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Shape-Switchable Azo-Macrocycles

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The synthesis of four shape-switchable macrocycles comprising different peripheral substituents is described. The macrocycles **1**–**4** consist of *m*-terphenyl semicircles interlinked by two azo joints. These macrocycles were assembled from nitro-functionalized *m*-terphenyl moieties through reductive dimerization. The semicircles were assembled through Suzuki cross-coupling reactions. The molecular weights of the macrocycles were determined by vapour pressure osmometry, because mass spectrometry failed in the cases of **2** and **3**. The $E \rightarrow Z$ photoisomerization reactions were analysed by UV/Vis spectroscopy complemented by ^{1}H NMR studies. A very slow thermal back-reaction indicated considerable stabilization of the *Z* isomer. The reduced efficiency of the thermal back-reaction probably arises from the reduced degree of freedom due to the mechanical interlinking of the two azo groups. The photostationary state consisted of all-*Z* (85 %) and all-*E* isomers (15 %). The $E \rightarrow Z$ transformation induced by irradiation displayed simple exponential kinetics, which indicates pairwise switching of the two azo groups in a macrocycle, at least on the timescale under investigation.

Introduction

The $E \rightarrow Z$ photoisomerization of azobenzene is a well-understood photochromic transformation reaction[1–5] and has already been used in the development of light-driven functional molecules.[5–7] Chemical substances exhibiting photoinduced structural changes are not only suitable candidates for the storage of light energy, but also for the conversion of light energy into mechanical motion.[5,8–10] The photoinduced reversible $E \rightarrow Z$ isomerization of azobenzene derivatives causes considerable structural changes.[5,7,11,12] The azobenzene motive is thus an ideal building block for integrating light-induced conformational changes into molecular structures and for creating patterns and nanostructures in polymeric and glass substrates.[13–17] Bulky substituents or cyclic structures cause steric hindrance and thus may influence the isomerization behaviour of azo-functionalized systems. Of particular interest are macrocycles comprised of several azo groups as their structural rearrangement upon isomerization becomes interdependent due to mechanical interlinkage. Macrocyclic model compounds consisting of two azobenzene subunits interlinked by alkyl chains have already been synthesized to investigate the influence of steric restrictions on the photochemical properties of these photoactive subunits.[2] Recently, Tamaoki and co-workers reported the synthesis of a (3,3′)-azobenzophane displaying inverted thermodynamic stabilities.[18] Owing to steric strain, the *Z* isomer of this azobenzophane was more stable, whereas steric repulsion usually favours the *E* isomers of azo derivatives. Thus, the thermal back-reaction of (3,3′)-azobenzophane was from the *E* to the *Z* isomer, and under irradiation the amount of *E* isomer was increased.

Synthetically, only a few different strategies have been reported for the synthesis of azo derivatives. However, owing to their importance as readily available and inexpensive dyes in industry, various procedures for their synthesis have been developed and patented.[19,20] Most of these procedures are based on so-called azo coupling,[21] which is an electrophilic substitution of aryldiazonium salts with electron-rich aromatic compounds.[22,23] However, the moderate electrophilicity of aryldiazonium cations requires rather nucleophilic arenes, which limits the scope of the synthetic strategy. Furthermore, symmetrical azo compounds have been assembled by the oxidation of primary arylamines[24–26] or by the reduction of nitrobenzene derivatives.[27] Both strategies, which alter the oxidation state of the aryl nitrogen atom, are expected to have a common nitroso intermediate that reacts with an arylamine to provide the targeted azo group. Thus, to form azo derivatives comprising two different aryl subunits, a nitroso derivative as precursor of the azo group is isolated that subsequently re-

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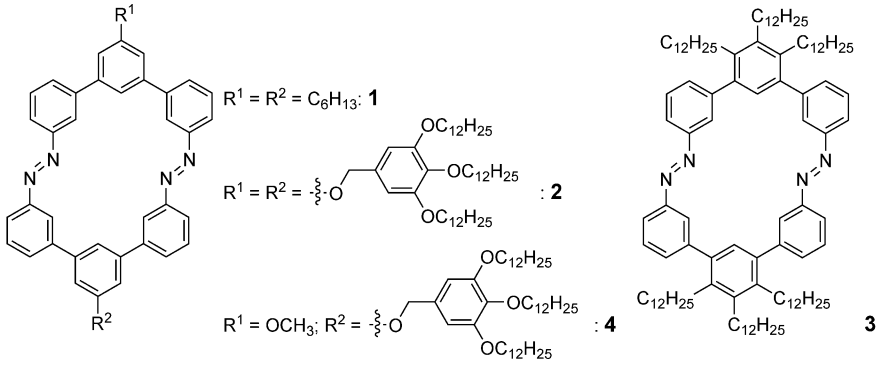


acts with an arylamine in the Mills reaction.[28,29] More recently, an alternative strategy towards asymmetric azo derivatives based on the palladium-catalysed coupling of aryl hydrazides with aryl halides followed by an oxidation was reported.[30,31]

Herein we report the synthesis and shape-switching behaviour of macrocycles **1**–**4** consisting of two rigid *m*-terphenyl semicircles interlinked by two azo groups. Although the central photochemically active macrocycle is common to all the macrocycles **1**–**4**, they differ considerably in the substituents on the central ring of their terphenyl subunits. With the variation of these substituents not only are chemical properties like solubility, processability or adhesion features expected to differ, but also physical properties like size, shape, or momentum of inertia. Whereas the target structures **1**–**3** are symmetric azobenzene macrocycles consisting of two identical semicircles, in the asymmetric macrocycle **4** the central substituents on both semicircles are different.

The shape-switchable macrocycles **1**–**4** are paving the way towards photoswitchable macrocycles, the isomers of which have improved thermodynamic stability features as well as considerably different spatial appearances. However, the combination of efficient photochemical switching with large differences in appearance requires a subtle balance between the rigidity and flexibility of the macrocycle subunits. Although a macrocyclic backbone that is too rigid will handicap the isomerization reaction, subunits that are too flexible will not stabilize the thermodynamically less favoured configuration sufficiently.

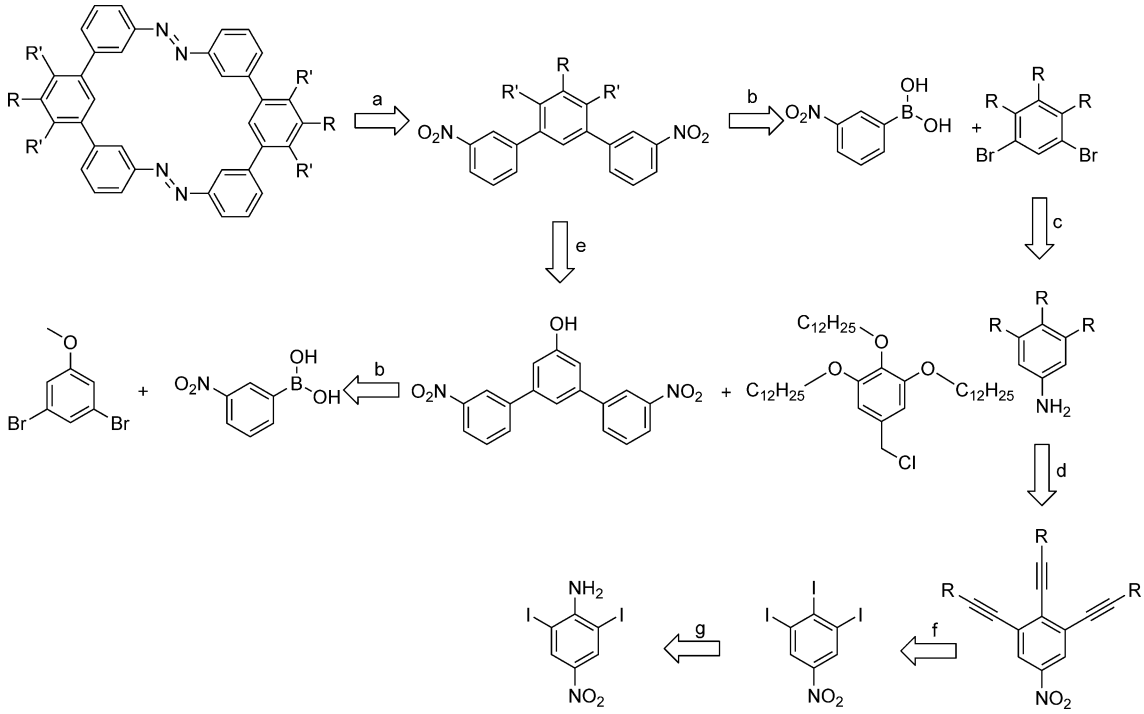
Results and Discussion

Synthetic Strategy

An overview of the synthetic strategy is shown in Scheme 1. All target structures **1**–**4** are macrocycles consisting of two *m*-terphenyl semicircle subunits and two azo groups on opposite sides, and thus similar synthetic strategies were considered in all four cases. Owing to the synthetic availability of its precursors, a reductive dimerization between nitro-functionalized *m*-terphenyl semicircles was favoured as the ring-closing reaction. In the case of the asymmetric macrocycle **4**, the coupling between a nitroso- and an amino-functionalized semicircle (Mills reaction), which would enable two different precursors to be distinguished, might be more favourable. This consideration was even more supporting of the general strategy, as the precursors for the Mills reaction should be available by reduction of the original starting materials, namely the corresponding nitro-functionalized semicircles. A Suzuki cross-coupling reaction should provide the *m*-terphenyl semicircles. 3,5-Dibromoanisole as the starting material for the Suzuki reaction will provide a phenolic hydroxy group on the *m*-terphenyl semicircle after deprotection, which would enable its further functionalization by nucleophilic substitution reactions. Finally, to obtain a suitable 2,3,4-trialkyl-1,5-dibromobenzene precursor for the Suzuki reaction, 2,6-diiodo-4-nitroaniline was considered as a starting material. A Sandmayer reaction will provide 3,4,5-triiodo-1-nitrobenzene and subsequent substitution of the iodine atoms by alkynyl chains in a Sonogashira–Hagihara reaction should yield the required carbon chains. Hydrogenation should reduce both the triple bonds and the nitro group to provide 3,4,5-trialkylaniline, a suitable precursor for introducing bromine atoms at the 2- and 6-positions. Subsequent deamination should give the desired 2,3,4-trialkyl-1,5-dibromobenzene precursor.

