PAPER www.rsc.org/njc | New Journal of Chemistry

Introduction of useful peripheral functional groups on [2]catenanes by combining Cu(I) template synthesis with "click" chemistry†

Jackson D. Megiatto, Jr.* and David I. Schuster*

Received (in Montpellier, France) 15th September 2009, Accepted 19th October 2009
First published as an Advance Article on the web 11th November 2009
DOI: 10.1039/b9nj00486f

Two protocols based on Cu(I) template synthesis and "click" reactions for the synthesis of functionalized [2]catenanes are described. A straightforward procedure, involving high dilution conditions at high temperatures (70 °C), affords [2]catenanes bearing two identical peripheral groups in high yields. For the preparation of non-symmetrically functionalized [2]catenanes, a second milder and simpler protocol was developed, generalizing and extending the method. The introduction of peripheral functional groups into the catenane structure opens up possibilities of using [2]catenanes as building blocks for preparation of even more complex structures.

1. Introduction

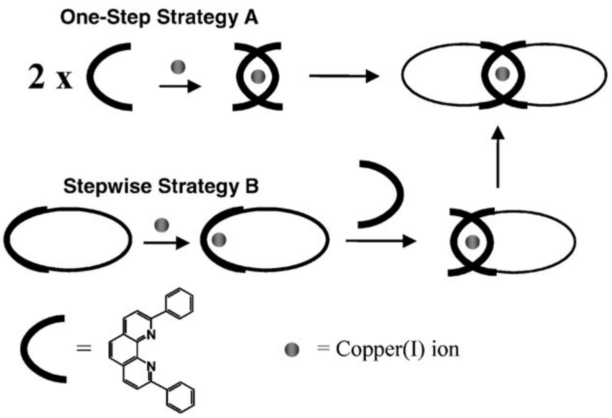
Recent developments in the synthesis of interlocked molecules have allowed the preparation of a great variety of rotaxanes, catenanes and more complex structures, such as three foil knots.[1] The easy access to such interlocked molecules has allowed an extensive exploration of their interesting submolecular motion properties as principles for construction of molecular machines, molecular muscles, nanoelectromechanical systems and nanovehicles.[2] This flourishing field of research has also impacted other fields such as artificial photosynthetic systems,[3] catalysis,[4] and drug delivery.[5]

The preparation of interlocked molecules relies on two key steps: (i) recognition and arrangement of the non-interlocked components in an entwined orientation, and (ii) covalent bond-forming reactions, which prevent the fragments from disentangling, creating a mechanical bond between the subunits.[6] Different templates based on non-covalent bonding interactions, including hydrogen bonding, donor–acceptor interactions, and metal complexation, have been successfully used as synthetic tools to organize the motifs in the orthogonal arrangement necessary to afford interlocked molecules.[1]

For the final covalent bond-forming step, different reactions have been explored as protocols for stoppering (rotaxanes) or cyclization (catenanes) reactions. Ring closing metathesis (RCM), imine formation, oxidative coupling of alkynes, and Huisgen copper(I)-catalyzed alkyne–azide 1,3-dipolar cycloaddition (the CuAAC or "click" reaction) have proved to be efficient methodologies for the final step in the synthesis of interlocked molecules.[1a,7]

Among the entwined templates described in the literature, the metal-template approach, developed by Sauvage and co-workers,[8] is a highly effective strategy for the preparation of catenanes, rotaxanes and knots. This idea is based on the strong preference of Cu(I) ions for two bidentate phenanthroline (phen) ligands, which form a pseudotetrahedral (phen)$_2$–Cu(I) complex, generating the cross-over points needed for interlocked structure formation. Sauvage and co-workers[8] have elegantly demonstrated that catenanes can be prepared by two different basic strategies using Cu(I) template synthesis. In the one-step approach (strategy A, Scheme 1), the two phen ligands assemble around the Cu(I) ion, and the subsequent pairwise connection of the reaction centers leads to catenanes. In the step-wise approach (strategy B, Scheme 1), which is one step longer but results in better yields than strategy A, a "threading" reaction of a phen-string-like fragment through a previously synthesized phen-containing ring, promoted by binding to the Cu(I) center, generates a pseudorotaxane precursor, which can be subjected to cyclization reactions, affording catenanes.

The biggest challenge in the preparation of interlocked molecules using Cu(I) template synthesis is the ring closure of the pre-oriented phen moieties. The precursor (phen)$_2$–Cu(I) complex is inherently unstable,[8] since it may dissociate from the metal core when subjected to changes in temperature, solvent polarity, or the presence of strong bases or competing complexation ligands. Kinetically controlled reactions, where the (phen)$_2$–Cu(I) pseudotetrahedral configuration is retained



Scheme 1 Sauvage's Cu(I) template synthesis principle.[8]

Chemistry Department, New York University, New York, NY 10003, USA. E-mail: david.schuster@nyu.edu, jackson.megiatto@nyu.edu

† Dedicated to Jean-Pierre Sauvage on the occasion of his 65th birthday.

in the transition state, minimize this dissociation problem and give mechanically interlocked compounds in high yields.

The CuAAC or "click" reaction[9] has emerged as a powerful and robust synthetic tool for construction of complex materials due to its unusual tolerance towards functional groups, regioselectivity and often quantitative yields. Synthesis of elaborate structures, such as dendrimers, macrocycles, polymers, donor–acceptor materials, as well as derivatization of biological substrates (*e.g.*, virus particles, enzymes and proteins), has been efficiently accomplished using the CuAAC reaction.[10]

Inspired by these promising results, we have developed effective straightforward strategies based on "click" chemistry and Sauvage's Cu(I) template technique, for preparation of interlocked molecules, such as [2] and [3]catenanes.[11] Taking advantage of the mild conditions employed in these protocols, we have been able to introduce useful functional groups on the periphery of the interlocked rings, which allow further structural elaboration.

We have explored both Cu(I) template strategies (A and B, Scheme 1) in conjunction with the CuAAC reaction for preparation of functionalized interlocked molecules. In a previous communication,[11a] we reported that formation of a bis-diethynyl(phen)$_2$–Cu(I) complex, according to one-step strategy A (Scheme 1), followed by "double click" ring closure at 70 °C with functionalized 3,5-aryl-diazides under high dilution conditions, afforded [2]catenanes with identical functionalized rings. Catenanes with two different interlocked rings are appealing targets since they open up the possibility of using interlocked structures as building blocks for preparation of even more complex materials. To prepare such materials, we first attempted the step-wise Cu(I) approach B (Scheme 1) using our previous methodology.[11a] Analysis of the product mixtures revealed that the pseudorotaxane precursor (phen)$_2$–Cu(I) complex dissociates from the metal core under these conditions.[11a] To minimize this dissociation problem, a slightly different and simpler procedure, which does not require high dilution conditions, had to be developed.[11b,c] Indeed, employing milder conditions allowed the preparation of non-symmetrical-functionalized [2]catenanes in high yields, as illustrated below by the synthesis of a non-symmetrical [2]catenane bearing peripheral styrene and benzaldehyde groups.

