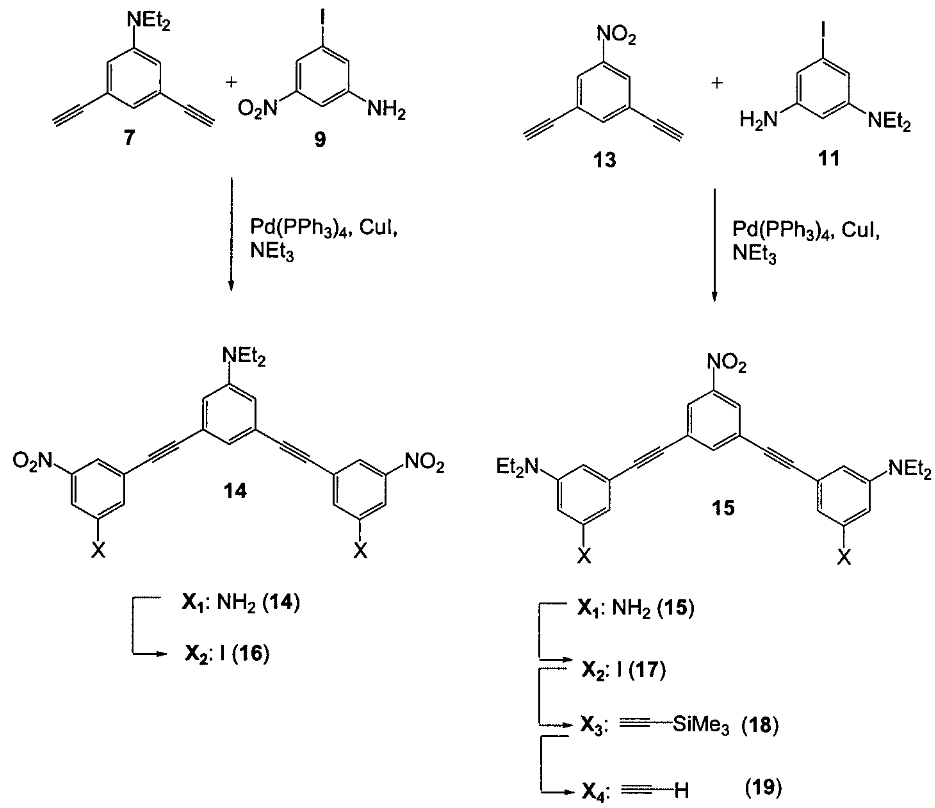
In a second procedure we applied a stepwise approach to the preparation of **1a**. As starting materials we used **7a**, 3-iodo-5-nitroaniline (**9**),[37] 3-(diethylamino)-5-iodoaniline (**11**) and 1-nitro-3,5-bis(trimethylsilylethynyl)benzene (**13**). The last two species were readily available by the procedures shown in Scheme 3.



Scheme 1.



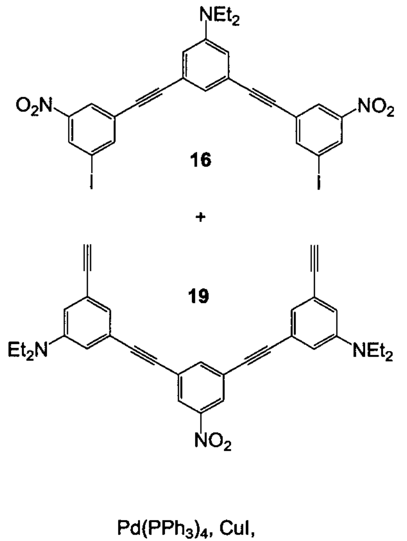
Scheme 2.



Scheme 4.

In two parallel runs we utilized Pd catalysis (Scheme 4). The Sonogashira coupling of **7a**[16,37,38] and **9** afforded **14**, whilst from **11** and **13** we obtained **15** in 72% yield. The free amino groups in **14** and **15** were converted to afford the corresponding diiodo species **16** and **17**, respectively, by a Sandmeyer reaction.[39] In both cases the yields were above 70% when the reaction was carried out at –15 to –10 °C. The bisiodide **17** was transformed into **18** by coupling with two equivalents of trimethylsilylacetylene under Sonogashira conditions.[37,38,40] The removal of the TMS groups to yield **19** was achieved with diluted KOH in EtOH.

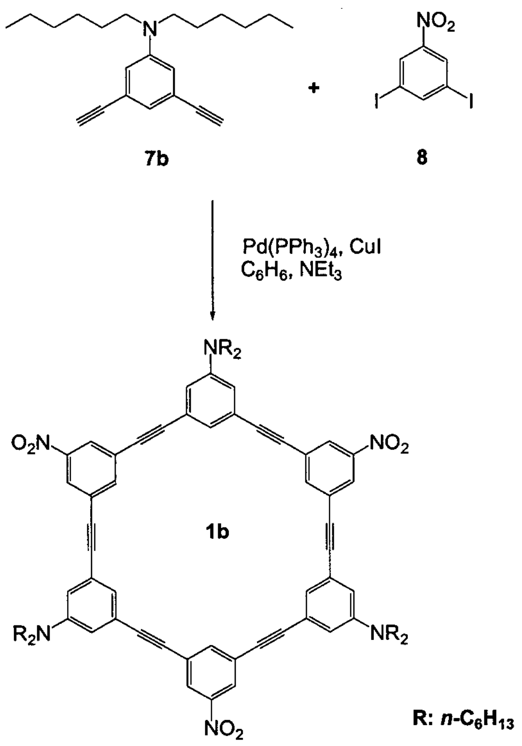
Now the stage was set for the final coupling reaction. The two components **16** and **19** were added dropwise to a Pd(PPh$_3$)$_4$/CuI catalyst solution in dry THF as solvent at 65 °C (Scheme 5). It was possible to detect **1a** by mass spectrometry in the raw material, but because of its low solubility it was not possible to isolate and purify the desired product.



Scheme 5.

To increase the solubility of the target molecule we planned the introduction of two hexyl substituents at the amino groups of **16** and **19**. Before embarking in the synthesis of the di(*n*-hexylamino)-substituted congeners of **16** and **19** (see Scheme 5) we again explored a one-pot synthesis, arguing that our first effort (Scheme 2) might have also been in vain because of the low solubility of **1a**. One component for our new product was 3,5-bis(ethynyl)-*N*,*N*-di(*n*-hexyl)aniline **7b**, prepared analogously to **7a** (Scheme 1) by dialkylation of 3,5-diiodoaniline (**3**) with 1-iodohexane.[41] This produced *N*,*N*-di(*n*-hexyl)-3,5-iodoaniline, which was subsequently ethynylated to produce **7b** (see also Experimental Part).

The coupling reaction between **7b** and **8** (Scheme 6) was carried out at different addition rates to the catalyst (Pd(PPh$_3$)$_4$/CuI) with triethylamine in benzene. We found that the highest yields of **1b** were obtained with addition rates of starting material to a 10 mol% catalyst solution of

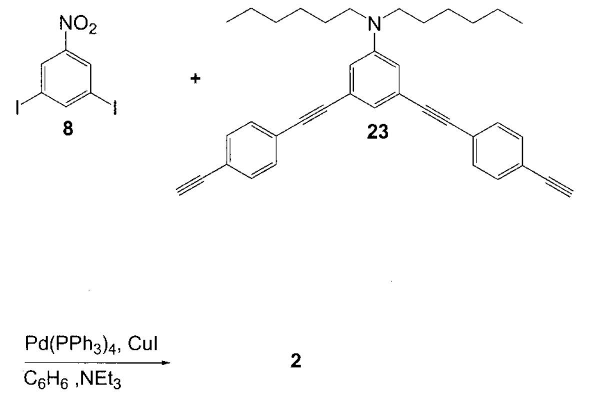


Scheme 6.