Synthesis

The dibromo intermediate **7** was obtained from commercially available 4-hexylaniline. Treatment of 4-hexylaniline (**5**) with *N*-bromosuccinimide (NBS) in DMF gave the doubly brominated product **6** as a dark-red solid in a good yield of 86%.[32] Deamination with concentrated sulfuric acid and sodium nitrite at 75 °C provided after 3 h the desired dibromo compound **7**, which was isolated by column chromatography (CC) in 55% yield over both steps. Treatment of 2.6 equiv. of the commercially available (3-nitrophenyl)boronic acid and the dibromoaryl compound **7** with 8 mol-% of tetrakis(triphenylphosphane)palladium [$Pd(PPh_3)_4$] in toluene/ethanol (3:1) at 85 °C for 3 h provided the desired semicircle **8** as a light-green solid in a good yield of 95% after CC.[33] To assemble the macrocycle



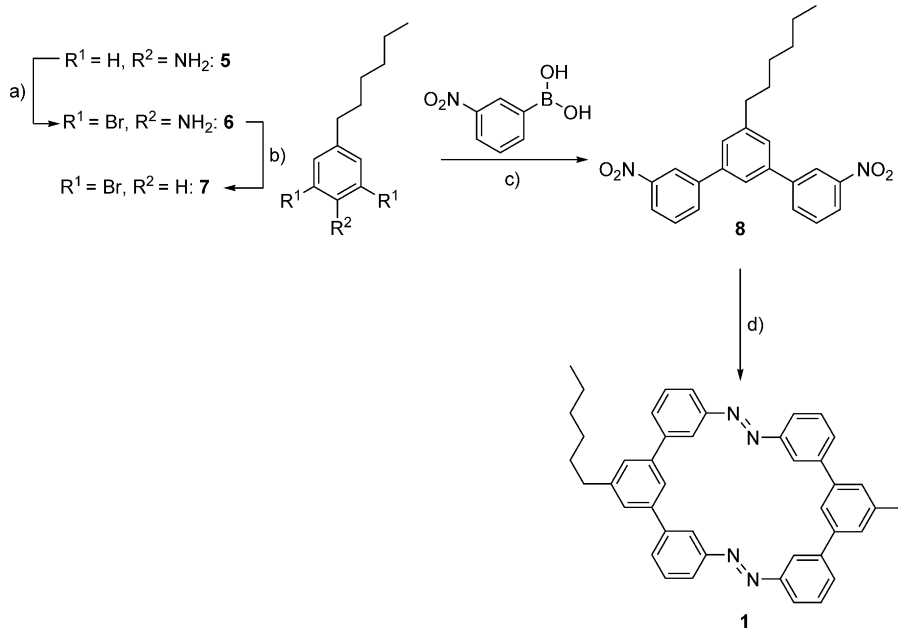
Scheme 1. Retrosynthetic scheme for the synthesis of symmetric macrocycles. (a) Reductive dimerization, (b) Suzuki cross-coupling reaction, (c) bromination and deamination, (d) hydrogenation, (e) nucleophilic substitution, (f) Sonogshira–Hagihara cross-coupling, (g) Sandmayer reaction.

1 (Scheme 2), the dinitro semicircle **8** was treated with lithium aluminium hydride ($LiAlH_4$) in dry THF at room temperature (r.t.) for 75 min. Interestingly, precipitation indicating the formation of insoluble polymers was not observed in spite of the bifunctional building blocks. The crude product was collected by filtration of the precipitate formed after the addition of water. Subsequent extraction by CH_2Cl_2 and purification by gel permeation chromatography (GPC) provided the macrocycle **1** as a bright-orange solid in 37% yield. With the pure compound in hand, an alternative purification procedure was found. Dissolution of the crude extract in hot toluene/ethanol (6:5) and collection of the oily residue after storage at –20 °C for 10 d gave the macrocycle **1** in 50% yield and in a pure form according to analytical GPC.

To further clarify the surprising efficiency of the cyclization reaction, the crude reaction mixture was also investigated by analytical GPC. And indeed, besides the dominant main peak corresponding to the macrocycle **1** with a retention time of 11.85 min, only a few rather weak peaks at shorter retention times, probably arising from larger oligomers, and a single small peak at a longer retention time, probably due to the fully reduced diamino semicircle, were observed. However, these side-products were not further investigated.

To increase the molecular weights of the subunits of the two semicircles moving relative to each other and thus to increase the spatial difference of the two isomers, the macrocycles **2** and **3** were envisaged. Shape-persistent macrocycles comprising similar polyalkyl substituents have already been reported by Höger et al.[34] Increased adsorption properties of these macrocycles with increasing number of alkyl chains were observed, an interesting aspect in view of a future scanning probe investigation of switching macrocycles.

The synthetic route to the target macrocycle **2** is shown in Scheme 3. The commercially available 1,3,5-tribromobenzene (**13**) was converted in an aromatic nucleophilic substitution reaction[35] with 1.4 equiv. of sodium methoxide in DMF at 80 °C. After CC, the desired monosubstituted product **14** was isolated in a good yield of 70%. Subsequent Suzuki cross-coupling[36,37] turned out to be challenging. With $[Pd(PPh_3)_4]$ as catalyst and K_2CO_3 as base, **14** was treated with 2.6 equiv. of (3-nitrophenyl)boronic acid in toluene/ethanol (8:3) at 85 °C for 150 min. The doubly arylated product **15** was obtained in a moderate yield of 33% after recrystallization from hot toluene. Although shorter reaction times provided the monocoupled compound as the main product, considerable degradation of the starting material was observed for elongated reaction times. After nearly quantitative deprotection to the free alcohol **16** with BBr_3, the semicircle **17** was assembled in an S_N2 reaction with the electrophile **12**. The polyalkylated chloromethylbenzene **12** was synthesized according to the literature[38] by starting from the commercially available methyl 3,4,5-trihydroxybenzoate (**9**) in three steps in an excellent overall yield of 85%.[39] The subsequent S_N2 reaction[31] with the phenol **16** was performed with potassium carbonate in DMF at 65 °C. After CC, the semicircle **17** was isolated as a white powder in a good yield of 89%. For the macrocycli-



Scheme 2. Synthetic route to target macrocycle **1**. Reagents and conditions: (a) NBS, DMF, 0 °C → r.t., 86%; (b) $NaNO_2$, H_2SO_4, EtOH, 75 °C, 60%; (c) $[Pd(Ph_3)_4]$, K_2CO_3, $C_6H_5CH_3$, EtOH, 85 °C, 95%; (d) $LiAlH_4$, THF, r.t., 37–50%.

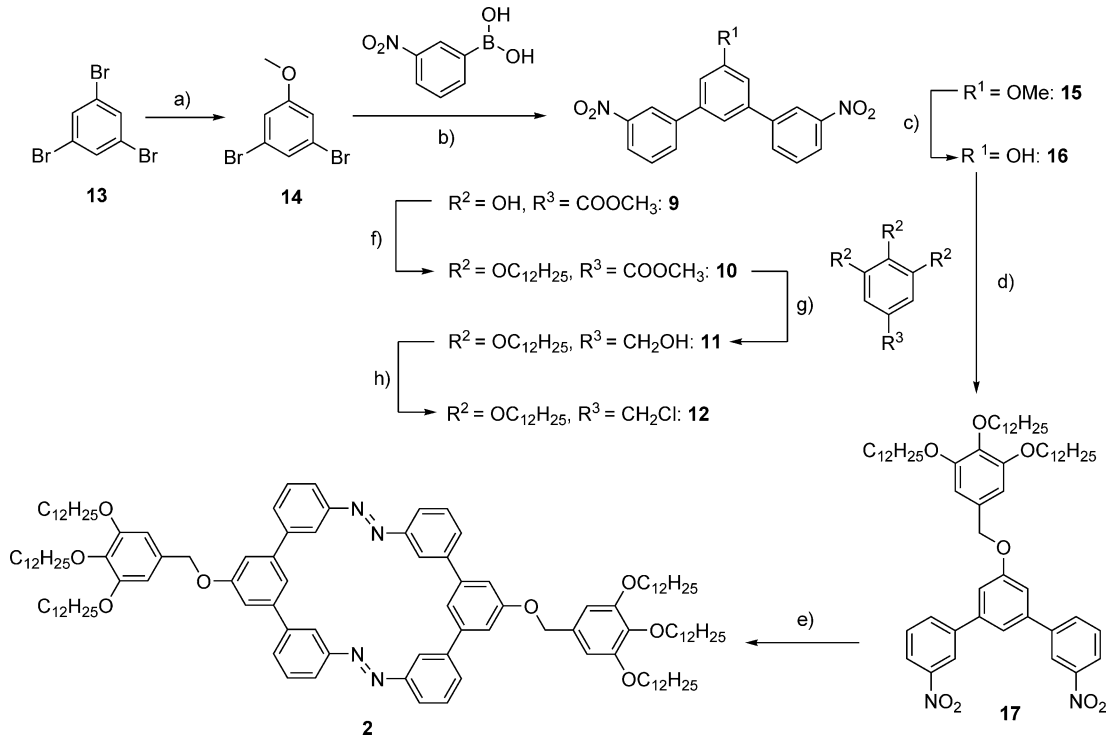
zation reaction similar conditions to those described above for the macrocycle **1** were applied. Thus, after treating **17** in THF with $LiAlH_4$, the macrocycle **2** was isolated in a yield of 34% by size-exclusion chromatography (SEC) as an intensely orange-coloured resin. A single peak in the analytical GPC (10.8 min) further confirmed the purity of the isolated macrocycle **2**.

As a more compact macrocycle consisting of trialkyl-functionalized semicircles, **3** was envisaged with three long alkyl chains directly connected to the central ring of the *m*-terphenyl subunit (Scheme 4). With three alkyl chains per semicircle the solubility and adsorption properties of the macrocycle **2** should be maintained, but the floppiness of the semicircle subunits should be reduced due to the absence of the flexible –O–CH_2 linker.