2. Results and discussion

Synthesis of symmetrical-functionalized [2]catenanes

At the outset of this study, it was anticipated that the mild conditions and the unusual tolerance of "click" reactions[9] toward the substrate would allow the introduction of useful functional groups into interlocked structures. We first studied a model reaction between the bis-ethynyl derivative **1** and the 3,5-diazidoaryl acetal **2** to afford phen-macrocycle **3** (see Scheme 2).

We found[11a] that the CuAAC cyclization reaction between **1** and **2** to give **3** in good yields requires high temperature (70 °C), high dilution conditions and the presence of the base 1,8-diaza[5.4.0]bicycloundec-7-ene (DBU) (full details are given in the Experimental). Another important aspect of the cyclization reaction shown in Scheme 2 is that sulfonated bathophenanthroline (SBP), a so-called "click" additive,[10g,h] must be employed as part of the "click brew". In biological systems, SBP has been used previously to sequester Cu(I) ions from the reaction medium, thereby preventing damage to substrate molecules, such as peptides and proteins.[10g] Due to the ability of **1** to complex Cu(I) ions, the absence of SBP as an auxiliary ligand results in a complex product mixture, which contains only 7% of target macrocycle **3** along with other unidentified products.

When a highly dilute equimolar mixture of **1** and **2** in 9 : 1 EtOH–toluene solvent mixture was added dropwise over 10 hours to a mixture containing CuI, sodium ascorbate (SA), DBU and SBP in an oxygen-free 7 : 3 : 1 EtOH–H_2O–toluene solvent mixture at 70 °C, macrocycle **3** was obtained in 70% isolated yield. The structure of **3** was unambiguously confirmed by its ^1H NMR spectrum (Fig. 1) and by MALDI-TOF analysis (Fig. 2), which showed a molecular ion peak at m/z 979.20 $[M + H]^+$. Remarkably, higher cyclic compounds, oligomers and linear structures were not formed under these conditions, confirming the specificity of our cyclization protocol.

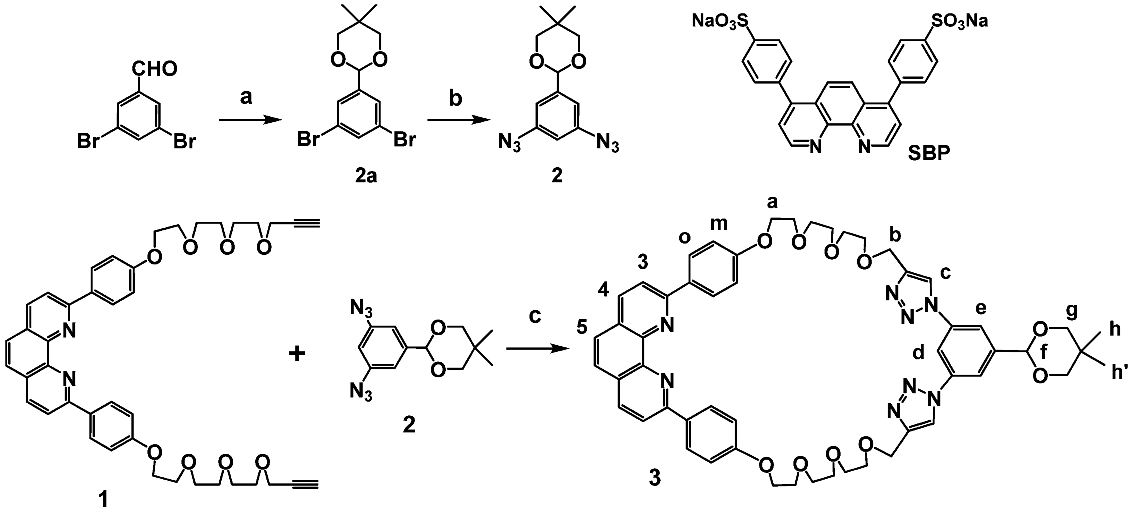
This promising result encouraged us to explore other variants of this methodology. We envisaged the straightforward preparation of a symmetrical-functionalized [2]catenane based on the Cu(I) template one-step strategy depicted in Scheme 3. The reaction was carried out as follows: bis-diethynyl(phen)$_2$–Cu(I) complex **4**, prepared following the one-step strategy A (Scheme 1), was added to a 7 : 3 : 1 EtOH–H_2O–toluene mixture of DBU, SA, SBP and CuI at 70 °C. A highly dilute solution of **2** in 9 : 1 EtOH–toluene was then added dropwise over 12 h, affording the symmetrically functionalized catenand **5** in 90% yield.

The material obtained after the workup procedure, which involved washing with ammonium hydroxide,[10a,b] was surprisingly the copper-free catenane. Its ^1H NMR spectrum is quite similar to that of the analogous macrocycle shown in Fig. 1; however, MALDI-TOF analysis (m/z calculated for **5**: 1956.86; found: 1957.48 $[M + 1]^+$, Fig. 3) confirmed the Cu-free catenane structure.[11a] Presumably, the cuprous ion was removed by complexation with ammonium hydroxide present in the reaction brew. No higher catenanes were formed under these conditions, demonstrating the remarkable efficiency of the final "double click" cyclization procedure.

Synthesis of non-symmetrical-functionalized [2]catenanes

We next turned our attention to the preparation of a non-symmetrically functionalized [2]catenane (Scheme 4). The synthesis of a [2]catenane bearing peripheral styrene and aldehyde groups was particularly appealing, since it would allow the preparation of more complex structures using well established methodologies, such as radical polymerization,[12a] olefin metathesis,[12b] Wittig[12c] or Schiff base[12d] reactions.

The synthetic pathway outlined in Scheme 4 is based on Sauvage's step-wise Cu(I) template approach (Scheme 1), which is expected to afford catenanes with two different interlocked rings.[8] Macrocycle **6** was prepared as described



Scheme 2 Building blocks and "double click" macrocyclization model reaction between diethynylphenanthroline derivative **1** and 3,5-diazidoaryl acetal **2** to afford macrocycle **3**. (a) Neopentylglycol, *p*-toluenesulfonic acid, THF, reflux, 8 h, quantitative; (b) NaN_3, sodium ascorbate (SA), *N*,*N*-dimethylethylenediamine, CuI, EtOH–H_2O, reflux, 3 h, 60% yield; (c) CuI, SA, SBP, H_2O–EtOH–toluene, high dilution, 70 °C, 30 h, 70% yield.