5 mL·h^{-1}. At higher concentrations of the catalyst (25 mol%) the amounts of byproducts were higher. From the raw material we were able to isolate **1b** by column chromatography in yields of up to 20%, although the yield was reduced if the reaction was scaled up.

Encouraged by the success in synthesizing **1b** we went on to prepare **2**, in which the π system is enlarged by a phenylethynyl unit relative to **1**. This system provides a larger cavity than **1** and is therefore better suited for hosting other molecules. Scheme 7 summarizes our approach to the preparation of the starting materials.

Sonogashira coupling between **7b** and 1-bromo-4-iodobenzene (**20**) produced **21** in good yields. Further Pd-catalysed coupling of **21** with **5** in diethylamine afforded **22**, which was converted into **23**. To prepare **2** we slowly and simultaneously added **8** and **23** to the catalyst in the presence of triethylamine in benzene solution (Scheme 8). Our evidence for the formation of **2** is based on the ^{1}H NMR spectroscopic data and mass spectrometric (MS(FD) and MALDI) data on a few milligrams recrystallized from dioxane.

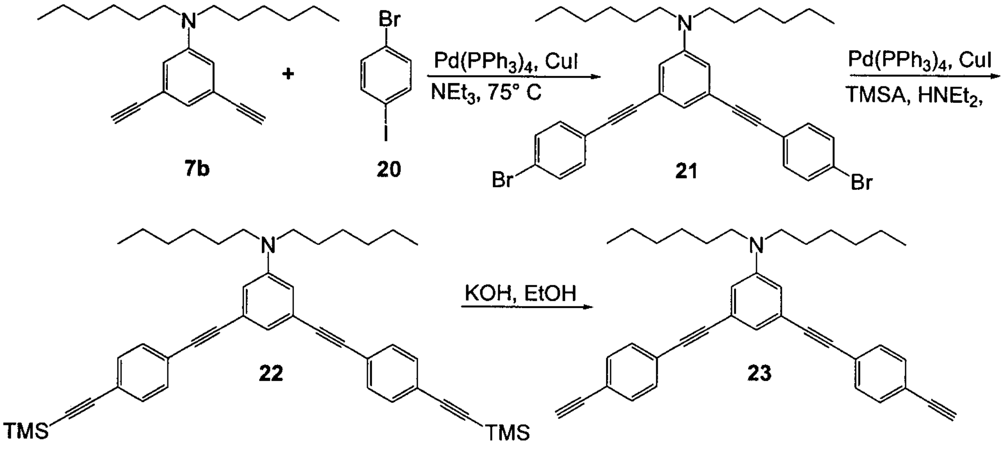


Scheme 8.

Structural and Optical Investigations

We were able to grow single crystals of **1b** suitable for X-ray investigations; the results are presented in Figure 1 and Figure 2. Crystals of **1b** were obtained from a hexane/CH_2Cl_2 solution. The molecular structure of **1b** shows the anticipated planar π ring system with a diameter of 10.9 Å (closest transannular distance between carbon centres) for the cavity. The nitro and amino groups, with the exception of the hexyl side chains, are oriented nearly coplanar to the adjacent phenyl rings.

A section of the unit cell shows a pairing of two rings in such a way that the amino group of one ring faces the nitro



Scheme 7.

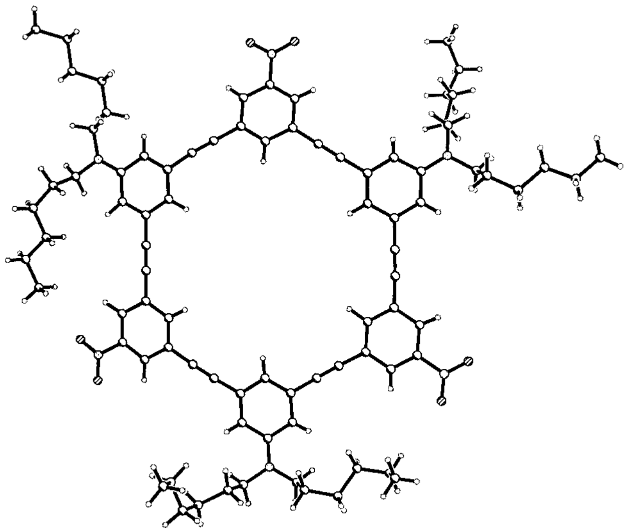


Figure 1.Molecular structure of **1b**. Nitrogen atoms are dotted, oxygen atoms are hatched.

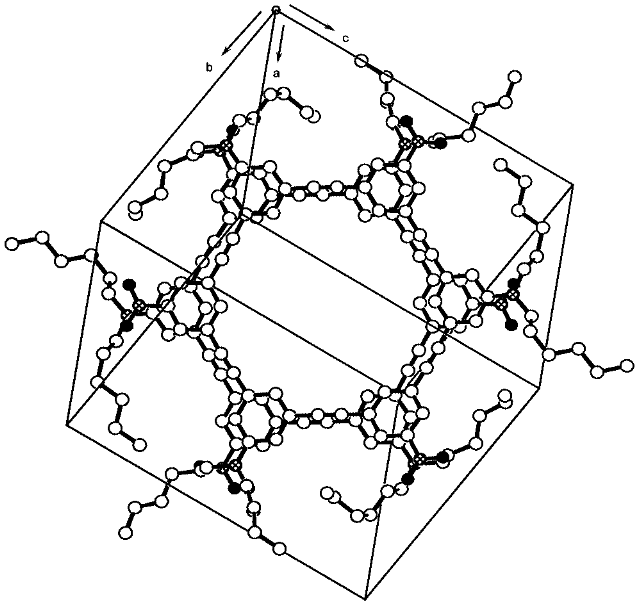


Figure 2. Packing arrangement of **1b**. View of two PAMs. Hydrogen atoms were omitted, nitrogen atoms are crossed, and oxygen atoms are filled in.

group of the other and vice versa (Figure 2). However, no occurrence of a tubular packing was detected, because the pairs of rings are shifted with respect to one another, so an ABCDABCD stacking results. The distances between the nitrogen centres of the NO_2 groups and those of the opposite dihexylamino groups vary between 4.2 Å and 5.0 Å for one pair. Probably the voluminous hexyl groups prevent a closer contact. The ring systems are not completely planar, but open a very flat cone. Within a pair of rings the centers of the two cones point towards each other, so the intermolecular distances to the ring planes are smaller at the inner perimeter of the π system and larger at the outer perimeter (3.7–4.6 Å distance between corresponding face-to-face carbon atoms). The UV/Vis spectrum of **1b** in dichloromethane is displayed in Figure 3. The spectrum shows an intense absorption below 300 nm and a band of low intensity at 400 nm. The chromophore has an enormously high absorbance coefficient with complete transparencyin the visible region.

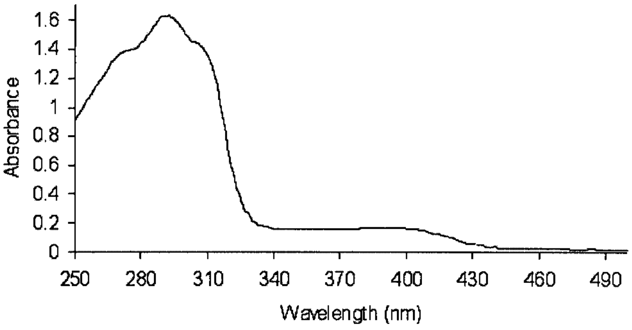


Figure 3. UV/Vis spectrum of **1b**.