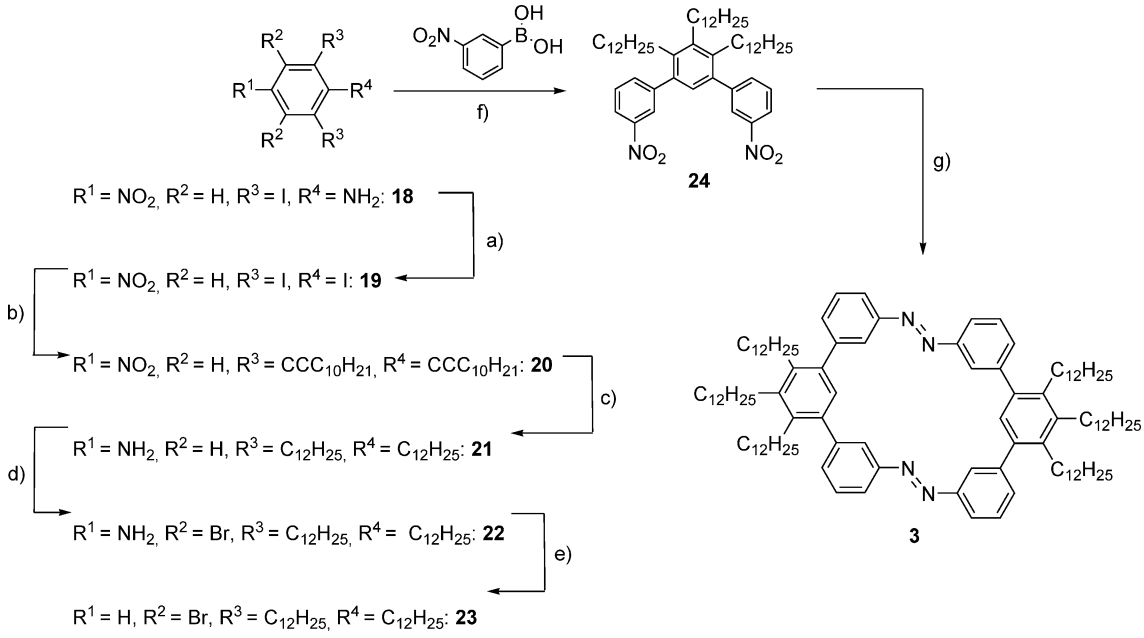
The commercially available 2,6-diiodo-4-nitroaniline (**18**) was first converted through a Sandmayer reaction[40] into triiodonitrobenzene **19** in 80% yield. According to the literature,[41] intermediate **21** was synthesized by a Sonogashira–Hagihara cross-coupling reaction followed by a palladium-catalyzed hydrogenation in 53% yield over both steps. The moderate yield of the hydrogenation reaction was due to incomplete hydration hydrogenation of the double bond in the *para* position to the nitro group, probably as a result of the sterically hindered formation of the π complex in the catalytic cycle.[22,42] However, neither increased hydrogen pressure nor an increased concentration of the catalyst provided a better yield.

The subsequent assembly of the macrocycle **3** was similar to the synthesis described above for macrocycle **1**. The reaction of the amine **21** with NBS in DMF gave the doubly brominated product **22** as a yellowish oil in 70% yield.[32] Deamination with concentrated sulfuric acid and sodium nitrite provided the desired dibromo compound **23**, which was isolated by CC in pure hexane in a good yield of 95%. A Suzuki cross-coupling reaction[36] with commercially available 3-nitrophenylboronic acid allowed the triply alkylated semicircle **24** to be prepared in 81% yield. The desired macrocycle **3** was obtained by a reductive dimerization with $LiAlH_4$ in THF at room temp. After purification with SEC by using toluene as eluent, the pure product was isolated in 49% yield as an intensely orange-coloured resin. Analytical GPC confirmed the purity of the compound with a single peak after 10.87 min.

To investigate the role of symmetry, an asymmetric macrocycle **4** was envisaged (Scheme 5). The Mills reaction[43] has previously turned out to be very efficient for constructing asymmetric azo compounds.[28,44] Because of the different functionalities required as precursors (R–NO and R′–NH_2), it is ideally suited for the assembly of two different building blocks. Amino-functionalized semicircles were readily available by reducing the corresponding dinitro semicircles with tin powder in concentrated hydrochloric acid. However, a dinitroso-functionalized semicircle as the second precursor of the Mills reaction could not be obtained in reasonable yields, neither by reduction of a dinitro semicircle nor by oxidation of a diamino semicircle. According to a second strategy, an amino semicircle was treated with potassium peroxymonosulfate in a CH_2Cl_2/H_2O solvent mixture.[45] Both ^1H NMR and MALDI-TOF MS investigations revealed the presence of the desired compound in the crude reaction mixture. However, all attempts to isolate this labile nitroso semicircle by CC or by crystallization failed. As an alternative, an in situ preparation of the dinitroso semicircle was envisaged. However, treatment of the reaction mixture comprising the dinitroso semicircle with a diamino semicircle only provided poor amounts of an inseparable mixture, probably of various oligomers.

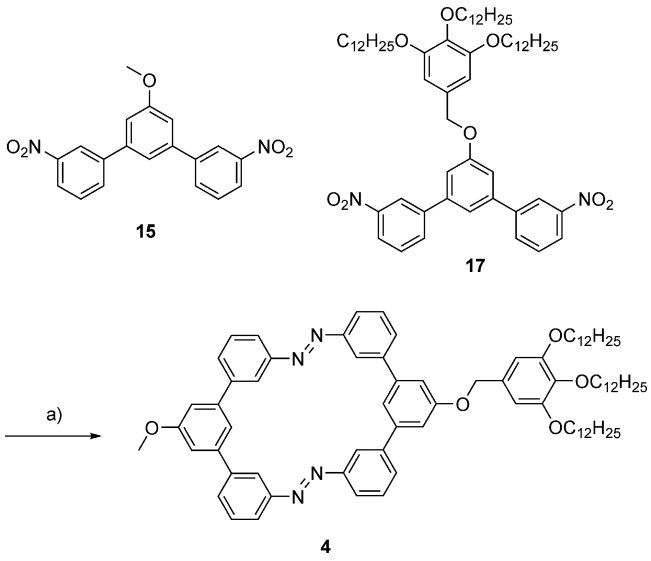


Scheme 3. Synthetic route to target macrocycle **2**. Reagents and conditions: (a) NaOMe, DMF, 80 °C, 70%; (b) $[Pd(Ph_3)_4]$, K_2CO_3, $C_6H_5CH_3$, EtOH, 85 °C, 33%; (c) BBr_3, DCM, –78 °C → r.t., 95%; (d) K_2CO_3, DMF, 65 °C, 89%; (e) $LiAlH_4$, THF, r.t., 34%, (f) $BrC_{12}H_{25}$, DMF, K_2CO_3, KI, 70 °C, 90%; (g) (1) $LiAlH_4$, Et_2O, r.t.; (2) NaOH, H_2O, r.t., 96%; (h) $SOCl_2$, DMF, DCM, r.t., 98%.



Scheme 4. Synthetic route to target macrocycle **3**. Reagents and conditions: (a) (1) AcOH, $NaNO_2$, H_2SO_4, 15 °C → r.t.; (2) KI, H_2O, CH_3COOH, H_2SO_4, 95 °C, 80%; (b) $HCCC_{10}H_{21}$, $[Pd(PPh_3)_2Cl_2]$, CuI, NEt_3, 85 °C, 89%; (c) H_2, Pd/C, EtOH, AcOEt, r.t., 59%; (d) NBS, DMF, 0 °C → r.t., 70%; (e) H_2SO_4, $NaNO_2$, EtOH, 85 °C, 95%; (f) $[Pd(Ph_3)_4]$, K_2CO_3, $C_6H_5CH_3$, EtOH, 85 °C, 85%; (g) $LiAlH_4$, THF, 40 °C, 49%.

An alternative strategy towards an asymmetric azomacrocycle consists of the statistical assembly of two different dinitro semicircles. Thus, the two semicircles **15** and **17** were subjected to the macrocyclization conditions described above. Equimolar amounts of the two different semicircles **15** and **17** were dissolved in THF. A 1 M $LiAlH_4$ solution in THF was slowly added at r.t. over a period of 20 min. After keeping the reaction mixture at 40 °C for



Scheme 5. Synthetic route to the asymmetric macrocycle **4**. Reagents and conditions: (a) $LiAlH_4$, THF, 40 °C, 44%.

110 min, it was poured into water and extracted with CH_2Cl_2. Owing to the statistical nature of the reaction, not only the desired macrocycle **4** but most probably also the two symmetric macrocycles were formed. Fortunately, the molecular weights of the three macrocycles are sufficiently different to allow their separation by SEC. Although analytical GPC was not able to separate the crude reaction mixture (see the Supporting Information, ESI 9), preparative SEC divided the sample into three well-separated main bands, of which the most intense central one was isolated. Owing to the limited amounts formed, the two accompanying bands were not further analyzed. The analytical data (^{1}H NMR, GPC, VPO) of the isolated central band indicated a pure chemical compound with the structure of macrocycle **4**. The isolated intensely orange-coloured resin corresponded to a yield of 44% of the non-symmetrical compound **4** and displayed a single symmetric peak with a retention time of 11.01 min in analytical GPC. The efficiency of the formation of the asymmetric macrocycle **4** remains to some extent puzzling. It might be related to the restricted formation of the symmetric macrocycle **2** comprising two sterically more demanding semicircles.

Characterization

Although the precursors **6**–**24** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis, the characterization of the macrocycles **1**–**4** turned out to be more challenging.

Although the ^{1}H NMR spectra corroborated the suggested structures of all the macrocycles **1**–**4**, one-dimensional ^{13}C NMR spectra could only be obtained for the macrocycles **1** and **4**. The size and the relatively high inertia of each of the larger macrocycles **2** and **3** cause long rotational correlation times τ. Because τ is proportional to the linewidths of the resonances in the NMR spectra, the signal-to-noise ratio for the relatively insensitive ^{13}C NMR spectra turned out to be too small to obtain meaningful one-dimensional $^{13}C\{^1H\}$ NMR spectra.[46] However, the more sensitive ^{1}H-detected HMBC and HMQC spectra allowed full characterization of the carbon resonances of both macrocycles **2** and **3**. Attempts to record the one-dimensional ^{13}C NMR spectra of these two macrocycles in their more compact *Z*,*Z* form by illumination at 313 nm prior to recording the ^{13}C NMR spectra were not successful.

Of particular importance is the determination of the purity and the molecular weight of each of the isolated macrocycles, as the synthetic strategy based on the dimerization of two bifunctional building blocks allows the formation of larger cyclic oligomers with comparable NMR spectra. Analytical gel permeation chromatograms were recorded to document the purity of the macrocycles **1**–**4** and are displayed in the Supporting Information. All four compounds displayed well-defined single peaks with retention times R_t(**1**) = 11.85 min, R_t(**2**) = 10.8 min, R_t(**3**) = 10.87 min and R_t(**4**) = 11.01 min in the expected order of decreasing molecular weight. However, owing to the particular shape and thus hydrodynamic volume of the macrocycles **1**–**4**, GPC is not suited to determining their molecular weights. Surprisingly, similar GPC conditions applied to polystyrene standards (see the Supporting Information) displayed systematically shorter retention times for the more compact macrocycles. Fortunately, the molecular signals of the macrocycles **1** and **3** were also detected in mass spectrometry by electron impact ionization for **1** and by matrix-assisted laser desorption ionization (MALDI) in the case of **3**, which enabled the peaks detected by analytical GPC to be calibrated. All attempts to ionize the macrocycles **2** and **4** for subsequent detection by mass spectrometry failed. Neither the molecular ions nor characteristic decomposition fragments were observed. As a complementary method for determining the molecular weights of the macrocycles **1**–**4** vapour pressure osmometry (VPO) was considered. Thus, the molecular weights of the macrocycles **1**–**4** were determined by VPO. All four compounds were measured in $CHCl_3$ at 42 °C, and the results are displayed in Table 1. Within the limits of experimental accuracy, the expected molecular weights were recorded for all macrocycles **1**–**4**, further corroborating their structures.