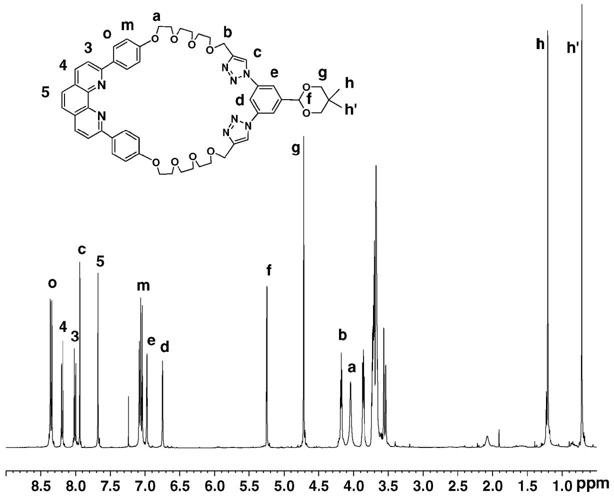


Fig. 1 ^1H NMR spectrum (400 MHz, $CDCl_3$, 300 K) of macrocycle **3**.

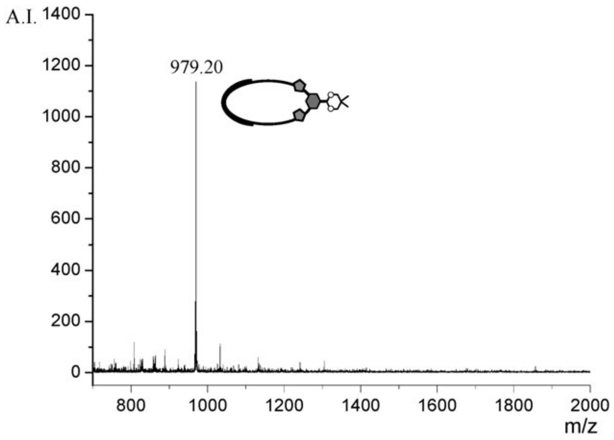


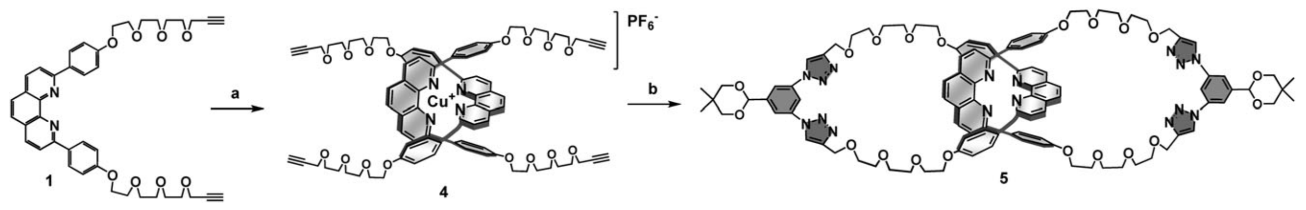
Fig. 2 MALDI-TOF mass spectrum of macrocycle **3** (positive mode, α-cyano-4-hydroxycinnamic acid (CCA) matrix).

elsewhere.[11b] Reduction followed by oxidation of the peripheral carboxymethyl ester group, using $LiAlH_4$ and MnO_2, respectively, resulted in aldehyde **7**. The threading of the diethynylphenanthroline derivative **1** through the macrocycle **6** gave precursor **8**. Compound **10** was prepared in two steps: Wittig reaction between 3,5-dibromobenzaldehyde and methyl triphenyl phosphonium bromide in presence of potassium *tert*-butoxide (*t*-BuOK) yielded 3,5-dibromostyrene **9**, which then was converted to **10** using NaN_3 following a literature procedure.[13]

The final cyclization reaction between **8** and **10** using the same "click" conditions described for **3** did not yield the desired catenate **11** after the usual workup. Instead, the symmetric bis-styrene-functionalized [2]catenate **12** (Scheme 5) was isolated in 35% yield together with the styrene-macrocycle **13** (10%) along with other unidentified byproducts, indicating that under these conditions unthreading of **8** took place. A plausible explanation[14] for the formation of catenate **12** is shown in Scheme 5, involving decomposition of the precursor **8** followed by the formation of the symmetrical complex **4**, which then undergoes "click" reactions with **10** to form **12**. The starting macrocycle **7** was not identified in the product mixture, suggesting that the peripheral aldehyde group on **7** may undergo side reactions under the reaction conditions.

These results indicate that the conditions used for the final cyclization reaction are too harsh, resulting in unthreading of **8** before the CuAAC reactions with **10** took place.[8,14] In order to minimize the detrimental unthreading process, the reaction medium had to be adjusted to stabilize precursor **8**, while simultaneously the kinetics of the critical cycloaddition reactions must be accelerated to prevent side reactions with the peripheral functional groups.

Thus, a new strategy to prepare non-symmetrical-functionalized [2]catenanes was required, shown in Scheme 6. To overcome the precursor stability problem, a heterogeneous reaction medium was used, composed of dichloromethane (DCM) and aqueous ethanol. The Cu(I)–$(phen)_2$ complex is



Scheme 3 One-step strategy to the preparation of symmetrical-functionalized [2]catenand **5**, (a) $Cu(CH_3CN)_4][PF_6]$, DCM–CH_3CN, rt, 30 min; quantitative; (b) (ii) **2**, CuI, SA, SBP, H_2O–EtOH–toluene, high dilution, 70 °C, 30 h; (ii) DCM–H_2O–NH_4OH, rt, 12 h, 90% yield.