The absorbance coefficient of **1b** at $\lambda_{\max} = 292$ nm is $\varepsilon = 177600\ \mathrm{l{\cdot}mol^{-1}{\cdot}cm^{-1}}$. Hyper Rayleigh experiments were carried out, unfortunately without any measurable NLO signal in spite of the high absorbance. To find out if this is due to association of **1b** in solution as found in the solid state (c.f. Figure 2), we recorded the electronic absorption spectrum of **1b** in dichloromethane in concentrations between $2{\cdot}10^{-5}$ and $8{\cdot}10^{-5}\ \mathrm{mol{\cdot}L^{-1}}$ and found no derivation from the Lambert–Beer law. We also found no shift of the proton signals of **1b** in the ^1H NMR spectrum in the concentration range between $2{\cdot}10^{-3}$ and $7{\cdot}10^{-3}\ \mathrm{mol{\cdot}L^{-1}}$ in chloroform. These observations led us to assume that the absence of any measurable NLO signals is due to the *meta* connection of the donor and acceptor groups in **1b**. The resulting conjugation is apparently too weak to give rise to distinct interactions resulting in a stronger charge-transfer transition.

Conclusions

Our experiments have shown that the macrocyclic metacyclophanes **1a** and **1b** can be synthesized either in a stepwise fashion or in a one-pot reaction under high-dilution conditions. A key step for both approaches was a Sonogashira reaction between an alkyne unit and an iodobenzene fragment. The resulting macrocyclic system possessed a planar ring with a D_{3h} symmetry. The rings are oriented in a pairwise fashion in the solid state in such a way that the dihexylamino groups of one ring face the nitro groups of the other. The associated pairs are shifted towards each other, so a tubular arrangement is prevented. Although **1b** shows a strong absorption band at 300 nm, no measurable NLO signal could be detected, probably due to the weak donor–acceptor coupling through the *meta* conjugation.

Experimental Section

General: Reactions were carried out in oven-dried (120 °C) glassware under argon and with magnetic stirring. Solvents: THF was dried by distillation over sodium, DMF (Acros) and diethylamine (Merck) were purchased. Starting materials and chemicals were obtained from commercial sources. The 1-iodohexane (Aldrich) and 1-bromo-4-iodobenzene (Aldrich) were used without further purification. Trimethylsilylacetylene,[42] tetrakis(triphenylphosphane)palladium,[43] 3,5-diiodoaniline,[36] 1,3-diiodo-5-nitrobenzene[35] and 3-iodo-5-nitroaniline[37] were synthesized by literature methods. For reactions under inert gas, the Schlenk technique was used. Melting points (Büchi B-540) are given uncorrected. NMR spectra: 300 MHz for ^{1}H, 75 MHz for ^{13}C. Microanalyses: Analytical Laboratory, Universität Heidelberg.

***N,N*-Diethyl-3,5-diiodoaniline (4a):** A mixture of 3,5-diiodoaniline(**3**, 10.0 g, 29.0 mmol) and triethyl phosphate (5.3 g, 29.0 mmol) was heated under argon for 2 h at 205 °C, during which the solution darkened. After the mixture had cooled to room temp., NaOH (3.9 g, 96.0 mmol) in water (30 mL) was added and the mixture was stirred for further 2 hours. The aqueous phase was separated and washed three times with diethyl ether. The combined organic phase was washed with brine and dried, and the solvent was removed in vacuo. Acetic anhydride (40 mL) and catalytic amounts of DMAP (20 mg) were added to the crude product, and the mixture was warmed briefly and then diluted with diethyl ether. After the mixture had cooled to 0 °C, HCl (20%) was added, the phases were separated, and the organic phase was washed with HCl. The acid solution was neutralised with NaOH solution and washed with diethyl ether. The organic phase was washed with brine and dried, and the solvent was removed in vacuo. Column chromatography (silica gel, light petroleum ether/dichloromethane 9:1) gave **4a** (4.9 g, 12.2 mmol, 42.0%) as a white, crystalline solid. M.p. 59.8–62.8 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.12 (t, ^3J = 7.1 Hz, 6 H), 3.25 (q, ^3J = 7.1 Hz, 4 H), 6.90 (s, 2 H), 7.25 ppm (s, 1 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 12.3, 44.5, 95.7, 119.8, 131.7, 149.4 ppm. IR (KBr): $\tilde{\nu}$ = 3077, 2969, 2924, 2890, 2860, 1569, 1522, 1486 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 238 (22100), 272 (17460), 320 (3140). MS (EI+, 70 eV): 401 (65) [M]$^+$; 386 (100) [M – CH_3]$^+$, 357 (16), 231 (6).

***N,N*-Diethyl-3,5-bis(trimethylsilylethynyl)aniline (6a):** A mixture of *N,N*-diethyl-3,5-diiodoaniline (**4a**,5.2 g, 13.0 mmol), trimethylsilylacetylene (**5**, 3.6 g, 35.2 mmol), $Pd(PPh_3)_4$ (680 mg, 0.7 mmol) and CuI (220 mg, 1.2 mmol) in degassed Et_2NH (40 mL) was heated at reflux under argon for 2 h. The solvent was evaporated in vacuo and the residue was dissolved in dichloromethane and washed three times with water. The organic phase was dried and the solvent was removed in vacuo. Column chromatography (silica gel, light petroleum ether/dichloromethane 1:1) gave **6a** (3.6 g, 10.5 mmol, 80.6%) as colourless crystals. M.p. 140 °C. ,^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 18 H), 1.12 (t, ^3J = 7.1 Hz, 6 H), 3.29 (q, ^3J = 7.1 Hz, 4 H), 6.66 (d, ^4J = 1.3 Hz, 2 H), 6.87 ppm (m, ^4J = 1.3 Hz, 1 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): , $CDCl_3$): δ = 0.02, 12.5, 44.2, 93.1, 105.5, 115.3, 123.1, 123.8, 147.4 ppm. IR (neat): $\tilde{\nu}$ = 3062, 2956, 2923, 2853, 1799, 1760, 1633, 1525 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 242 (22300), 286 (2350), 334 (118). MS (EI+, 70 eV): 240.9 (44) [M]$^+$, 325.8 (100) [M – CH_3]$^+$. $C_{20}H_{31}NSi_2$ (341.64): calcd. C 70.31, H 9.15, N 4.10; found C 70.11, H 9.20, N 4.25.

***N,N*-Diethyl-3,5-bis(ethynyl)aniline (7a):** KOH (1.3 g, 23.2 mmol) in H_2O (5 mL) was added to a solution of *N,N*-diethyl-3,5-bis(trimethylsilylethynyl)aniline (**6a**) (3.6 g, 10.5 mmol) in EtOH (71 mL) and the mixture was heated at reflux for 15 min. The solvent was removed and the residue was dissolved in Et_2O. The organic layer was washed with half conc. brine (100 mL) and dried. After evaporation, **7a** (2.1 g, 10.5 mmol, 100%) was obtained as an orange oil and was used for analysis without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.0 Hz, 6 H), 3.06 (s, 2 H), 3.33 (q, ^3J = 7.0 Hz, 4 H), 6.77 (d, $^4J_{2,6-4}$ = 1.5 Hz, 2 H), 6.85 ppm (t, $^4J_{4-2,6}$ = 1.5 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.6, 44.7, 76.6, 84.1, 115.9, 122.6, 123.3, 148.0 ppm. IR (neat): $\tilde{\nu}$ = 3289, 3082, 2971, 2101, 1799, 1583, 1444 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 246 (25500), 286 (11300), 358 (3100). MS (EI+, 70 eV): 197 (40) [M]$^+$, 182 (100) [M – CH_3]$^+$, 154 (22). $C_{14}H_{15}N$ (197.28): calcd. C 85.24, H 7.66, N 7.10; found C 85.20, H 7.95, N 7.11.