The chemical structures of all four macrocycles **1**–**4** were fully confirmed by the analytical investigations described above. Additional supporting evidence was obtained from their UV/Vis and IR spectra. For example, the UV/Vis absorption in the region of 320 nm and the visible band at about 450 nm, responsible of the bright-orange colour of the compounds, are characteristic features of the azo derivatives. The cyclization reaction was further monitored by comparison of the IR spectra of the macrocycles **1**–**4** and their precursors. The disappearance of the characteristic aromatic nitro band in the region of 1520 cm^{-1} together with the appearance of the signals at 1450 and 1240 cm^{-1}, which were assigned to a (*Z*)-azo subunit, further document the transformation of the nitro groups of the semicircles

Table 1. Molecular weights of **1**–**4** measured by VPO.

Macrocycle	Measured molecular weight [g/mol]	Calculated molecular weight [g/mol]	Concentration [mg/g]	Standard deviation[a]
1	709.1	680.4	3.93	0.06
2	1739.7	1830.8	5.22	0.05
3	1500.7	1522.5	4.69	0.07
4	1174.4	1201.7	1.44	0.09

[a] Standard deviation of the measured samples derived from at least three independent measurements.

into the azo groups in the macrocycles. Furthermore, even linear oligomers could be excluded by IR spectroscopy, as neither signals expected for aromatic nitro functions (1660–1440 cm^{-1}) nor those expected for aromatic amines (3500–3300 cm^{-1}) were observed.

UV/Vis Measurements

All four macrocycles **1**–**4** showed absorption bands at about 450 nm as well as at about 320 and 285 nm. In particular, the high-energy bands were attributed to π→π* transitions and the broad low-energy absorption was attributed to n→π* transitions.[9,47]

All the macrocycles **1**–**4** displayed similar spectra that differ mainly in the UV region, that is, at about 250 nm. This has been attributed to the different substituents on the central phenyl ring, which cause a twisting of the phenylene units resulting in electronic decoupling of the aromatic moieties. Thus, a blueshift of this band was observed for the sterically more hindered compounds **2** and **3** (Figure 1). Emission was not detected for any of these macrocycles, neither at r.t. nor at 77 K.

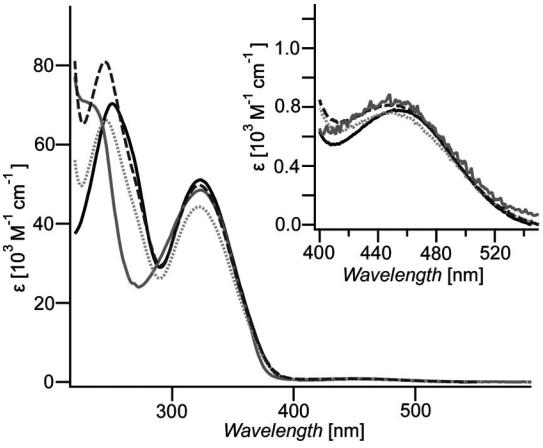


Figure 1. Absorption spectra of the macrocycles **1**–**4** (**1**: solid black line; **2**: dashed line; **3**: solid grey line; **4**: dotted line) in THF solution.

Upon exposure to ambient light, considerable changes in the UV/Vis spectra were observed, as expected for azo derivatives. Photoisomerization reactions were investigated for all compounds **1**–**4** in THF by observing the changes in their absorption spectra. Furthermore, to quantify the *E*/*Z* ratio of isomers, the concentrations of the isomers formed were determined in deuteriated THF by ^{1}H NMR spectroscopy.

To investigate the $E \rightarrow Z$ isomerization mechanism, all the macrocycles **1**–**4** were irradiated at 313 nm. For the irradiation, a 200 W mercury lamp with a dichromic filter (280–400 nm) and a 320 nm band-pass filter to select only the peak at 313 nm were used. All four macrocycles **1**–**4** displayed very similar spectral changes. As a typical example, the behaviour of macrocycle **1** in THF at a concentration of 1.7×10^{-5} mol/L is shown in Figure 2.

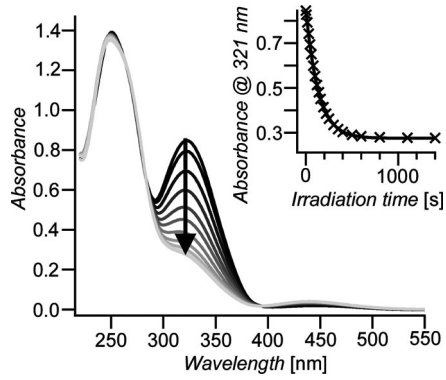


Figure 2. Changes in the absorption spectra of macrocycle **1** in THF upon irradiation at 313 nm. Inset: absorbance change versus irradiation time.

The decrease in the absorbance of the π→π* band and the increase in the n→π* absorbance upon light irradiation over time was attributed to the formation of the *Z* isomer. The photoisomerization reaction presented two isosbestic points at 285 and 395 nm and reached the photostationary state within 8 min of irradiation under the experimental conditions applied.

The inset in Figure 2 displays the absorbance at 321 nm plotted against the irradiation time. The evolution of the 321 nm signal (see inset) followed an exponential trend. This suggests a switching dynamic for the pair of azo chromophores in the macrocycle **1**, which should involve, at least within the temporal resolution of the optical investigation, the switching of both azo groups.

The reaction was monitored by ^{1}H NMR spectroscopy in order to determine the amounts of *Z* and *E* isomers and to calculate the molar extinction coefficient of the *Z* isomer. Isomerization was performed in a deuterated THF solution, and measurements were taken at different irradiation times. The ^{1}H NMR spectra and the corresponding UV/Vis absorptions of macrocycle **1** are displayed in Figure 3; the other compounds **2**–**4** behave similarly, and their results are summarized in Table 2.

The *Z* isomers displayed signals in the ^{1}H NMR spectra at frequencies different to those of the *E* isomers. Both the

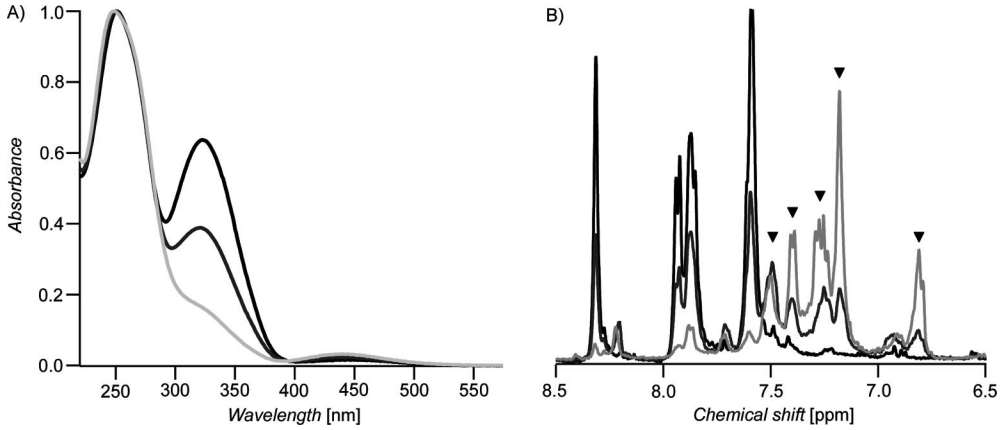


Figure 3. (A) UV/Vis spectra of macrocycle **1** of the corresponding *E*/*Z* ratio (black: thermally stable state; dark grey: 50% isomerized; light grey: photostationary state). (B) Corresponding ^{1}H NMR spectra (markers indicate the peaks corresponding to the *Z* isomer).

Table 2. Quantum yields of photoisomerization and molar extinction coefficients (at 321 nm) of macrocycles **1**–**4**.

Macrocycle	Φ_{E-Z}	Φ_{Z-E}	ε_E [dm^3/mol cm]	ε_Z [dm^3/mol cm]
1	0.29	0.43	50800	7100
2	0.33	0.56	49300	15900
3	0.28	0.45	48300	8600
4	0.26	0.51	44000	14500

UV/Vis and ^{1}H NMR spectra were used to calculate the concentration of the *Z* compound formed. On the timescale of the ^{1}H NMR measurements, no detectable thermal back-isomerization was observed, as shown by measuring the absorption spectra before and after the NMR experiments.

By integration of the corresponding ^{1}H NMR signals, the amount of *E* isomer in the photostationary state was determined to be 15%. Furthermore, the ε values of the *Z* isomers of the macrocycles **1**–**4** were determined and are listed in Table 2.

By using the acquired data, the photoisomerization quantum yields for the $E \rightarrow Z$ reactions were calculated (see Table 2) according to the procedure reported by Zimmerman et al.[48] (see the Exp. Sect.).

The ε values differed considerably for the macrocycles and were slightly higher than those found in comparable systems.[2] However, the calculated quantum yields were comparable considering that both azo moieties underwent photoisomerization. Despite the fact that the two azobenzene groups are linked together, the formation of an intermediate *E*,*Z* isomer upon irradiation with UV light was not observed. The UV/Vis and ^{1}H NMR spectra gave no evidence of an *E*,*Z* intermediate, as all the spectra can be expressed as the sum of the absorbances of the *Z* and *E* isomers. The macrocycles **1**–**4** are extremely rigid, and therefore a small motion of half of the macrocycle forces the other half to switch accordingly. This explains the absence of *E*,*Z* intermediates, which have been observed in comparable, but less rigid azo systems.[2]

The back $Z \rightarrow E$ back-isomerization was either triggered by light or was observed as a thermal back-reaction. For the light-induced back-reaction, the sample was irradiated at the maximum of the peak of the *Z* isomer (450 nm). To monitor the thermal back-reaction with time, the sample was kept in the dark until the azo compound **1** had switched back to its thermodynamically more stable *E* form. The dynamics of the thermal back-reaction were investigated by monitoring the increasing absorbance at 321 nm (Figure 4). The thermal back-isomerization turned out to be a very slow reaction, which indicates a very stable *Z* isomer. The re-equilibration of the *Z*-enriched solution back to a solution comprising exclusively the thermodynamically favoured *E* form took several days. The rate constant for the thermal back-isomerization was 1.15×10^{-6} s^{-1}, which is of a magnitude comparable to those of similar systems with multiple azobenzene moieties.[47]

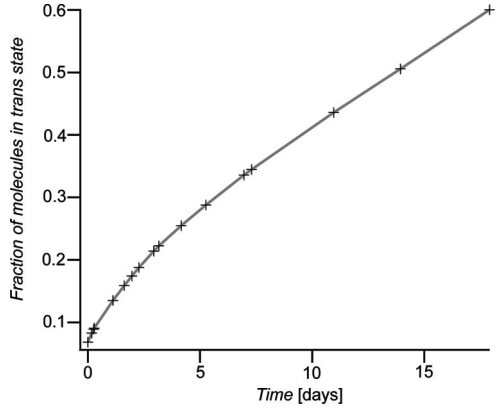


Figure 4. Thermal back-reaction $Z \rightarrow E$ of macrocycle **1** monitored over time.