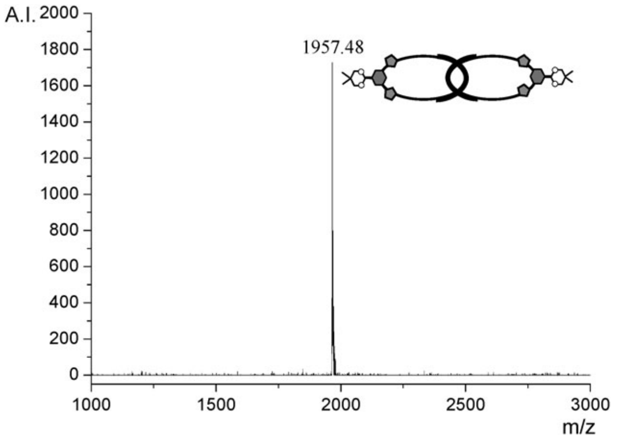


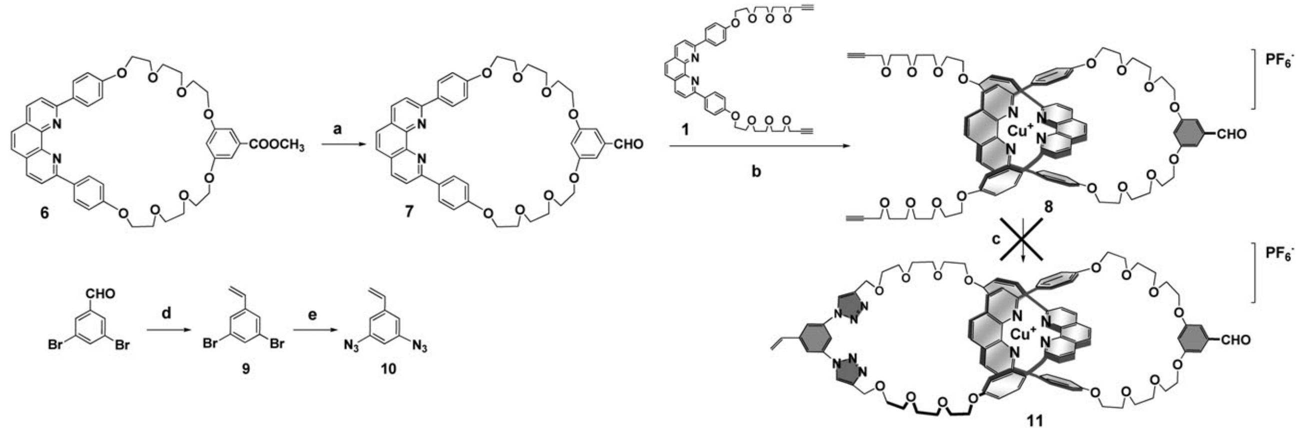
Fig. 3 MALDI-TOF mass spectrum of triazole-linked Cu-free [2]catenand **5** (positive mode, α-cyano-4-hydroxycinnamic acid (CCA) matrix).

less susceptible to unthreading in the DCM phase, while the other CuAAC reagents remain mainly in the aqueous phase; since the reaction to connect the pieces takes place at the interface, high dilution conditions are not required in this new scenario.

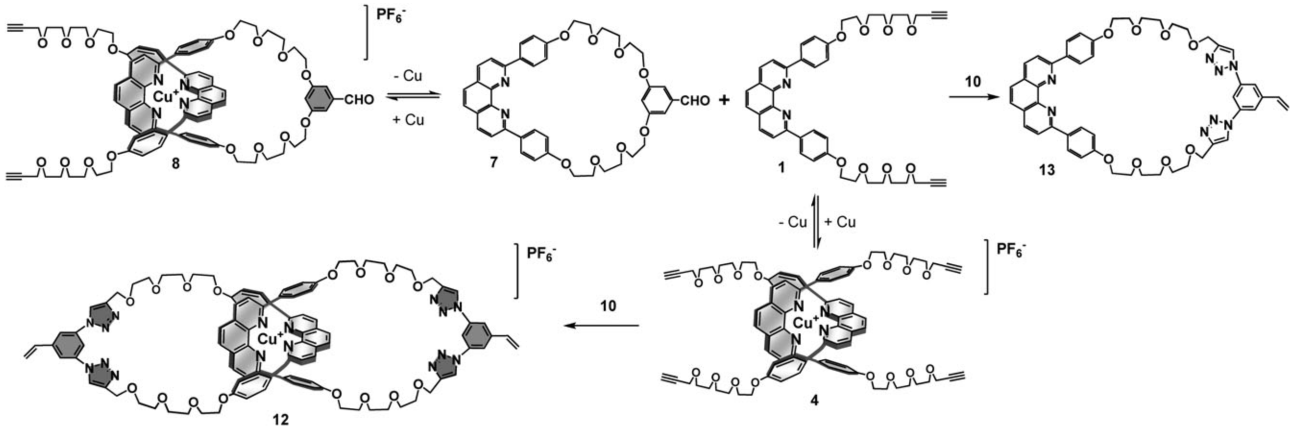
To enhance the reaction kinetics, we again used the "click additives" SBP and the base DBU.[10h,11] Switching the azide and alkyne positions on the building blocks allowed the final CuAAC cyclization reactions to occur at room temperature, increasing the tolerance toward the peripheral functional groups. Thus, the diazido phen string-like fragment **14**[11b] and 3,5-diethynylstyrene **15** were synthesized and used as building blocks for the preparation of the target [2]catenate **17**. Compound **15** (Scheme 6) was prepared by a Sonogashira coupling reaction between **9** and a large excess of (trimethylsilyl)-acetylene,[15] followed by treatment with tetrabutylammonium fluoride (TBAF) in THF at rt, affording compound **15** in 70% overall yield. The threading reaction of **14** through macrocycle **7**, using Cu(I) ion as template,[8] afforded the pseudorotaxane precursor **16** in quantitative yield.

The final macrocyclization reaction was carried out as follows:[11b] CuI, SA and SBP were dissolved in degassed aqueous ethanol (1 : 1, v/v), and the pink suspension was heated at reflux for 2 min under nitrogen in order to increase the solubility of the catalyst brew before being cooled to room temperature. The red DCM–acetonitrile solution containing **16** was then diluted to 10 mL with degassed DCM and added by syringe to the reaction flask. Finally, diethynylstyrene derivative **15**, dissolved in 3 mL of degassed DCM, and DBU were added and the resulting red mixture was stirred under nitrogen for 12 h at rt. The crude mixture was washed with 10% aqueous HCl solution, then water, and finally extracted with DCM. The organic phase was then stirred for 3 h with a saturated methanol solution of KPF_6 to effect the anion exchange. Final purification was achieved by column chromatography (silica gel) using DCM–methanol (99/1 v/v) as eluent, affording **17** as a red solid in 60% yield.