***N,N*-Diethyl-3-iodo-5-nitroaniline (10):** $NaHCO_3$ (60 g, 714 mmol) was added to a stirred solution of 3-iodo-5-nitroaniline (**9**, 35.1 g, 133 mmol) in diethyl sulfate (150 mL) and the mixture was stirred at 120 °C overnight. Gas formation could be observed. The reaction was interrupted when the suspension could not be stirred any more. After the mixture had cooled to room temp., NH_3 solution was added and the mixture was stirred for a further hour. The suspension was dissolved in Et_2O and washed with half conc. brine (100 mL). The organic phase was dried and the solvent was removed in vacuo. The dark red oil was chromatographed (silica gel, light petroleum ether/diethyl ether 9:1) to give **10** (10.5 g, 72.0%) as an orange-red powder. M.p. 37 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, ^3J = 7.1 Hz, 6 H), 3.38 (d, ^3J = 7.1 Hz, 4 H), 7.01 (dd, $^4J_{2-6}$ = 2.5, $^4J_{4-6}$ = 1.4 Hz, 1 H), 7.21 (dd, $^4J_{2-6}$ = 2.5, $^4J_{2-4}$ = 1.6 Hz, 1 H), 7.45 ppm (dd, $^4J_{4-2}$ = 1.6, $^4J_{4-6}$ = 1.4 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.5, 44.5, 95.9, 108.8, 116.4, 122.1, 149.3, 154.1 ppm. IR (KBr): $\tilde{\nu}$ = 3121, 2969, 2928, 2892, 1608, 1553, 1526, 1495 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 254 (19100), 280 (11450), 328 (2920), 426 (1850). MS (EI+, 70 eV): 320 (35) [M]$^+$; 306 (100) [M – CH_3]$^+$, 277 (13), 259 (12), 132 (14). $C_{10}H_{13}IN_2O_2$ (320.13): calcd. C 37.52, H 4.09, N 8.75, I 39.64; found C 37.53, H 4.15, N 8.68, I 39.58.

3-(Diethylamino)-5-iodoaniline (11): Tin(II) chloride (95.3 g, 421.2 mmol) was added to a stirred solution of ethanol (143 mL) and conc. HCl (95 mL). Afterwards, *N,N*-diethyl-3-iodo-5-nitroaniline (**10**, 28.9 g, 90.2 mmol) was added in small portions, the reaction temperature being held at 35 °C. The system was stirred overnight. NaOH was added until the pH of the solution was alkaline, while the suspension was cooled with ice water. The suspension was extracted into Et_2O and washed with conc. brine (100 mL). The organic phase was dried and the solvent was removed in vacuo. Column chromatography (silica gel, CH_2Cl_2) gave **11** (24.1 g, 83.0 mmol, 91.9%) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, ^3J = 7.5 Hz, 6 H), 3.25 (d, ^3J = 7.5 Hz, 4 H), 5.89 (dd, $^4J_{2-4}$ = 1.9, $^4J_{2-6}$ = 2.3 Hz, 1 H), 6.35 (dd, $^4J_{4-6}$ = 1.4, $^4J_{2-4}$ = 1.9 Hz, 1 H), 6.42 ppm (dd, $^4J_{4-6}$ = 1.4, $^4J_{2-6}$ = 2.3 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.6, 44.2, 96.2, 97.6, 111.9, 112.0, 148.4, 149.7 ppm. MS (EI+, 70 eV): 290 (65) [M]$^+$, 275 (100) [M – CH_3]$^+$, 247 (8). $C_{10}H_{15}IN_2$ (290.14): calcd. C 41.40, H 5.21, N 9.66, I 43.74; found C 41.28, H 5.24, N 9.62, I 43.74.

1,3-Bis(ethynyl)-5-nitrobenzene (13): A mixture of 1,3-diiodo-5-nitrobenzene (34.4 g, 92.1 mmol), trimethylsilylacetylene (18.9 g, 192.8 mmol), $Pd(PPh_3)_4$ (1.2 g, 1.0 mmol) and CuI (0.4 g, 2.1 mmol) in degassed Et_2NH (150 mL) was stirred at r.t overnight. The reaction is slightly exothermic. The solvent was evaporated in vacuo. Column chromatography (silica gel, light petroleum ether/dichloromethane 1:2) gave 1,3-(bistrimethylsilylethynyl)-5-nitrobenzene (**12**, 24.2 g, 76.8 mmol, 83.4%) as colourless crystals, which were not purified for subsequent use.

KOH (10.3 g, 184.6 mmol) in H_2O (10 mL) was added to a solution of **12** (24.2 g, 76.8 mmol) in EtOH (100 mL) and the mixture was stirred for 1 h. After the reaction was finished (TLC monitoring) the solvent was removed and the residue was dissolved in Et_2O. The organic layer was washed with brine (100 mL) and dried. After evaporation and recrystallisation from ethanol, **13** (10.0 g, 58.5 mmol, 76.1%) was obtained as colourless crystals. M. p. 113.5–115 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.23 (s, 2 H), 7.84 (d, $^4J_{4-2,6}$ = 1.5 Hz, 1 H), 8.25 ppm (d, $^4J_{2,6-4}$ = 1.5 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 80.3, 80.7, 124.3, 126.8, 140.8, 148.0 ppm. IR (KBr): $\tilde{\nu}$ = 3285, 3079, 2883, 2112, 1799, 1613, 1544 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, $L\cdot M^{-1}\cdot cm^{-1}$) = 244 (26200), 272 (4360), 328 (1340). MS (EI+, 70 eV): 171 (100) $[M]^+$, 125 (41) $[M - NO_2]^+$, 99 (16) $[M - NO_2\text{-}(CH)_2]^+$, 75 (21) $[M - NO_2 - (CCH)_2]^+$. $C_{10}H_5NO_2$ (171.15): calcd. C 70.18, H 2.95, N 8.18; found C 69.97, H 3.03, N 8.16.

3,5-Bis(3-amino-5-nitrophenylethynyl)-*N*,*N*-diethylaniline (14): A mixture of *N*,*N*-diethyl-3,5-bis(ethynyl)aniline (**7a**, 2.0 g, 10.3 mmol), 3-iodo-5-nitroaniline (**9**, 5.7 g, 21.5 mmol), $Pd(PPh_3)_4$ (0.6 g, 0.6 mmol) and CuI (0.2 g, 1.1 mmol) in dry triethylamine (50 mL) was heated at reflux under argon overnight. After the mixture had cooled to room temp. the solvent was removed. The crude product was pulverized, washed several times with water and recrystallized from water/acetone. Several fractions with different degree of purity were obtained, the overall yield of **14** was 3.7 g (7.8 mmol, 75.9%) as an ochre-coloured powder. M. p. 223–227 °C. ^1H NMR (300 MHz, DMSO -d_6): δ = 1.09 (t, ^3J = 7.0 Hz, 6 H), 3.34 (m, 4 H), 6.02 (br., 4 H), 6.85 (m, 2 H), 6.93 (m, 1 H), 7.07 (m, 2 H), 7.40 (m, 2 H), 7.42 ppm (m, 2 H). ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 12.2, 43.5, 87.3, 89.9, 107.6, 112.4, 114.6, 120.8, 121.4, 123.0, 123.7, 147.4, 148.9, 150.2 ppm. IR (KBr): $\tilde{\nu}$ = 3231, 2971, 2215, 1625, 1582, 1529 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, $L\cdot M^{-1}\cdot cm^{-1}$) = 266 (49100), 282 (59440), 302 (35600), 356 (10480), 378 (9860). MS (FAB^+, NBA-Matrix): 469 $[M]^+$, 470 $[M + H]^+$, 454 $[M - CH_3]^+$. $C_{26}H_{23}N_5O_4$ (469.49): calcd. C 66.51, H 4.94, N 14.92; found C 66.21, H 4.95, N 14.57.