To obtain a faster $Z \rightarrow E$ isomerization and to monitor the reversibility of the photoisomerization reaction, the n→π* band at 450 nm was irradiated by using a xenon lamp and an appropriate set of filters (water filter and 450 BP). After the thermal back-reaction, the macrocycle **1** was

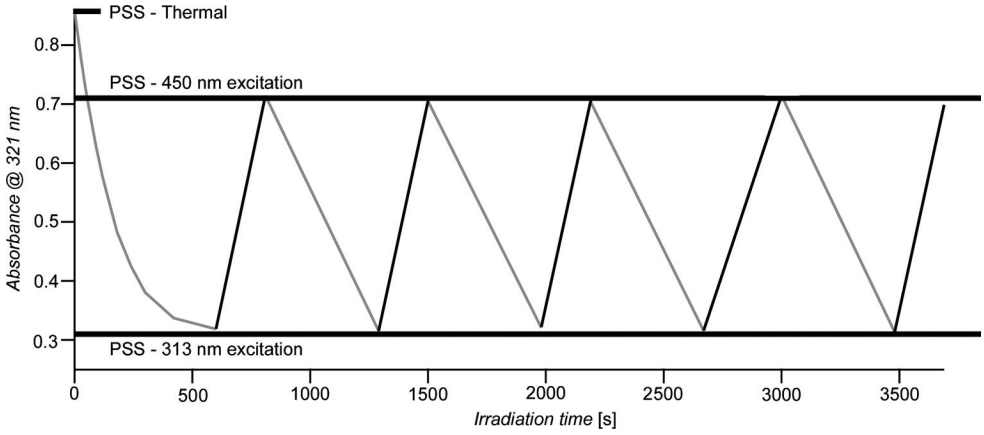


Figure 5. Photoinduced back-reaction of macrocycle **1**, alternatingly irradiating with UV (313 nm) and blue (450 nm) light to switch between the two photostationary states (PSS).

completely switched back to the *E* isomer, whereas in the photochemical back-reaction in the photostationary state 15% of the macrocycle still remained in its *Z* form. To gain information on the stability and fatigue resistance of the system, macrocycle **1** was cycled five times. Reversible switching between the two photostationary states was observed (Figure 5). Figure 5 shows data obtained by irradiating the macrocycle **1** at 313 nm for the $E \rightarrow Z$ isomerization and at 450 nm for the $Z \rightarrow E$ conversion. The data is representative for all the target compounds **1**–**4**.

Conclusions

Four shape-switchable macrocycles **1**–**4** consisting of *m*-terphenyl semicircles interlinked by two azo joints have been synthesized and characterized. All four macroycles were obtained by reductive dimerization of the corresponding dinitro semicircles. Considering the polymerization potential of the synthetic strategy, all four azo-macrocycles were isolated in surprisingly good yields, ranging from 34% for **2**, to 44 and 49% for **4** and **3**, respectively, up to 50% for **1**. These macrocycles were characterized by ^{1}H and ^{13}C NMR spectra, profiting from the more sensitive ^{1}H-detected HMBC and HMQC techniques in the cases of **2** and **3**. Although the purity of **1**–**4** was shown by analytical GPC, their molecular weights were determined by VPO. Mass spectra were also obtained for **1** and **3**.

All four macrocycles **1**–**4** displayed comparable $E \rightarrow Z$ photoisomerization upon irradiation at 313 nm. An *E*/*Z* ratio of 15:85 of the isomers was determined in their photostationary states. The full thermal back-reaction required several weeks. Hence, the thermodynamically less favoured *Z* isomer showed substantial stabilization by the rigid macrocyclic structure. Despite having two azo groups in the macrocyclic periphery, an intermediate mixed *E*,*Z* isomer was not observed; the stiff terphenyl semicircles probably disfavour a strained mixed state.

These shape-switchable macrocycles **1**–**4** were designed to investigate their spatial transformations by scanning probe methods. So far, all attempts to immobilize these macrocycles on graphite have failed in spite of their long alkyl chains.

Experimental Section

Reagents and Solvents: All chemicals were directly used for the synthesis without further purification unless otherwise stated. Solvents for chromatography and crystallization were distilled once before use; technical grade solvents were used for extraction. Dry tetrahydrofuran (THF) was distilled from sodium and potassium, and dry dichloromethane (DCM) was distilled from calcium hydride or purchased over molecular sieves from Fluka.

Synthesis: All reactions with reagents that are easily oxidized or hydrolysed were performed under argon by using Schlenk techniques; only dry solvents were used, and the glassware was heated prior to use.

Analyses and Instruments: Bruker DPX NMR (400 MHz) and BZH NMR (250 MHz) instruments were used to record ^{1}H NMR spectra. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks or trimethylsilane (TMS), and coupling constants (*J*) are reported in Hertz (Hz). NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The spectra were recorded at room temperature. The multiplicities are denoted as the following: s = singlet, d = doublet, q = quartet, quint = quintet, m = multiplet and br. = broad. In addition, ^{1}H NMR spectra during isomerization studies were recorded with a Bruker AM 400 MHz spectrometer. A Bruker DPX (101 MHz) instrument was used to record ^{13}C NMR spectra. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks. NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The measurements were performed at room temperature. The carbon atom assignments are classified by the following: Cp = primary, Cs = secondary, Ct = tertiary, Cq = quaternary. The peaks were related to the carbon atoms by estimations and calculations of incremental values. A Bruker (600 MHz) instrument was used to record 2D NMR spectra. HMQC spectra were recorded with an acquisition time in *f*2 of 85 ms and 1 K data points and an acquisition time in *f*1 of 20 ms and 0.5 K data points. HMBC spectra were recorded with an acquisition time in *f*2 of 170 ms and 2 K data points and an acquisition time in *f*1 of 34 ms and 1 K data points.[49] Mass

spectra were recorded with a Bruker Esquire 3000 Plus for electron spray ionization (ESI), a Finnigan MAT 95Q for electron impact (EI), a Finnigan MAT 8400 for fast atom bombardment (FAB) or a Voyager-De™ Pro for MALDI-TOF. The peaks were measured in *m*/*z* (%). Elementary analyses were carried out with a Perkin-Elmer Analysator 240. The samples for UV analysis were irradiated by using a Lot-Oriel 200 W high-pressure mercury lamp with a 280–400 nm dichroic mirror (to remove IR and visible light) and a Perkin-Elmer 320 nm band-pass filter to allow only light from the 313 nm Hg line. The intensity of the light source was determined by chemical actinometry using a 6.4×10^{-4} mol L^{-1} azobenzene (Sigma–Aldrich, 99%) solution in methanol. All samples were constantly stirred upon irradiation. Spectra were recorded with a Varian Cary 5000 two-beam spectrophotometer with baseline correction and pure solvent as the reference. Spectroscopic grade THF and methanol were used as obtained from Merck. Samples for IR spectroscopy were measured neat with a Shimadzu FTIR 8400S Fourier transform IR spectrometer. A Shimadzu LC-8A instrument was used to record gel permeation chromatograms. The measurements were performed at room temperature with an OligoPore 300 × 7.5 mm column (particle size 6 μm) from Polymer Laboratories by eluting with toluene at a flow rate of 0.5 mL/min at λ = 220 nm. Calibrations were performed with polystyrene from Polymer Laboratories under the same conditions as used for the analysis. Vapour pressure osmometry (VPO) experiments were performed with a Knauer K-7000 vapour pressure osmometer. For the calculations the software EuroOsmo 7000, Version 1.5, was used. For column chromatography (CC), silica gel 60 (40–63 μm) from Merck or silica gel 60 (40–63 μm) from Fluka was used. Preparative size-exclusion chromatography (SEC) was performed with Bio-Beads® S-X Beads from BIO RAD with distilled toluene as eluent. For thin-layer chromatography (TLC), silica gel 60 F_{254} glass plates with a thickness of 0.25 mm from Merck were used. Detection was carried out by using a UV lamp at 253 or 366 nm.

2,6-Dibromo-4-hexylbenzenamine (6): 4-Hexylaniline (**5**; 4.520 g, 25.480 mmol) was dissolved in DMF (30 mL) and cooled to 0 °C. *N*-Bromosuccinimide (11.34 g, 63.710 mmol) in DMF (30 mL) was added dropwise over a period of 30 min while stirring. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for another 3 h. Afterwards, the DMF was removed by rotary evaporation. The residue was purified by CC (silica gel, toluene/DCM, 2:1, R_f = 0.73) to afford the product **6** (7.27 g, 86%) as dark-red crystals after standing overnight. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.19 (s, 2 H), 4.39 (br. s, 2 H, NH_2), 2.45 (t, $^3J_{HH}$ = 7.4 Hz, 2 H), 1.53 (m, 2 H), 1.28 (m, 6 H), 0.88 (m, $^3J_{HH}$ = 6.0 Hz, 3 H, CH_3) ppm.

1,3-Dibromo-5-hexylbenzene (7): 2,6-Dibromo-4-hexylbenzenamine (**6**; 7.26 g, 21.800 mmol) was dissolved in ethanol (130 mL) and concd. sulfuric acid (10 mL). Sodium nitrite (4.50 g, 65.400 mmol) was slowly added in small portions while stirring. Afterwards, the reaction mixture was stirred at 75 °C for 2 h. The reaction mixture was then cooled with an ice bath to 5 °C, water (50 mL) was added, and the suspension was extracted with DCM (2 × 30 mL). The combined organic layers were dried with $MgSO_4$ and the solvents evaporated. The black oily residue was dissolved in hexane (2 mL) and ethyl acetate (1 mL) and purified by column chromatography (silica gel, hexane, R_f = 0.56) to afford the product **7** (4.170 g, 60%) as a light-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (t, $^4J_{HH}$ = 2.0 Hz, 1 H), 7.24 (d, $^4J_{HH}$ = 2.0 Hz, 2 H), 2.53 (t, $^3J_{HH}$ = 7.6 Hz, 2 H), 1.57 (tt, $^3J_{HH}$ = 7.6, $^3J_{HH}$ = 6.6 Hz, 2 H), 1.29 (m, 6 H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.3 (s, 1 C, Cq), 131.7 (s, 1 C, Ct), 130.7 (s, 2 C, Ct), 123.1 (s, 2 C, Cq), 35.8 (s, 1 C, Cs), 32.0 (s, 1 C, Cs), 31.4 (s, 1 C, Cs), 29.2 (s, 1 C, Cs), 23.0 (s, 1 C, Cs), 14.5 (s, 1 C, Cp) ppm. MS (EI): *m*/*z* (%) = 318 (17), 320 (36), 322 (17), 250 (100), 169 (51), 89 (22).