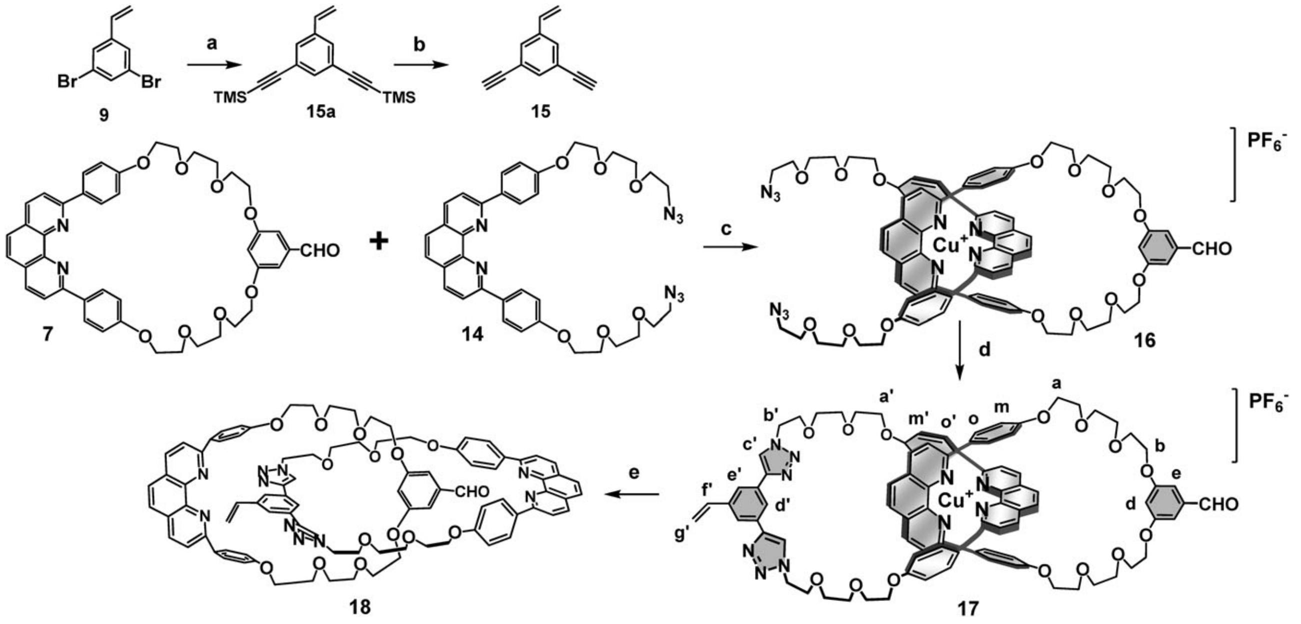
The MALDI-TOF spectrum (Fig. 4) shows a peak at *m*/*z* 1623.12, corresponding to the target structure **17** $(M - PF_6)^+$.



Scheme 4 Building blocks and unsuccessful attempt to synthesize non-symmetrical-functionalized [2]catenate **11**; (a) (i) $LiAlH_4$, THF, rt, 6 h, quantitative; (ii) MnO_2, DCM, reflux, 12 h, 65% overall yield; (b) two steps: (i) $[Cu(CH_3CN)_4][PF_6]$, DCM–CH_3CN, rt, 30 min; (ii) **1**, rt, 3 h, quantitative; (c) CuI, SA, SBP, H_2O–EtOH–toluene, high dilution, 70 °C, 30 h; (d) (i) methyltriphenylphosphonium bromide, *t*-BuOK, THF, 0 °C, 30 min; (ii) −78 °C, **9**, then rt, 1 h, yield 45%; (e) NaN_3, SA, *N*,*N*-dimethylethylenediamine, CuI, EtOH–H_2O, reflux, 3 h, 55% yield.



Scheme 5 Proposed synthetic pathway leading to formation of symmetrical-functionalized [2]catenate **12** and macrocycle **13** under the conditions explored for the synthesis of target catenate **11**.



Scheme 6 Strategy for preparation of non-symmetrical-functionalized [2]catenate **17**, (a) (i) $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N, (trimethylsilyl)acetylene, 50 °C; (b) TBAF, THF, rt, 30 min, 70% overall yield; (c) (i) $[Cu(CH_3CN)_4][PF_6]$, DCM–CH_3CN, rt, 30 min; (ii) **14**, rt, 3 h, quantitative; (d) **15**, CuI, SA, SBP, DBU, DCM–H_2O–EtOH, rt, 12 h, 78% yield; (e) KCN, DCM–H_2O, rt, 30 min, quantitative yield.

The fragmentation pattern observed in the mass spectrum, which can be unambiguously assigned to the individual macrocycles, is very characteristic of catenane structures.[16] Loss of N_2 from the triazole rings[17] was also observed in the spectrum, suggesting that fragmentation of the styrene-containing ring occurs through cleavage of the triazole moieties. The absence of fragments between the molecular ion peak and the peaks corresponding to the individual macrocycles confirms the assigned catenate structure **17**, possessing two different functionalized interlocked rings.

^1H NMR analysis (Fig. 5) clearly supports the non-symmetrical interlocked structure **17** depicted in Scheme 6. The aldehyde proton is observed at 9.63 ppm, while those belonging to the olefinic moiety are at 6.36, 5.51, and 4.90 ppm (identified as f' and g' in Fig. 5). The methylene groups adjacent to the triazole ring appear at 4.57 ppm, while the resonance of the proton on the triazole ring itself is at 7.91 ppm (identified as b' and c' in Fig. 5).[11a] The expected upfield shift for the phenyl protons on the two phen fragments entwined around the Cu(I) core[8] is observed, while the protons attached to the phenanthroline moieties give signals at the expected regions for a Cu(I) catenate.[8] The protons on the trioxoethyl linkers appear in the usual region between 4.40 and 3.00 ppm. Interestingly, the corresponding protons of the styrene moiety (labeled as d' and e', in Fig. 5) give peaks at significantly higher field, which can be explained by a deshielding effect exerted by the two triazole rings at the *meta* positions of the styrene ring.[18]

Removing the Cu(I) ion in **17**, following the classical KCN procedure,[8] resulted in the Cu-free catenand **18** (Scheme 6), which was isolated as a waxy material in quantitative yield. The mass spectrum shows the ion peaks corresponding to

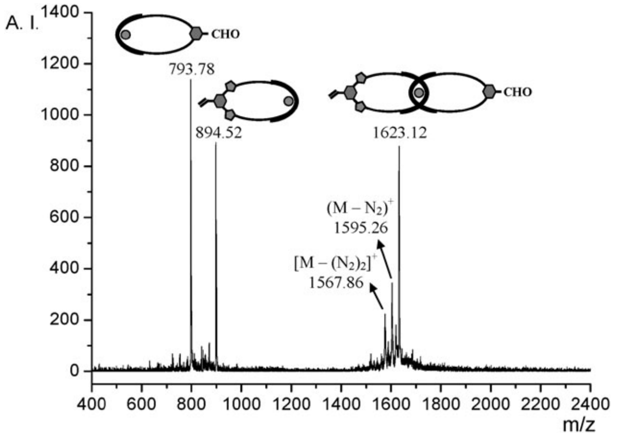


Fig. 4 MALDI-TOF mass spectrum of styrene-aldehyde-Cu(I)-[2]-catenate **17** (positive mode, α-cyano-4-hydroxycinnamic acid (CCA) matrix). ● = Cu(I) ion.