3,5-Bis(3-amino-(diethylamino)-phenylethynyl)nitrobenzene (15): A mixture of 1,3-bis(ethynyl)-5-nitrobenzene (**13**, 6.6 g, 38.3 mmol), diethylamino-3-iodo-5-nitroaniline (**11**, 22.2 g, 76.5 mmol), $Pd(PPh_3)_4$ (1.2 g, 1.0 mmol) and CuI (0.4 g, 2.1 mmol) in dry triethylamine (100 mL) was heated at reflux under argon overnight. After the mixture had cooled to room temp., the solvent was removed. Column chromatography (SiO_2, CH_2Cl_2/ethyl acetate 5:1) yielded **15** (13.6 g, 27.5 mmol, 71.9%) as a yellow powder. M. p. 179.3–180.4 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.14 (t, ^3J = 7.0 Hz, 12 H), 3.30 (q, ^3J = 7.0 Hz, 8 H), 3.66 (br., 4 H), 6.00 (t, ^4J = 2.1 Hz, 2 H), 6.19 (dd, ^4J = 1.3, ^4J = 1.8 Hz, 2 H), 6.30 (dd, ^4J = 1.2, ^4J = 2.3 Hz, 2 H), 7.90 (t, ^4J = 1.5 Hz, 1 H), 8.22 ppm (d, ^4J = 1.5 Hz, 2 H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.8, 44.7, 84.8, 94.3, 99.9, 106.2, 106.5, 123.3, 125.5, 126.1, 139.9, 148.3, 148.6 149.3 ppm. IR (KBr): $\tilde{\nu}$ = 2969, 2929, 2895, 2871, 2212, 1586, 1533, 1490, 1449 cm^{-1}.UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, $L\cdot M^{-1}\cdot cm^{-1}$) = 240 (54700), 270 (62600), 310 (28800), 360 (8060), 376 (5760). MS (FAB^+, NBA-Matrix): 495 $[M]^+$, 496 $[M + H]^+$, 480 $[M - CH_3]^+$, 465 $[M - CH_3 - CH_3]^+$. $C_{30}H_{33}N_5O_2$ (495.62): calcd. C 72.70, H 6.71, N 14.13; found C 72.79, H 6.65, N 13.84.

***N*,*N*-Diethyl-3,5-bis(3-iodo-5-nitrophenylethynyl)aniline (16):** 3,5-Bis(3-amino-5-nitrophenylethynyl)-*N*,*N*-diethylaniline (**14**, 3.3 g, 7.1 mmol) was added to hydrochloric acid (20%, 50 ml), during which a yellow suspension was formed. $NaNO_2$ (1.2 g, 4.4 mmol) was dissolved in water, and the solution was cooled and added dropwise to the suspension at –20 °C. The solid dissolved and a clear orange solution was obtained. The solution was stirred for a further hour at this temperature; afterwards some amounts of urea were added. The mixture was poured into an ice–water solution of potassium iodine (10 g, 60.3 mmol) with vigorous stirring. The mixture was stirred overnight without cooling. The formed iodine was destroyed by addition of $NaHSO_3$, and the solution was made alkaline (pH = 12) and extracted several times with dichloromethane. The combined organic phases were washed several times with water and dried. The solvent was removed in vacuo, the obtained solid was washed several times with dichloromethane until the residue was free of any side products, and the filtrate was chromatographed (SiO_2: CH_2Cl_2/light petroleum ether 1:9) The overall yield of **16** was 3.5 g (5.1 mmol, 71.6%) as ochre-coloured crystals. M.p.>200 °C (decomp.). ,^1H NMR (300 MHz, DMSO -d_6): δ = 1.19 (t, ^3J = 7.0 Hz, 6 H), 3.44 (q, ^3J = 7.0 Hz, 4 H), 6.93 (d, ^4J = 1.09 Hz,2 H), 7.01 (dd, ^4J = 1.1, ^4J = 1.4 Hz, 2 H), 8.29 (dd, ^4J = 1.4, ^4J = 1.6 Hz, 2 H), 8.35 (dd, ^4J = 1.4, ^4J = 1.6 Hz, 2 H), 8.55 ppm (t, ^4J = 1.91 Hz, 1 H). ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 12.7, 44.9, 85.8, 93.2, 94.2, 116.2, 122.6, 124.0, 126.3, 127.2, 132.6, 146.4, 148.8, 149.6 ppm. IR (KBr): $\tilde{\nu}$ = 3091, 2971, 2215, 1623, 1582, 1530, 1446, 1347 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, $L\cdot M^{-1}\cdot cm^{-1}$) = 238 (49400), 276 (57300), 286 (55300), 302 (45410), 338 (9860), 376 (5900). MS (FAB^+, NBA-Matrix): 691 $[M]^+$, 692 $[M + H]^+$, 676 $[M - CH_3]^+$.

1,3-Bis[(3-diethylamino-5-iodophenyl)ethynyl]-5-nitrobenzene (17): 1,3-Bis(3-amino-5-nitrophenylethynyl)-5-nitrobenzene (**15**, 6 g, 12.1 mmol) was added to hydrochloric acid (20%, 96 mL), during which an orange suspension was formed. $NaNO_2$ (2.1 g, 30.3 mmol) was dissolved in water, and the solution was cooled and added dropwise to the suspension at –20 °C. The solid dissolved and a clear red, foaming solution was obtained. The solution was stirred for 30 min at this temperature; afterwards some amounts of urea were added. The mixture was poured into an ice–water solution of potassium iodide (10 g, 60.3 mmol) with vigorous stirring and stirred overnight without cooling. The formed iodine was destroyed by addition of $NaHSO_3$, and the solution was made alkaline (pH = 12) and extracted several times with dichloromethane. The combined organic phases were washed several times with water and dried, and the solvent was removed in vacuo. The obtained crude product was washed several times with dichloromethane until the residue was free of any side products to give **17** (9.2 g, 9.9 mmol, 81.8%) as ochre-coloured crystals. M. p. 224.6–225.5 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.17 (t, ^3J = 7.1 Hz, 12 H), 3.34 (q, ^3J = 7.1 Hz, 8 H), 6.80 (dd, ^4J = 2.5, ^4J = 1.2 Hz, 2 H), 7.01 (dd, ^4J = 1.5, ^4J = 2.4 Hz, 2 H), 7.14 (t, ^4J = 1.5 Hz, 2 H), 7.94 (t, ^4J = 1.5 Hz, 1 H), 8.29 ppm (d, ^4J = 1.5 Hz, 2 H). ^{13}C NMR(75 MHz, CD_2Cl_2): δ = 12.5, 44.7, 86.3, 92.2, 92.2, 95.3, 114.3, 121.6, 124.4, 125.7, 127.0, 140.0, 148.7, 148.9 ppm. IR (KBr): $\tilde{\nu}$ = 2970, 2929, 2872, 2214, 2105, 1584, 1539, 1486, 1452 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, $L\cdot M^{-1}\cdot cm^{-1}$) = 234 (53400), 276 (68700), 288 (60800), 306 (44000), 356 (10900). MS (FAB^+, NBA-Matrix): 717 $[M]^+$, 718 $[M + H]^+$, 702 $[M - CH_3]^+$. $C_{30}H_{29}I_2N_3O_2$ (717.38): calcd. C 50.23, H 4.07, N 5.86, I 35.38; found C 50.35, H 4.17, N 5.85, I 35.60.