1-Hexyl-3,5-bis(3-nitrophenyl)benzene (8): 3-Dibromo-5-hexylbenzene (**7**; 1.00 g, 3.150 mmol), 3-nitrophenylboronic acid (1.41 g, 8.180 mmol), tetrakis(triphenylphosphane)palladium (290 mg, 0.252 mmol) and potassium carbonate (3.48 g, 25.200 mmol) were added to a solution of dry toluene (100 mL) and dry ethanol (30 mL) under argon. The potassium carbonate did not completely dissolve. The reaction mixture was stirred vigorously at 85 °C for 3 h. After cooling to room temperature, the reaction mixture was filtered through a 1 cm pad of silica, eluting with toluene and ethanol. The residue was absorbed with dichloromethane on silica and then purified by chromatography (silica gel, ethyl acetate/hexane, 1:5, R_f = 0.32) to give the product **8** as a light-yellow oil, which precipitated to give a light-green solid after standing (1.21 g, 95%, m.p. 86–89 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (t, $^4J_{HH}$ = 2.0 Hz, 2 H), 8.24 (ddd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 2.0, $^5J_{HH}$ = 1.0 Hz, 2 H), 7.98 (ddd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 2.0, $^5J_{HH}$ = 1.0 Hz, 2 H), 7.66 (t, $^3J_{HH}$ = 8.1 Hz, 2 H), 7.65 (t, $^4J_{HH}$ = 1.5 Hz, 1 H), 7.50 (d, $^4J_{HH}$ = 1.5 Hz, 2 H), 2.79 (t, $^3J_{HH}$ = 7.6 Hz, 2 H), 1.73 (quint, $^3J_{HH}$ = 7.6 Hz, 2 H), 1.42 (quint, $^3J_{HH}$ = 7.6 Hz, 2 H), 1.35 (m, 4 H), 0.91 (t, $^3J_{HH}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.2 (s, 2 C, Cq), 145.6 (s, 1 C, Cq), 143.0 (s, 2 C, Cq), 140.2 (s, 2 C, Cq), 133.6 (s, 2 C, Ct), 130.2 (s, 2 C, Ct), 127.9 (s, 2 C, Ct), 123.9 (s, 1 C, Ct), 122.8 (s, 2 C, Ct), 122.5 (s, 2 C, Ct), 36.5 (s, 1 C, Cs), 32.1 (s, 1 C, Cs), 32.0 (s, 1 C, Cs), 29.5 (s, 1 C, Cs), 23.0 (s, 1 C, Cs), 14.5 (s, 1 C, Cp) ppm. MS (EI): *m*/*z* (%) = 404.2 (69), 405.2 (18), 334 (100), 287 (25), 239 (43), 226 (23). $C_{24}H_{24}N_2O_4$ (404.46): calcd. C 71.27, H 5.98, N 6.93; found C 71.10, H 5.96, N 6.87.

Macrocycle 1: 1-Hexyl-3,5-bis(3′-nitrophenyl)benzene (**8**; 300 mg, 0.742 mmol) was dissolved under argon in dry THF (3 mL). A 1 M lithium aluminium hydride solution in THF (3.0 mL, 2.969 mmol) was carefully added over a period of 15 min. After complete addition, the reaction mixture was stirred at room temperature for 70 min and at 55 °C for an additional 20 min. After cooling to room temperature, water (7 mL) was added carefully, and, after stirring for 5 min, the reaction mixture was filtered. The filtrate was extracted with dichloromethane (2 × 10 mL), and the combined organic layers were dried with $MgSO_4$ and the solvents evaporated. The almost pure crude product was dissolved in a warm mixture of ethanol/toluene (6:5, 5 mL). After 10 d in the freezer at –20 °C, the solvent was decanted, and the dark-orange oily residue was washed with ethanol and dried at high vacuum for 5 h to give the macrocycle **1** as a bright-orange solid (504 mg, 50%, m.p. 155–157 °C). TLC (silica gel, DCM/hexane, 2:1): R_f = 0.32 (due to the limited solubility of **1** in the eluent, the spot was observed to have a long tail). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 4 H), 7.96 (m, 4 H), 7.80 (m, 6 H), 7.60 (m, 4 H), 7.53 (s, 4 H), 2.77 (m, 4 H), 1.74 (m, 4 H), 1.41 (m, 4 H), 1.33 (m, 8 H), 0.89 (m, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.6 (s, 4 C, Cq), 144.7 (s, 4 C, Ct), 142.8 (s, 4 C, Cq), 141.5 (s, 4 C, Cq), 130.3 (s, 2 C, Cq), 130.0 (s, 4 C, Ct), 127.3 (s, 4 C, Ct), 124.1 (s, 4 C, Ct), 122.6 (s, 2 C, Ct), 122.0 (s, 4 C, Ct), 36.7 (s, 2 C, Cs), 32.2 (s, 2 C, Cs), 32.1 (s, 2 C, Cs), 29.6 (s, 2 C, Cs), 23.1 (s, 2 C, Cs), 14.6 (s, 2 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3051 (w), 3024 (w), 2924 (s), 2852 (m), 1593 (m), 1504 (w), 1445 (4), 1441 (m), 1155 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 680.3 (6), 681 (3), 344 (100), 85 (11), 71 (17), 57 (33), 44 (35).

1,3-Dibromo-5-methoxybenzene (14): Sodium methoxide (1.20 g, 22.24 mmol) was added to a solution of 1,3,5-tribromobenzene (**13**; 5.10 g, 15.88 mmol) in DMF (50 mL). The reaction mixture was

stirred at 80 °C for 8 h, quenched with a 10% aq. HCl solution (20 mL) and extracted with *tert*-butyl methyl ether (3 × 30 mL). The combined organic layers were washed with brine (35 mL), dried with magnesium sulfate and the solvents evaporated. The crude product was purified by CC (silica gel, hexane, R_f = 0.3) to afford the title compound **14** (2.95 g, 70%) as a white solid (m.p. 42–43 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, $^4J_{HH}$ = 1.8 Hz, 1 H), 6.99 (d, $^4J_{HH}$ = 1.8 Hz, 2 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.2 (s, 1 C, Cq), 126.8 (s, 1 C, Ct), 123.5 (s, 2 C, Cq), 116.9 (s, 2 C, Ct), 56.1 (s, 1 C, Cq) ppm. MS (EI): *m*/*z* (%) = 265.8 (100), 263.8 (49), 266.8 (7), 267.8 (47), 235.8 (19). $C_7H_6Br_2O$ (265.93): calcd. C 31.62, H 2.27; found C 31.49, H 2.27.

5-Methoxy-1,3-bis(3-nitrophenyl)benzene (15): (3-Nitrophenyl)boronic acid (816 mg, 4.89 mmol), tetrakis(triphenylphosphane)palladium (217 mg, 0.19 mmol) and potassium carbonate (2.07 g, 15.04 mmol) were added to a solution of **14** (500 mg, 1.88 mmol) in dry toluene (40 mL) and dry ethanol (15 mL) under argon. The reaction mixture was stirred vigorously at 85 °C for 150 min. After cooling to room temperature, the reaction mixture was filtered through a 1 cm pad of silica gel, the pad was washed with toluene (150 mL), and the solvents were evaporated to dryness. The dark crude product was recrystallized from hot toluene to afford the title compound **15** (219 mg, 33%) as a white powder (m.p. 203–205 °C). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.57 (t, $^4J_{HH}$ = 2.0 Hz), 8.28 (d, $^3J_{HH}$ = 7.8 Hz), 8.23 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 2.0 Hz), 7.77 (t, $^3J_{HH}$ = 7.8 Hz, 2 H), 7.71 (t, $^4J_{HH}$ = 1.4 Hz, 1 H), 7.39 (d, $^4J_{HH}$ = 1.4 Hz, 2 H), 3.93 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 161.4 (s, 1 C, Cq), 149.3 (s, 2 C, Cq), 142.3 (s, 2 C, Cq), 141.1 (s, 2 C, Cq), 134.7 (s, 2 C, Ct), 131.3 (s, 2 C, Ct), 123.4 (s, 2 C, Ct), 122.6 (s, 2 C, Ct), 119.3 (s, 1 C, Ct), 113.7 (s, 2 C, Ct), 56.5 (s, 1 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3072 (w), 2939 (w), 1595 (m), 1518 (s), 1456 (m), 1344 (s), 1278 (m), 1209 (m), 1072 (m), 1041 (m), 854 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 350.1 (100), 351.1 (21), 352.1 (3), 258.1 (13), 215.1 (17). $C_{19}H_{14}N_2O_5$ (350.32): calcd. C 65.14, H 4.03, N 8.00; found C 64.80, H 4.21, N 7.93.

3,5-Bis(3-nitrophenyl)phenol (16): BBr_3 (174 μL, 1.84 mmol) was slowly added to a solution of **15** (150 mg, 0.43 mmol) in dry DCM (15 mL) at –78 °C. The orange reaction mixture was stirred for 2.5 h at room temperature and poured onto ice (10 g). After extraction with DCM (3 × 10 mL), the combined organic layers were washed with brine (20 mL), dried with magnesium sulfate and the solvents evaporated to dryness to afford the desired compound **16** (136 mg, 95%) as a pale-yellow solid (m.p. 190–192 °C). The product **16** was used in the next step without further characterization. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (t, $^4J_{HH}$ = 1.9 Hz, 2 H), 8.28 (m, 2 H), 7.98 (m, 2 H), 7.67 (t, $^3J_{HH}$ = 8.1 Hz, 2 H), 7.41 (t, $^4J_{HH}$ = 1.5 Hz, 1 H), 7.17 (d, $^4J_{HH}$ = 1.5 Hz, 2 H) ppm. MS (MALDI-TOF): *m*/*z* (%) =336.7 (30), 335.7 (100).