Cu-free catenand **18** and the two different macrocyclic components, revealing again the characteristic fragmentation pattern of catenated species under the ionization conditions of MALDI-TOF mass spectrometry.[16]

The ^{1}H NMR spectrum of **18** indicates that, upon demetalation of **17**, the two interlocked rings undergo a reorientation relative to one another (Fig. 5). In particular, the signals of protons o and o', and m and m' of the phenyl substituent of the phenanthroline moieties move downfield, indicating that the two chelates are no longer entwined around the Cu(I) ion template.[8] These assignments were made with the help of 2D COSY ^{1}H NMR spectral data. The protons on the styrene ring are shifted upfield, reflecting proximity to other aromatic residues.[14] These considerations suggest that **18** adopts a conformation similar to that shown in Scheme 6, in agreement with conformations previously reported for other demetalated catenands.[8]

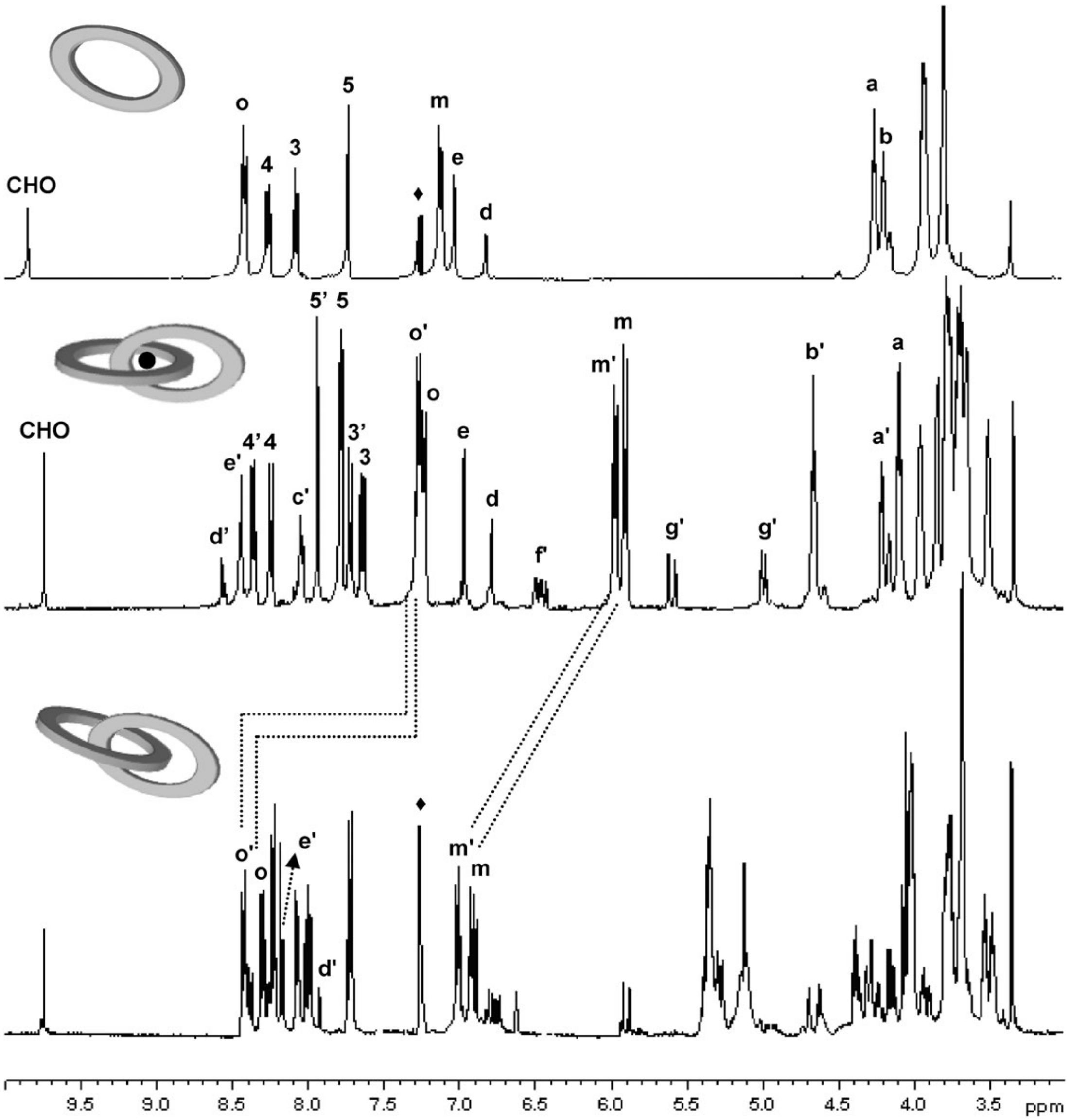


Fig. 5 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of benzaldehyde-macrocycle **7**, styrene-benzaldehyde-Cu(I)-[2]catenate **17** and Cu-free [2]catenand **18**. ● = Cu(I) ion and ♦ = solvent peak.

The ^1H NMR spectrum of **18** shows no concentration dependence in $CDCl_3$ at room temperature, implying no significant intermolecular π–π stacking.[14,19] Variable temperature ^1H NMR studies (298–233 K) in the same solvent show only increasing broadening of the peaks as the temperature is lowered, indicating that the molecule exists in several interconverting conformations.[14] Presumably, this lack of order is a result of the large size and shape of the macrocycle components (42 and 37-atom membered rings) of catenand **18**. The two rings are apparently free to reorient around and through one another at a rate which is fast on the ^1H NMR time scale, even at low temperatures (213 K) in $CDCl_3$.

These results clearly demonstrate that the introduction of peripheral styrene and aldehyde groups and the presence of triazole rings does not noticeably alter the physical properties of the [2]catenane in solution.[8,14,19] The free circumrotation of one ring within the other and the relatively facile conformational changes are desirable features, since the peripheral groups are available for further reactions, opening up the possibility of using functionalized catenanes as synthetic building blocks, even after removing the metal-template ion needed to assemble the structure.

3. Conclusions

Two "click" protocols for the preparation of functionalized [2]catenanes, using a Cu(I) template synthesis, are described. A straightforward strategy allowed the synthesis of symmetrical-functionalized [2]catenanes, although it failed for the synthesis of non-symmetrical [2]functionalized catenanes. A different strategy using milder conditions, which is compatible with the instability of precursors and the presence of peripheral functional groups, was developed for the preparation of non-symmetrical-functionalized [2]catenanes in high yields. The introduction of peripheral functional groups into [2]catenane structures will be useful for the preparation of structurally elaborated materials, such as polymers, dendrimers, mechanically linked donor–acceptor systems and higher interlocked structures. The large size of the macrocycle components allows the interlocked structure to adopt different conformations after removing the central Cu(I) ion needed for structural assembly, suggesting that the metal-free system should be suitable for further reactions to prepare more complex purely organic systems. These possibilities are under current investigation.