1,3-Bis([3-diethylamino-5-(trimethylsilylethynyl)phenyl]ethynyl)-5-nitrobenzene (18): A mixture of **17** (3.0 g, 4.1 mmol), trimethylsilylacetylene (3.0 g, 31.0 mmol), $Pd(PPh_3)_4$ (0.9 g, 0.8 mmol) and CuI (0.3 g, 1.6 mmol) in dry diethylamine (80 mL) was heated at reflux at 50 °C for 2 h. A further amount of trimethylsilylacetylene (1.45 g) was added and the mixture was heated for an additional 2 hours. After the mixture had cooled to room temp., the solvent was removed. Column chromatography (SiO_2, CH_2Cl_2/light petroleum ether 6:4) yielded **18** (2.0 g, 3.0 mmol, 71.9%) as a yellow-brown powder. M. p. 152.3–153.3 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ = 0.26 (s, 18 H), 1.18 (t, ^3J = 7.1 Hz, 12 H), 3.36 (q, ^3J = 7.1 Hz, 8 H), 6.77 (dd, ^4J = 2.6, ^4J = 1.3 Hz, 2 H), 6.81 (dd, ^4J = 1.3, ^4J =

2.6 Hz, 2 H), 6.91 (t, ^{4}J = 1.3 Hz, 2 H), 7.95 (t, ^{4}J = 1.5 Hz, 1 H), 8.29 ppm (d, ^{4}J = 1.5 Hz, 2 H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 0.01, 12.6, 44.7, 85.8, 93.1, 93.9, 105.5, 115.3, 115.9, 122.3, 123.2, 124.6, 125.8, 125.9, 140.0, 148.1, 148.7 ppm. MS (FAB$^+$, NBA-Matrix): 656 $[M]^+$, 657 $[M + H]^+$, 642 $[M - CH_3 + H]^+$. $C_{40}H_{47}N_3O_2Si_2$ (657.99): calcd. C 73.01, H 7.20, N 6.39; found C 72.68, H 7.27, N 6.40.

1,3-Bis[(3-diethylamino-5-ethynylphenyl)ethynyl]-5-nitrobenzene (19): KOH (76 mg, 1.4 mmol) in H_2O (5 mL) was added to a solution of 1,3-bis([3-diethylamino-5-(trimethylsilylethynyl)phenyl]ethynyl)-5-nitrobenzene (**18**, 450 mg, 0.7 mmol) in EtOH (20 mL) and the mixture was heated at reflux for 15 min. The reaction was monitored by TLC. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was dried, the solvent was removed, and **19** and 1-([3-diethylamino-5-(ethynyl)phenyl]-ethynyl)-3-[(3-diethylamino-5-(trimethylsilylethynyl)phenyl)-ethynyl]-5-nitrobenzene were separated and purified by column chromatography (SiO_2; CH_2Cl_2/light petroleum ether 1:1) to yield **19** (345 mg, 0.7 mmol, 98.3%) as orange crystals. M.p. 202.5–203.3 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.18 (t, ^{3}J = 7.1 Hz, 12 H), 3.10 (s, 2 H), 3.37 (q, ^{3}J = 7.1 Hz, 8 H), 6.81 (dd, ^{4}J = 1.3, ^{4}J = 2.6 Hz, 2 H), 6.84 (dd, ^{4}J = 1.3, ^{4}J = 2.6 Hz, 2 H), 6.93 (t, ^{4}J = 1.3 Hz, 2 H), 7.97 (t, ^{4}J = 1.5 Hz, 1 H), 8.29 ppm (d, ^{4}J = 1.5 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.6, 44.7, 76.8, 84.0, 85.9, 93.0, 115.5, 116.3, 122.3, 123.3, 123.5, 125.8, 125.9, 140.0, 148.1, 148.7 ppm. IR (neat): $\tilde{\nu}$ = 3290, 2970, 2929, 2214, 2106, 1579, 1535, 1483, 1445 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 246 (69000), 288 (65400), 306 (46000), 352 (12400), 424 (3540). MS (FAB$^+$, NBA-Matrix): 513 $[M]^+$, 514 $[M + H]^+$, 498 $[M - CH_3]^+$;

5,21,37-Tris(diethylamino)-13,29,45-trinitro-[2.2.2.2.2.2]-metacyclophane-1,9,17,25,33,41-hexayne (1a): A mixture of $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) and CuI (38 mg, 0.2 mmol) was suspended in dry THF (20 mL) under argon, and diisopropylamine (240 mg, 2.4 mmol) was added. Compounds **19** (513 mg, 1.0 mmol) and **16** (691 mg, 1.0 mmol), both dissolved in dry THF (200 mL), were added dropwise by dropping funnel while the reaction mixture was slowly heated to 68 °C. After the addition was complete, the reaction was heated at reflux overnight. The solution was filtered off and the solvent was removed. A yellow brown solid containing the expected mass spectroscopic peak for **1a** was obtained, but it was not possible to separate the product from the byproducts.

***N,N*-Dihexyl-3,5-diiodoaniline (4b):** 1-Iodohexane (19.9 mL, 93.9 mmol) and Na_2CO_3 (5.2 g, 49.0 mmol) were added to a solution of 3,5-diiodoaniline (**3**, 9.8 g, 28.5 mmol) in DMF (87 mL) and the mixture was stirred at 125 °C for 20 h. Further 1-iodohexane (10 mL, 67.4 mmol) was added to this solution and the mixture was stirred at 125 °C for two more hours. After the mixture had cooled to room temp. the solution was separated from the resulting salts by filtration and the solvent was removed in vacuo. The residue was dissolved in Et_2O, washed with half conc. brine (100 mL) and dried. The residue was chromatographed (silica gel, light petroleum ether/CH_2Cl_2 7: 3) to give **4b** (10.5 g, 72.0%) as a clear oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, ^{3}J = 7.1 Hz, 6 H), 1.30 (s, 12 H), 1.51 (m, 4 H), 3.16 (t, ^{3}J = 7.1 Hz, 4 H), 6.85 (d, ^{4}J = 1.4 Hz, 2 H), 7.23 ppm (t, ^{4}J = 1.4 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0, 22.7, 26.8, 27.0, 31.7, 51.0, 95.7, 119.8, 131.7, 149.4 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2928, 2856, 1729, 1573, 1526, 1462 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 234 (109900), 272 (86600), 322 (15200). MS (EI+, 70 eV): 513 (42) $[M]^+$, 441 (100) $[M - C_5H_{11}]^+$, 372 (57) $[M - C_5H_{11} - C_5H_{10}]^+$. HR-EI$^+$: calcd. $C_{18}H_{29}NI_2$ 513.0388, found 513.0389 (–0.1).