1,3-Bis(3-nitrophenyl)-5-{[3,4,5-tris(dodecyloxy)phenyl]methoxy}-benzene (17): Potassium carbonate (245 mg, 1.78 mmol) was added to a solution of **16** (60 mg, 0.18 mmol) and **12** (133 mg, 0.20 mmol) in DMF (25 mL). The orange reaction mixture was stirred at 65 °C for 22 h. The violet reaction mixture was cooled to room temperature and quenched with water (20 mL). After extraction with DCM (3 × 20 mL), the combined organic layers were washed with water (2 × 20 mL), dried with magnesium sulfate and concentrated to dryness. The crude product was purified by CC (silica gel, ethyl acetate/hexane, 1:7, R_f = 0.25) to afford the title compound (155 mg, 89%) as a white powder (m.p. 88–90 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (t, $^4J_{HH}$ = 1.9 Hz, 2 H), 8.25 (m, 2 H), 7.95 (m, 2 H), 7.65 (t, $^3J_{HH}$ = 8.0 Hz, 2 H), 7.44 (t, $^4J_{HH}$ = 1.5 Hz, 1 H), 7.29 (d, $^4J_{HH}$ = 1.5 Hz, 2 H), 6.69 (s, 2 H), 5.11 (s, 2 H), 4.00 (m, 6 H), 1.81 (m, 6 H), 1.48 (m, 6 H), 1.25 (m, 48 H), 0.87 (m, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.4 (s, 1 C, Cq), 153.9 (s, 2 C, Cq), 149.2 (s, 2 C, Cq), 142.6 (s, 2 C, Cq), 141.5 (s, 2 C, Cq), 138.6 (s, 1 C, Cq), 133.6 (s, 2 C, Ct), 131.6 (s, 1 C, Cq), 130.3 (s, 2 C, Ct), 123.0 (s, 2 C, Ct), 122.5 (s, 2 C, Ct), 119.2 (s, 1 C, Ct), 114.2 (s, 2 C, Ct), 106.6 (s, 2 C, Ct), 73.9 (s, 1 C, Cs), 71.3 (s, 1 C, Cs), 69.6 (s, 2 C, Cs), 32.3(s, 3 C, Cs), 29.8 (m, 21 C, Cs), 26.5 (s, 3 C, Cs), 23.1 (s, 3 C, Cs), 14.5 (s, 3 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3089.8 (w), 2916.2 (s), 2848.7 (m), 1593.1 (m), 1521.7 (s), 1342.4 (s), 1244.0 (m), 1195.8 (s), 1114.8 (s), 1012.6 (m), 808.1 (s) cm^{-1}. MS (FAB): *m*/*z* (%) = 978.4 (1.4), 979.4 (1.1), 980.2 (0.6), 643.4 (7.6), 383.0 (13), 138.9 (31), 90.9 (60), 57.0 (92), 55.0 (80), 43.0 (100). $C_{61}H_{90}N_2O_8$ (979.38): calcd. C 74.81, H 9.26, N 2.86; found C 74.87, H 9.00, N 2.65.

Macrocycle 2: A 1 M lithium aluminium hydride solution in THF (0.6 mL, 0.601 mmol) was slowly added to a solution of **17** (58 mg, 0.059 mmol) in dry THF (10 mL) under argon at room temperature. The reaction mixture was stirred at room temperature for 2.5 h, and then the black suspension was quenched with water (10 mL). After extraction with toluene (3 × 15 mL), the combined organic layers were washed with brine (20 mL), dried with magnesium sulfate and the solvents evaporated to dryness. The crude product was purified by size-exclusion CC (Bio-Beads® S-X Beads, toluene) to afford the macrocycle **2** (18 mg, 34%) as an orange resin (m.p. 98–101 °C). TLC (silica gel, DCM/hexane, 2:1): R_f = 0.52 (due to the limited solubility of **2** in the eluent, the spot was observed with a long tail). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (m, 4 H), 7.95 (m, 4 H), 7.77 (m, 4 H), 7.60 (m, 6 H), 7.34 (m, 4 H), 6.69 (m, 4 H), 5.10 (m, 4 H), 3.96 (m, 12 H), 1.75 (m, 12 H), 1.44 (m, 12 H), 1.22 (m, 96 H), 0.85 (m, 18 H) ppm. ^{13}C NMR ($CDCl_3$, determined by HMBC and HMQC): δ = 159.8 (2 C, Cq), 153.4 (4 C, Cq), 153.2 (4 C, Cq), 142.4 (4 C, Cq), 142.0 (4 C, Cq), 138.1 (2 C, Cq), 131.6 (2 C, Cq), 130.0 (4 C, Ct), 129.7 (4 C, Ct), 122.2 (4 C, Ct), 121.9 (4 C, Ct), 119.0 (4 C, Ct), 113.3 (2 C, Ct), 106.1 (4 C, Ct), 73.5 (2 C, Cs), 70.9 (2 C, Cs), 69.2 (4 C, Cs), 32.0 (6 C, Cs), 30.4 (6 C, Cs), 29.6 (36 C, Cs), 26.1 (6 C, Cs), 22.7 (6 C, Cs), 14.1 (6 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3059 (w), 3024 (w), 2920 (s), 2851 (m), 1591 (m), 1504 (w), 1466 (m), 1437 (m), 1334 (m), 1112 (s) cm^{-1}.

Macrocycle 4: A 1 M lithium aluminium hydride solution in THF (1.25 mL, 1.250 mmol) was slowly added to a solution of **15** (43.6 mg, 0.125 mmol) and **17** (122 mg, 0.125 mmol) in dry THF (30 mL) over a period of 20 min. After complete addition, the reaction mixture was heated to 40 °C and stirred for 110 min. The mixture was cooled to room temperature and quenched with water (20 mL). After extraction with DCM (2 × 15 mL), the combined organic layers were washed with brine (20 mL), dried with magnesium sulfate and the solvents evaporated to dryness. The orange crude product was purified by size-exclusion CC (Bio-Beads® S-X Beads, toluene) to afford macrocycle **4** (66 mg, 44%) as an orange resin (m.p. 120–125 °C). TLC (silica gel, DCM/hexane, 2:1): R_f = 0.33 (due to the limited solubility of **4** in the eluent, the spot was observed with a long tail). ^{1}H NMR (400 MHz, $CDCl_3$,): δ = 8.26 (m, 4 H), 7.95 (m, 4 H), 7.77 (m, 4 H), 7.59 (m, 6 H), 7.35 (m, 2 H), 6.70 (m, 2 H), 5.11 (m, 2 H), 3.96 (m, 9 H), 1.77 (m, 6 H), 1.46 (m, 6 H), 1.25 (m, 48 H), 0.87 (m, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.9 (s, 1 C, Cq), 160.0 (s, 1 C, Cq), 153.8 (s, 4 C, Cq), 153.5 (s, 2 C, Cq), 142.9 (s, 4 C, Cq), 142.4 (s, 4 C, Cq), 138.4 (s, 1 C, Cq), 132.1 (s, 1 C, Cq), 130.3 (s, 4 C, Ct), 130.0 (s, 4 C, Ct), 122.4 (s, 4 C, Ct), 122.3 (s, 4 C, Ct), 113.5 (s, 2 C, Ct), 112.7 (s, 4 C, Ct), 106.7 (s, 2 C, Ct), 73.9 (s, 1 C, Cs), 71.2 (s, 1 C, Cs), 67.1 (s, 2 C, Cs), 56.0 (s, 1 C, Cq), 32.4 (s, 3 C, Cs), 30.2 (s, 21 C,

Cs), 26.6 (s, 3 C, Cs), 23.1 (s, 3 C, Cs), 14.6 (s, 3 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3063 (w), 2920 (s), 2851 (m), 1591 (m), 1500 (w), 1437 (m), 1337 (m), 1211 (w), 1113 (s) cm^{-1}.

1,2,3-Triiodo-5-nitrobenzene (19): 2,6-Diiodo-4-nitroaniline (**18**; 10.3 g, 25.65 mmol) was dissolved in acetic acid (60 mL) at 15 °C, and then a solution of sodium nitrite in sulfuric acid (15 mL) was added dropwise at room temperature. The reaction mixture was stirred for 90 min until everything had dissolved. The yellow reaction mixture was poured into ice/water (200 mL), stirred vigorously, quenched with urea (4.0 g) and filtered. The filtrate was diluted with water (30 mL), potassium iodide (6.0 g, 36.23 mmol) in water (30 mL) was added and the mixture stirred vigorously. Afterwards, the brown reaction mixture was heated to 95 °C and stirred for 2 h. The cold mixture was then quenched with sodium bisulfite (5.0 g) and the precipitate filtered. The crude product was dried at high vacuum and recrystallized from 2-methoxyethanol (20 mL) to afford the desired product **19** (10.3 g, 80%) as brown crystals (m.p. 166–168 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.68 (s, 1 C, Cq), 133.06 (s, 2 C, Ct), 131.26 (s, 1 C, Cq), 107.20 (s, 2 C, Cq) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3082 (w), 3049 (w), 1503 (s), 1498 (s), 1326 (s), 874 (s), 734 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 500.8 (100), 501.8 (6.7), 454.9 (15), 327.9 (15), 201.0 (23), 74.0 (30). $C_6H_2I_3NO_2$ (500.80): calcd. C 14.39, H 0.40, N 2.80; found C 14.41, H 0.42, N 2.85.

1,2,3-Tri(dodec-1-ynyl)-5-nitrobenzene (20): 1,2,3-Triiodo-5-nitrobenzene (**19**; 2.0 g, 3.99 mmol), 1-dodecyne (2.85 mL, 13.18 mmol), bis(triphenylphosphane)palladium(II) dichloride (140 mg, 0.199 mmol) and copper(I) iodide (76 mg, 0.399 mmol) were added to degassed triethylamine (60 mL) under argon. After 150 min at 85 °C, the black reaction mixture was cooled to room temperature, filtered, the filtrate washed with water (30 mL) and dried with magnesium sulfate. The crude product was purified by CC (silica gel, ethyl acetate/hexane, 1:20, R_f = 0.41) to afford the title compound **20** (2.18 g, 89%) as a black oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 2 H), 2.54 (t, $^3J_{HH}$ = 7.0 Hz, 2 H), 2.46 (t, $^3J_{HH}$ = 7.0 Hz, 4 H), 1.63 (m, 6 H), 1.48 (m, 6 H), 1.27 (m, 36 H), 0.87 (t, $^3J_{HH}$ = 7.0 Hz, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.0 (s, 1 C, Cq), 134.8 (s, 1 C, Cq), 128.4 (s, 2 C, Ct), 125.4 (s, 2 C, Ct), 104.5 (s, 1 C, Cq), 97.4 (s, 2 C, Cq), 78.6 (s, 1 C, Cq), 78.5 (s, 2 C, Cq), 32.3 (s, 3 C, Cs), 30.1–29.0 (m, 18 C, Cs), 23.1 (s, 3 C, Cs), 20.1 (s, 3 C, Cs), 14.5 (s, 3 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3002 (w), 2921 (s), 2853 (m), 1521 (m), 1465 (w), 1347 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 615.4 (35), 616.3 (16), 617.3 (0.6), 585.4 (16), 530.3 (18), 474.2 (22), 446.2 (19), 404.2 (20), 390.2 (30), 378.2 (49), 83.1 (45), 69.1 (51), 55.0 (67), 43.0 (100). $C_{42}H_{65}NO_2$ (615.97): calcd. C 81.89, H 10.64, N 2.27; found C 81.73, H 10.69, N 1.93.