4. Experimental section

General

NMR spectra were obtained on either a Bruker AVANCE 400 (400 MHz) or an AVANCE 500 (500 MHz) spectrometer using deuterated solvents as the lock. The spectra were collected at 25 °C and chemical shifts (δ, ppm) were referenced to residual solvent peak. *J* values are given in Hz. In the ^1H NMR assignment (δ), H_o and H_m refer to the hydrogen atoms at the *ortho* and *meta* positions, respectively, of the phenyl ring attached to the phenanthroline ring system, whose hydrogen atoms are numbered $H_{3,8}$, $H_{4,7}$, $H_{5,6}$, respectively. Ar is used as an abbreviation for aromatic ring. Mass spectra were obtained on an Agilent 1100 Series Capillary LCMSD Trap XCT Spectrometer in positive or negative-ion mode and a ThermoFinnigan PolarisQ ion-trap GCMS Spectrometer. MALDI-TOF mass spectra were recorded in a Bruker OmniFLEX MALDI-TOF MS Spectrometer. This instrument was operated at an accelerating potential of 20 kV in linear mode. The mass spectra represent an average over 256 consecutive laser shots. The mass scale was calibrated using the matrix peaks and the calibration software available from Bruker OmniFLEX. The mentioned *m*/*z* values correspond to monoisotopic masses. The compound solutions (10^{-3} mol L^{-1}) were prepared in THF. Matrix compound was purchased from Aldrich and used without further purification. The matrix, α-cyano-4-hydroxycinnamic acid (CCA), was dissolved (10 g L^{-1}) in a solvent mixture composed of $H_2O–CH_3CN$–TFA (25/75/1, v/v). Two microlitres of compound solution were mixed with 10 μL of matrix solution. The final solution was deposited onto the sample target and allowed to dry in air. All chemicals were purchased from Sigma-Aldrich and Alfa Aesar and used without further purification. For moisture sensitive reactions, solvents were freshly distilled. Methylene chloride (DCM) and acetonitrile (CH_3CN) were dried over calcium hydride while tetrahydrofuran (THF) was dried using sodium–benzophenone. Anhydrous dimethylformamide (DMF) was used as received. All syntheses were carried out using Schlenk line techniques. Moisture sensitive liquids were transferred by canula or syringe. The progress of the reactions was monitored by thin-layer chromatography (TLC) whenever possible. TLC was performed using precoated glass plates (Silica gel 60, 0.25 mm thickness) containing a 254 nm fluorescent indicator. Column chromatography was carried out using Merck Silica gel 60 (0.063–0.200 mm). Macrocycle **6** and diazido phenanthroline derivative **14** were prepared in accordance with previously reported procedures.[11b]

Synthesis

Bis-ethynylphenanthroline derivative 1. 2,9-Bis(4-{2-[2-hydroxyethoxy(ethoxy)-(ethoxy)]}phenyl)-1,10-phenanthroline (4.00 g, 6.380 mmol), prepared in accordance with the literature procedure,[8c] and propargyl bromide (15.00 g, 12.740 mmol) were dissolved in 200 mL of dry DMF and stirred for 15 min under an argon atmosphere at room temperature. Sodium hydride (0.450 g, 18.90 mmol) was then added and the reaction mixture was heated to 80 °C. After 4 h, another portion of NaH (0.220 g, 9.450 mmol) and propargyl bromide (7.50 g, 6.370 mmol) were added and the reaction mixture was stirred for an additional 8 h at 80 °C. The reaction was carefully quenched with cold water and concentrated under reduced pressure. DCM (300 mL) was added and the organic layer was then separated. The aqueous phase was extracted with DCM (3 × 100 mL). The combined organic layers were washed with water (3 × 150 mL), dried over magnesium sulfate, filtered through paper and concentrated. Final purification was achieved by column chromatography (SiO_2) using DCM–MeOH as the eluent (gradient from 0 to 3%, v/v), affording **1** (3.60 g, 85%) as a brown oil. δ_H (400 MHz;

$CDCl_3$) 8.34 (4H, d, J = 8.8, 4H, H_o), 8.27 (2H, d, J = 8.5, $H_{4,7}$), 8.11 (2H, d, J = 8.5, $H_{3,8}$), 7.76 (2H, s, $H_{5,6}$), 7.08 (4H, d, J = 8.8, H_m), 4.20 (4H, t, J = 4.9, Ar-O-CH_2), 4.16 (4H, t, J = 4.9, O-CH_2-C≡CH), 3.86–3.55 (18H, m, O-CH_2-CH_2-O), 2.42 (2H, m, O-CH_2-C≡CH); δ_c (400 MHz; $CDCl_3$) phenanthroline nuclei: 159.5, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8, trioxoethyl linker: 72.7, 69.7, 69.5, 69.2, 67.6, 66.0, ethynyl group: 78.2 (CH_2-C≡CH); 76.2 (CH_2-C≡CH); 59.9 (CH$_2$-C≡CH); m/z (LC-MSD) found 705.40 ([M + H]$^+$), $C_{42}H_{44}N_2O_8$ requires 704.31.

2-(3,5-Diazidophenyl)-5,5-dimethyl-1,3-dioxane (2). Commercially available 3,5-dibromobenzaldehyde (1.00 g, 3.780 mmol), neopentylglycol (0.786 g, 7.56 mmol) and p-toluenesulfonic acid (0.360 g, 1.890 mmol) were dissolved in 50 mL of dry THF and heated at reflux for 8 h. The solvent was evaporated and DCM (200 mL) was added. The crude product was washed with water (5 × 100 mL), dried over Na_2SO_4, filtered through paper and evaporated to dryness to yield quantitatively the glycol-protected benzaldehyde **2a** as a colorless oil, which was used in the next step without further purification. Sodium azide (0.740 g 11.40 mmol), sodium ascorbate (0.340 g, 1.710 mmol), N,N-dimethylethylenediamine (0.225 g, 2.565 mmol), NaOH (0.034 g, 0.850 mmol), glycol-protected 3,5-dibromobenzaldehyde (1.00 g, 2.850 mmol) and CuI (0.162 g, 0.855 mmol) were dissolved in 50 mL of a degassed (argon for 30 min) EtOH–H_2O solvent mixture (7 : 3) and heated at reflux for 3 h. The crude product was concentrated under reduced pressure and extracted with DCM (3 × 100 mL). The combined organic phases were washed with water (3 × 150 mL), dried over Na_2SO_4, filtered through paper and concentrated. Final purification was achieved by column chromatography using DCM–MeOH (99 : 1) as the eluent to give the glycol-protected 3,5-diazidobenzaldehyde **2** (0.546 g, 65%) as a gold oil. ν_{max} (KBr)/cm^{-1} 2099 (N=N stretch); δ_H (400 MHz; $CDCl_3$) 6.61 (2H, d, J = 2.3, *ortho* Ar-H), 6.22 (1H, t, J = 2.3, *para* Ar-H), 5.26 (1H, s, Ar-CH-acetal), 3.85 and 3.55 (4H, d, acetal CH_2), 1.27 and 0.79 (6H, s, CH_3 on acetal); δ_c (400 MHz; $CDCl_3$) 140.6 ($C_{3,5}$), 136.2 (C_1), 134.3 (C_4), 128.8 ($C_{2,6}$), 108.32 (Ar-C-O-CH_2), 79.1 (O-CH$_2$-C-CH_3), 33.5 (O-CH_2-C-CH_3), 19.5 (O-CH_2-C-CH$_3$).