***N,N*-Dihexyl-3,5-bis(trimethylsilylethynyl)aniline (6b):** A mixture of **4b** (15.7 g, 30.5 mmol), trimethylsilylacetylene (7.2 g, 73.2 mmol), $Pd(PPh_3)_4$ (783 mg, 0.7 mmol) and CuI (258 mg, 1.4 mmol) in degassed Et_2NH (60 mL) was heated at reflux under argon for 3 h. The solvent was evaporated in vacuo, and the residue was dissolved in dichloromethane and washed three times with water. The organic phase was dried and the solvent was removed in vacuo. Column chromatography (silica gel, light petroleum ether/diethyl ether 99:1) gave **6b** (11.0 g, 79.1%) as a clear oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.23 (s, 18 H), 0.90 (t, ^{3}J = 7.1 Hz, 6 H), 1.32 (s, 12 H), 1.54 (m, 4 H), 3.23 (t, ^{3}J = 7.7 Hz, 4 H), 6.85 (d, ^{4}J = 1.1 Hz, 1 H), 6.77 ppm (t, ^{4}J = 1.3 Hz, 2 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 0.0, 14.2, 23.1, 27.1, 27.3, 32.1, 51.1, 93.5, 105.7, 115.4, 122.6, 124.2, 148.4 ppm. IR (neat): $\tilde{\nu}$ = 2958, 2929, 2857, 2153, 1580 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 242 (42800), 254 (35600), 292 (8140), 362 (3050). MS (EI+, 70 eV): 453 (30) $[M]^+$, 382 (100) $[M - C_5H_{11}]^+$, 312 (39) $[M - C_5H_{11} - C_5H_{10}]^+$.

3,5-Bis(ethynyl)-*N,N*-dihexylaniline (7b): KOH (3.3 g, 57.9 mmol) in H_2O (5 mL) was added to a solution of **6b** (11.0 g, 24.1 mmol) in EtOH (150 mL) and the mixture was heated at reflux for 15 min. The solvent was removed and the residue was dissolved in Et_2O. The organic layer was washed with half conc. brine (100 mL) and dried. After evaporation, **7b** (7.5 g, 100%) was obtained as an orange oil and was used for analysis without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, ^{3}J = 7.2 Hz, 6 H), 1.30 (s, 12 H), 1.50–1.54 (m, 4 H), 3.00 (s, 2 H), 3.21 (t, ^{3}J = 7.2 Hz, 4 H), 6.70 (s, 2 H), 6.88 ppm (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0, 22.6, 26.7, 27.0, 31.6, 50.9, 78.3, 83.9, 115.7, 122.6, 122.8, 147.8 ppm. IR (neat): $\tilde{\nu}$ = 3294, 2956, 2929, 2856, 2107, 1581, 1461, 1370, 1308 cm^{-1}.UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 246 (26950), 288 (11800), 362 (2630). MS (EI+, 70 eV): 309 (24) $[M]^+$, 238 (100) $[M - C_5H_{11}]^+$, 168 (39, $[M - C_5H_{11} - C_5H_{10}]^+$, 154 $[M - C_5H_{11} - C_5H_{10} - CH_2]^+$. $C_{22}H_{31}N$ (309.49): calcd. C 85.38, H 10.10, N 4.53; found C 85.26, H 10.13, N 4.76.

Phenylacetylene Macrocycle 1b: A suspension of $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) and copper(I) iodide (16 mg, 0.08 mmol) in triethylamine (60 mL) was heated under argon to 75 °C, during which the suspension turned dark. A mixture of 1,3-diiodo-5-nitrobenzene (**8**, 149 mg, 0.4 mmol) and 3,5-diethynyl-*N,N*-dihexylaniline (**7b**, 124 mg, 0.4 mmol), dissolved in benzene (50 mL) and triethylamine (50 mL), was added to the catalyst suspension by syringe pump. The rate of addition was 5 mL·h^{-1}. After the completion of addition the reaction mixture was heated at 75 °C for 2 more hours, and then cooled down to room temp. The solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, light petroleum/CH_2Cl_2) to yield 118 mg (23%) of **1b**. M.p.>250 °C (decomposition). The purity of the sample was monitored by HPLC. ^{1}H NMR(300 MHz, $CDCl_3$): δ = 0.94 (t, ^{3}J = 6.8 Hz, 18 H), 1.36 (s, 36 H), 1.50–1.60 (m, 12 H), 3.13 (t, ^{3}J = 6.8 Hz, 12 H), 6.51 (d, ^{4}J = 1.1 Hz, 6 H), 6.77 (t, ^{4}J = 1.1 Hz, 3 H), 7.75 (t, ^{4}J = 1.5 Hz, 3 H), 8.04 ppm (d, ^{4}J = 1.5 Hz, 6 H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.3, 23.1, 27.2, 27.3, 32.1, 51.1, 86.3, 93.0, 115.1, 122.4, 123.4, 125.3, 125.6, 140.0, 148.1, 148.2 ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2928, 2856, 2218, 1610, 1581, 1536 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 274 (149500), 292 (177600), 308 (153000), 394 (15200). MS(FD$^+$): *m*/*z* = 1285 (100) $[M]^+$, 1255 (22), 1201 (18), 1164 (13). $C_{84}H_{96}N_6O_6$ (1285.7) calcd. C 79.26, H 7.54, N 6.16, found C 79.20, H 7.73, N 6.04.

3,5-Bis(4-bromophenylethynyl)-*N,N*-dihexylaniline(21): A mixture of 3,5-diethynyl-*N,N*-dihexylaniline (**16**, 2.5 g, 8.1 mmol), 1-bromo-4-iodobenzene (**20**, 5.5 g, 19.4 mmol), $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol) and CuI (20 mg, 0.1 mmol) in dry triethylamine was heated at reflux under argon overnight. After the mixture had cooled to room temp., the solvent was removed and the residue was dissolved in CH_2Cl_2,. The organic phase was washed with water, dried and evaporated in vacuo. Column chromatography (silica gel, light petroleum/CH_2Cl_2 gradient) yielded **21** (3.3 g, 66.6%) as yellow, waxy crystals. M.p. 85 °C. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ = 0.87 (t, ^3J = 7.0 Hz, 6 H), 1.30 (s, 12 H), 1.56–1.60 (m, 4 H), 3.24 (t, ^3J = 7.0 Hz, 4 H), 6.73 (d, ^4J = 1.4 Hz, 2 H), 6.90 (t, ^4J = 1.4 Hz, 1 H), 7.38 (d, ^3J = 9.1 Hz, 4 H), 7.48 ppm (d, ^3J = 9.1 Hz, 4 H). ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$): δ = 14.2, 23.1, 27.1, 27.4, 32.1, 51.3, 87.7, 91.2, 115.1, 121.6, 122.7, 124.1, 132.0, 133.4, 147.9, 148.5 ppm. IR (KBr): $\tilde{\nu}$ = 2950, 2930, 2867, 2852, 2211, 1895, 1576, 1527 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 262 (44500), 274 (57400), 284 (63200), 290 (72200), 300 (58350), 308 (57400), 376 (5800). MS (EI$^+$, 70 eV): 621 (21) [M]$^+$ ($^{81}Br_2$), 619 (45) [M]$^+$ ($^{79}Br^{81}Br$), 617 (22) [M]$^+$ ($^{79}Br_2$), 550 (43) [M – C_5H_{11}]$^+$ ($^{81}Br_2$), 548 (100) [M – C_5H_{11}]$^+$ ($^{79}Br^{81}Br$), 546 (46) [M-C_5H_{11}]$^+$ ($^{79}Br_2$), 480 (13) [M – C_5H_{11} – C_5H_{10}]$^+$ ($^{81}Br_2$), 478 (27) [M – C_5H_{11} – C_5H_{10}]$^+$ ($^{79}Br^{81}Br$), 476 (14) [M – C_5H_{11} – C_5H_{10}]$^+$ ($^{79}Br_2$). HR-EI$^+$ calcd. for $C_{34}H_{37}N^{81}Br_2$ (621.1251), found 621.1238 (–1.3), calcd. for $C_{34}H_{37}N^{79}Br^{81}Br$ (619.1272), found 619.1273 (+0.1) calcd. for $C_{34}H_{37}N^{79}Br_2$ (617.1309), found 617.1291 (–1.8).