3,4,5-Tri(dodecyl)aniline (21): 1,2,3-Tri(dodec-1-ynyl)-5-nitrobenzene (**20**; 1.28 g, 2.08 mmol) and palladium on activated charcoal (440 mg, 0.416 mmol) were dissolved in dry ethanol (80 mL) and dry ethyl acetate (20 mL). The reaction mixture was hydrogenated (two hydrogen balloons) at room temperature for 28 h while stirring vigorously. After filtration through Celite, the concentrated crude product was purified by CC (silica gel, DCM/hexane, 1:1, R_f = 0.32) to afford the title compound **21** (711 mg, 59%) as a pale-orange oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.38 (s, 2 H), 3.43 (br. s, 2 H, NH_2), 2.49 (m, 6 H), 1.56 (m, 6 H), 1.27 (m, 54 H), 0.88 (t, $^3J_{HH}$ = 6.5 Hz, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.0 (s, 1 C, Cq), 142.4 (s, 1 C, Cq), 129.5 (s, 2 C, Ct), 114.5 (s, 2 C, Ct), 33.7 (s, 3 C, Cs), 32.3 (s, 3 C, Cs), 30.1 (m, 24 C, Cs), 23.1 (s, 3 C, Cs), 14.5 (s, 3 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3004 (w), 2920 (s), 2852 (m), 1620 (w), 1466 (w), 847 (br. w), 631 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 597.6 (100), 598.6 (42), 599.6 (9), 442.4 (60), 288.2 (9), 134.1 (12). $C_{42}H_{79}N$ (598.08): calcd. C 84.34, H 13.31, N 2.34; found C 84.36, H 13.12, N 2.26.

2,6-Dibromo-3,4,5-tri(dodecyl)aniline (22): A solution of dry DMF (20 mL) and 3,4,5-tri(dodecyl)aniline (**21**; 1.90 g, 3.18 mmol) was cooled to 0 °C under argon. *N*-Bromosuccinimide (1.36 g, 7.62 mmol) in dry DMF (20 mL) was added at 0 °C over a period of 20 min. After the complete addition, the reaction mixture was stirred at room temperature for another 120 min. The dark-brown reaction mixture was quenched with water (30 mL) and extracted with *tert*-butyl methyl ether (3 × 20 mL); the combined organic layers were dried with magnesium sulfate and the solvents evaporated to dryness. The black crude product was purified by CC (silica gel, ethyl acetate/hexane, 1:30, R_f = 0.44) to afford the title compound **22** (1.68 g, 70%) as a pale-yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.56 (s, 2 H), 2.71 (m, 4 H), 2.55 (m, 2 H), 1.53–1.27 (m, 60 H), 0.88 (t, $^3J_{HH}$ = 6.5 Hz, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.5 (s, 1 C, Cq), 140.3 (s, 2 C, Cq), 130.6 (s, 1 C, Cq), 110.6 (s, 2 C, Cq), 34.2 (s, 3 C, Cs), 32.4 (s, 3 C, Cs), 30.1 (m, 24 C, Cs), 23.1 (s, 3 C, Cs), 14.5 (s, 3 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3485 (w), 3387 (w), 2954 (w), 2920 (s), 2852 (m), 1599 (m), 1466 (m), 1430 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 753.3 (51), 754.4 (24), 755.3 (100), 756.3 (45), 757.3 (56), 758.3 (23), 759.3 (5), 600.2 (6), 521.3 (7), 433.0 (7). $C_{42}H_{77}Br_2N$ (755.88): calcd. C 66.74, H 10.27, N 1.85; found C 66.78, H 10.23, N 1.70.

1,5-Dibromo-2,3,4-tri(dodecyl)benzene (23): 2,6-Dibromo-3,4,5-tri(dodecyl)aniline (**22**; 83 mg, 0.110 mmol) was dissolved in ethanol (5 mL) by sonication. After the addition of sulfuric acid (2 mL) and sodium nitrite (23 mg, 0.331 mmol), the reaction mixture was stirred at 85 °C for 4 h, cooled to room temperature and quenched with water (10 mL). The water phase was extracted with DCM (3 × 10 mL), the combined organic layers were dried with magnesium sulfate and the solvents evaporated to dryness. The crude product was purified by CC (silica gel, hexane, R_f = 0.58) to afford the title compound **23** (78 mg, 95%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1 H), 2.62 (m, 6 H), 1.51–1.24 (m, 60 H), 0.85 (t, $^3J_{HH}$ = 6.5 Hz, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.7 (s, 1 C, Cq), 140.1 (s, 2 C, Cq), 134.2 (s, 1 C, Ct), 122.8 (s, 2 C, Cq), 33.5 (s, 3 C, Cs), 32.4 (s, 3 C, Cs), 30.1 (m, 24 C, Cs), 23.1 (s, 3 C, Cs), 14.5 (s, 3 C, Cp) ppm. MS (EI): *m*/*z* (%) = 738.4 (49), 739.4 (22), 740.4 (100), 741.4 (44), 742.4 (55), 743.4 (23), 744.4 (5), 418.1 (15), 276.9 (33), 197.0 (10), 71.1 (14), 57.1(19). $C_{42}H_{76}Br_2$ (740.86): calcd. C 68.09, H 10.34; found C 68.02, H 10.11.

1,3-Bis(3-nitrophenyl)-4,5,6-tri(dodecyl)benzene (24): (3-Nitrophenyl)boronic acid (46 mg, 0.274 mmol), tetrakis(triphenylphosphane)-palladium (12 mg, 0.011 mmol) and potassium carbonate (116 mg, 0.842 mmol) were added to a solution of 1,5-dibromo-2,3,4-tri(dodecyl)benzene (**23**; 78 mg, 0.105 mmol) in dry toluene (10 mL) and dry ethanol (3 mL) under argon. The reaction mixture was stirred vigorously at 85 °C for 150 min. After cooling to room temperature, the reaction mixture was filtered through a 1 cm pad of silica, eluted with toluene (15 mL), and the solvents were evaporated to dryness. The dark crude product was purified by CC (silica gel, toluene/hexane, 1:1, R_f = 0.59) to afford the title compound **24** (73 mg, 85%) as a white solid (m.p. 37–39 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (m, 4 H), 7.64 (d, $^3J_{HH}$ = 8.8 Hz, 2 H), 7.55 (t, $^3J_{HH}$ = 8.8 Hz, 2 H), 6.79 (s, 1 H), 2.70 (m, 2 H), 2.53 (m, 4 H), 1.26–1.12 (m, 60 H), 0.87 (t, $^3J_{HH}$ = 6.7 Hz, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.3 (s, 2 C, Cq), 144.6 (s, 2 C, Cq), 139.4 (s, 2 C, Ct), 138.1 (s, 1 C, Cq), 135.9 (s, 2 C, Cq), 130.1 (s, 2 C, Cq), 129.3 (s, 2 C, Ct), 124.7 (s, 2 C, Ct), 122.2 (s, 2 C, Ct), 32.3 (s, 3 C, Cs), 30.0 (m, 27 C, Cs), 23.1 (s, 3 C, Cs), 14.5

(s, 3 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3080 (w), 2920 (s), 2851 (m), 1526 (s), 1466 (m), 1346 (m), 1099 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 824.5 (100), 825.5 (55), 826.5 (17), 827.5 (4), 794.6 (18), 502.2 (22), 361.1 (17), 315.1 (10). $C_{54}H_{84}N_2O_4$ (825.26): calcd. C 78.59, H 10.26, N 3.39; found C 78.56, H 10.09, N 3.22.

Macrocycle 3: A 1 M lithium aluminium hydride solution in THF (0.48 mL, 0.485 mmol) was slowly added to a solution of **24** (80 mg, 0.097 mmol) in dry THF (20 mL) under argon at room temperature. The reaction mixture was stirred at 40 °C for 3 h and the black suspension quenched with water (10 mL). After extraction with DCM (2 × 15 mL), the combined organic layers were washed with brine (20 mL), dried with magnesium sulfate and the solvents evaporated to dryness. The crude product was purified by size-exclusion CC (Bio-Beads® S-X Beads, toluene) to afford macrocycle **3** (36 mg, 49%) as an orange resin (m.p. 67 –69 °C). TLC (silica gel, DCM/hexane, 2:1): R_f = 0.92; (silica gel, DCM/hexane, 1:1): R_f = 0.66 (due to the limited solubility of **3** in the eluents, the spots were observed with long tails). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 4 H), 7.85 (m, 4 H), 7.49 (m, 4 H), 7.44 (m, 4 H), 6.96 (s, 2 H), 2.71 (m, 4 H), 2.60 (m, 8 H), 1.57 (m, 12 H), 1.41 (m, 12 H), 1.26–1.12 (m, 96 H), 0.84 (m, 18 H) ppm. ^{13}C NMR ($CDCl_3$, determined by HMBC and HMQC): δ = 152.2 (4 C, Cq), 143.9 (4 C, Cq), 139.2 (4 C, Cq), 138.4 (4 C, Cq), 135.8 (2 C, Cq), 132.1 (4 C, Ct), 129.7 (2 C, Ct), 128.6 (4 C, Ct), 123.7 (4 C, Ct), 121.5 (4 C, Ct), 31.9 (6 C, Cs), 31.4 (6 C, Cs), 29.7 (48 C, Cs), 22.7 (6 C, Cs), 14.1 (6 C, Cp) ppm. IR (ATR, neat): $\tilde{\nu}$ = 3057 (w), 2953 (w), 2920 (s), 2851 (m), 1597 (w), 1458 (m), 1047 (br. s) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 1523.1 (100), 1431.3 (25).

VPO Measurements: The pure compounds **1**–**4** were separately dissolved in chloroform. The apparatus was calibrated with a benzil standard. Each sample was measured at 42 °C at least three times and the average value calculated. All concentrations were higher then the critical lower concentration of about 0.005 mol/kg indicated for the VPO apparatus (Knauer VPO K-7000).

Determination of the Quantum Yields of Photoisomerization: Starting from Equation (1), in which Φ_{ct} and Φ_{tc} are the quantum yields of the $Z \rightarrow E$ and $E \rightarrow Z$ photoisomerization reactions, f is the optical density, N is the number of incident photons (in Einstein/cm^2 s), the factor 3 stems from the volume of the cuvette, being 3 cm^3, and 1000 from the conversion of L into cm^3, we can easily obtain a differential equation that correlates the relative concentration and change thereof to the absorbed light and from that obtain the quantum yields from the measurements.

$$\Delta c = \Phi_{ct} f_c (1-10^{\bar{A}}) \Delta t \frac{1000N}{3} - \Phi_{tc} f_t (1-10^{\bar{A}}) \Delta t \frac{1000N}{3} + k_t c_{cis} \quad (1)$$

The ε values for the *E* and *Z* isomers used for this analysis were calculated by correlating the height of the $S_1 \leftarrow S_0$ (π–π^*) band and the corresponding relative concentrations of the *E* and *Z* isomers obtained from the ^{1}H NMR analysis.

Supporting Information (see footnote on the first page of this article): GPC charts and ^{1}H NMR spectra of the macrocycles **1**–**4**, synthesis and characterization of the building block **12** and its precursors.

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