Table 1. Crystallographic data.

Compound	**1b**
Empirical formula	$C_{84}H_{96}N_6O_6$
Molecular mass [g·mol^{-1}]	1285.67
Crystal size (mm)	0.35 × 0.25 × 0.07
Crystal colour	yellow
Crystal shape	irregular plate
Space group	*P*-1
Crystal system	triclinic
a [Å]	13.135(4)
b [Å]	16.688(4)
c [Å]	17.429(5)
α [°]	89.897(6)
β [°]	77.443(6)
γ [°]	73.787(6)
V [Å^3]	3574(2)
$D_{calcd.}$ [Mg·m^{-3}]	1.20
Z	2
F(000)	1380
Temperature [K]	100
h_{min}/h_{max}	–14/13
k_{min}/k_{max}	–18/18
l_{min}/l_{max}	–18/19
Θ range [°]	1.27–23.26
μ [mm^{-1}]	0.075
$T_{min.}$	0.974
$T_{max.}$	0.995
R_{int}	0.029
Refl. collected	17800
Refl. unique	10224
Refl. observed [$I > 2\sigma(I)$]	7362
Variables	963
$(\Delta/\sigma)_{max}$	0.001
R	0.066
R_w	0.177
S (Gof)	1.01
$(\Delta\rho)_{max}$ [e·Å^{-3}]	0.51
$(\Delta\rho)_{min}$ [e·Å^{-3}]	–0.31

3,5-Bis([4-trimethylsilylethynylphenyl]ethynyl)-*N*,*N*-dihexylaniline (22): A mixture of **21** (3.3 g, 5.4 mmol), trimethylsilylacetylene (2.0 g, 20.4 mmol), $Pd(PPh_3)_4$ (270 mg, 0.2 mmol) and CuI (89 mg, 0.5 mmol) in degassed Et_2NH (60 mL) was heated at reflux under argon for 3 h. The solvent was evaporated in vacuo, and the residue was dissolved in dichloromethane and washed three times with water. The organic phase was dried and the solvent was removed in vacuo. Column chromatography (silica gel, light petroleum ether/diethyl ether 99:1) gave **22** (3.1 g, 88.7%) as a yellow, vitreous oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.21 (s, 18 H), 0.87 (t, ^3J = 6.9 Hz, 6 H), 1.30 (s, 12 H), 1.50–1.55 (s, 4 H), 3.24 (t, ^3J = 6.9 Hz, 4 H), 6.73 (d, ^4J = 1.2 Hz, 2 H), 6.89 (t, ^4J = 1.2 Hz, 1 H), 7.44 (d, ^3J = 8.6 Hz, 4 H), 7.49 ppm (d, ^3J = 8.6 Hz, 4 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 0.1, 14.2, 23.1, 27.1, 27.4, 32.1, 51.3, 88.4, 92.0, 96.7, 104.8, 115.2, 121.7, 123.3, 123.8, 124.1, 131.8, 132.2, 148.5 ppm. MS (EI+, 70 eV): 653 (88) [M]$^+$, 582 (100) [M – C_5H_{11}]$^+$, 512 (26) [M – C_5H_{11} – C_5H_{10}]$^+$, 424 (5).

3,5-Bis(4-ethynylphenylethynyl)-*N*,*N*-dihexylaniline (23): KOH (0.6 g, 11.5 mmol) in H_2O (5 mL) was added to a solution of **22** (3.1 g, 4.8 mmol) in EtOH (150 mL) and the mixture was heated at reflux for 15 min. The solvent was removed and the residue was dissolved in Et_2O. The organic layer was washed with half conc. brine (100 mL) and dried. After evaporation, **23** (2.4 g, 100%) was obtained as a yellow solid, and was used for analysis without further purification. M.p. 76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.1 Hz, 6 H), 1.35 (s, 12 H), 1.50–1.60 (m, 4 H), 3.25 (s, 2 H), 3.29 (t, ^3J = 7.1 Hz, 4 H), 6.79 (s, 2 H), 6.95 (s, 1 H), 7.49 ppm (t, ^3J = 9.0 Hz, 8 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 23.1, 27.1, 27.4, 32.1, 51.2, 79.2, 83.4, 88.2, 92.1, 115.2, 121.7, 122.2, 124.1, 124.2, 131.9, 132.5, 148.5 ppm. IR (neat): $\tilde{\nu}$ = 3295, 3265, 2954, 2954, 2927, 2856, 2209, 2104, 1911, 1633, 1581 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, L·M^{-1}·cm^{-1}) = 270 (36400), 282 (47300), 290 (52700), 300 (64500), 308 (55400), 320 (53400), 384 (4550). MS (EI+, 70 eV): 509 (92) [M]$^+$, 438 (100) [M – C_5H_{11}]$^+$, 368 (27) [M – C_5H_{11} – C_5H_{10}]$^+$. $C_{34}H_{39}N$ (509.72) calcd. C 89.54, H 7.71, N 2.75; found: C 89.25, H 8.00, N 2.74.

Evidence for Formation of Phenylacetylene Macrocycle 2: A suspension of $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) and copper(I) iodide (16 mg, 0.08 mmol) in triethylamine (60 mL) was heated under argon to 75 °C, while the suspension turned dark. A mixture of 1,3-diiodo-5-nitrobenzene (**8**, 0.4 mmol, 149 mg) and **23** (204 mg, 0.4 mmol), dissolved in benzene (50 mL) and triethylamine (50 mL), was added to the catalyst suspension by syringe pump. The rate of the addition was 5 mL·h^{-1}. After the completion of addition the reaction mixture was heated at 75 °C for 2 more hours, and then cooled down to room temp. The solvent was removed in vacuo. The crude product was washed with CH_2Cl_2, and recrystallisation with dioxane yielded small amounts of a product consisting of six components (**2**). ^{1}H NMR(300 MHz, $C_2D_2Cl_4$): δ = 1.01 (s, 18 H), 1.45 (s, 12 H), 1.72 (s, 12 H), 3.29 (s, 12 H), 7.01 (s, 6 H), 7.20 (s, 3 H), 7.62 (s, 24 H), 8.03 (s, 3 H), 8.33 (s, 6 H). MS (FD$^+$): m/z = 1884 [M]$^+$, (MALDI): m/z = 1884 [M]$^+$. There was also mass spectroscopic evidence of a second product consisting of four components ($C_{88}H_{80}N_4O_4$): MS(FAB$^+$): m/z = 1256 [M]$^+$, 1257 [M + H]$^+$.

X-ray Structural Analysis: Table 1 contains the crystallographic data and details of the refinement procedure. The reflections were collected with a Bruker SMART APEX-diffractometer (Mo-*K*α-radiation, graphite monochromator). Data collection and reduction were performed with the BRUKER SMART and SAINT software.[44] A semiempirical absorption correction was performed with SADABS.[44] The structure was solved by direct methods (SHELXTL[45]). Structural parameters of the non-hydrogen atoms were refined anisotropically by a full-matrix, least-squares technique (F^2). The hydrogen atoms linked to aromatic rings were refined isotropically, all other H atoms were calculated. Refinement was carried out with SHELXTL.[45] Disorder was found in two of the *n*-hexyl groups:

C57, C58, C59 (70:30%) and C65, C66 (85:15%). CCDC-243853 contains the crystallographic data (excluding structure factors) for the structures reported in 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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