Macrocycle 3. Ethynylphenanthroline derivative **1** (0.200 g, 0.284 mmol) and protected 3,5-diazidobenzaldehyde **2** (0.078 g, 0.284 mmol) were dissolved in 100 mL of a degassed (argon for 30 min) ethanol–toluene (9/1) solvent mixture and transferred by canula into an addition funnel. In the three-neck round-bottomed flask, 1,8-diaza[5.4.0]bicycloundec-7-ene (DBU) (0.076 g, 4.00 mmol), sodium ascorbate (0.340 g, 1.704 mmol), sulfonated bathophenanthroline SBP (0.670 g, 1.136 mmol) and CuI (0.107 g, 0.568 mmol) were dissolved in 600 mL of a degassed (argon for 30 min) EtOH–H_2O–toluene (60/40/10) solvent mixture under an argon atmosphere. The resulting dark red solution was then heated to 70 °C and the solution in the addition funnel was added dropwise over 10 h (high dilution conditions). The reaction mixture was then stirred for another 4 h. The solvents were evaporated, and ethyl acetate (200 mL) and water (50 mL) were added. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed with ammonium hydroxide (2 × 50 mL) and water (5 × 150 mL), dried over magnesium sulfate, filtered through paper and finally evaporated to dryness. Final purification was achieved by column chromatography (neutral Al_2O_3) using DCM–MeOH (99/1) as the eluent to give macrocycle **3** (0.178 g, 70%) as a colorless solid. δ_H (400 MHz; $CDCl_3$) 8.38 (4H, d, J = 9.0, H_o), 8.22 (2H, d, J = 8.4 Hz, $H_{4,7}$), 8.03 (2H, d, J = 8.4, $H_{3,8}$), 7.95 (2H, s, H-triazole ring), 7.69 (2H, s, $H_{5,6}$), 7.10–7.00 (6H, m, H_m and *ortho* Ar-H), 6.76 (1H, s, *para* Ar-H), 5.26 (1H, s, Ar-CH-acetal), 4.73 (4H, s, O-CH_2-triazole ring), 4.19–3.60 (24H, m, all O-CH_2-CH_2-O), 3.58 (4H, m, acetal CH_2); 1.24 and 0.73 (6H, s, CH_3 on acetal); m/z (MALDI-TOF) found 979.20 ([M + H]$^+$), $C_{54}H_{58}N_8O_{10}$ requires 978.43.

Catenand 5. In the reaction flask, ethynylphenanthroline **1** (0.148 g, 0.200 mmol) was dissolved in 15 mL of dry DCM under an argon atmosphere. $Cu(CH_3CN)_4PF_6$ (0.038 g, 0.100 mmol) dissolved in 5 mL of CH_3CN was added to the flask dropwise by syringe and the resulting dark red solution was stirred at room temperature for 30 min, generating the Cu-complex **4**. A total of 600 mL of an oxygen-free mixture of EtOH–H_2O–toluene (60/40/10) was then added to the flask, followed by addition of DBU (0.608 g, 4.00 mmol), sodium ascorbate (0.160 g, 0.808 mmol) and SBP (0.708 g, 1.2 mmol). The reaction mixture was stirred for 10 min and CuI (0.076 g, 0.400 mmol) was then added. The solution was stirred for an additional 30 min at room temperature and heated to 70 °C. Protected diazidobenzaldehyde **2** (0.055 g, 0.200 mmol) was dissolved in 180 mL of a degassed (argon for 30 min) EtOH–toluene (90/10) solvent mixture and transferred by canula into an addition funnel under an argon atmosphere. The azide solution was added dropwise to the reaction flask over 10 h with magnetic stirring. At the end of the addition, the reaction mixture was stirred for another 4 h followed by removal of the solvents under reduced pressure. Ethyl acetate (200 mL) and water (50 mL) were added, the organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed with ammonium hydroxide (2 × 50 mL), then water (5 × 150 mL), dried over magnesium sulfate, filtered through paper and evaporated to dryness. Final purification was achieved by column chromatography (neutral Al_2O_3) using DCM–MeOH (gradient from 0 to 2%) as the eluent to give catenand **5** (0.360 g, 92%) as a beige solid. δ_H (400 MHz; $CDCl_3$) 8.32 (8H, d, J = 9.0, H_o), 8.15 (4H, d, J = 8.4 Hz, $H_{4,7}$), 8.01 (4H, d, J = 8.4, $H_{3,8}$), 7.86 (4H, s, H-triazole ring), 7.24 (4H, s, $H_{5,6}$), 7.10–6.95 (12H, m, H_m and *ortho* Ar-H); 6.71 (2H, s, *para* Ar-H), 5.14 (4H, s, acetal Ar-CH), 4.76 (8H, s, O-CH_2-triazole ring), 4.20–3.70 (48H, m, all O-CH_2-CH_2-O), 3.51 (8H, m, acetal CH_2), 1.22 and 0.71 (12H, s, CH_3 on acetal); m/z (MALDI-TOF) found 1957.48 ([M + H]$^+$), $C_{108}H_{116}N_{16}O_{20}$ requires 1956.86.

Macrocycle 7. Macrocycle **6** (0.152 g, 0.20 mmol) was dissolved in 30 mL of freshly distilled THF under an N_2 atmosphere and magnetic stirring. $LiAlH_4$ (2 mL, 1 M solution in THF) was slowly added by syringe and the blue suspension was stirred at rt for 6 h. Ethyl acetate (5 mL) was added to the mixture which was stirred for 10 min. The solvent was removed and the remaining solid was redissolved in 50 mL of $CHCl_3$. The solid was filtered through paper and thoroughly washed with $CHCl_3$. MnO_2 (3.0 g) was added to the filtrate and the mixture was heated at reflux for 5 h. The slurry solid was removed by filtration through celite and the solid washed with fresh $CHCl_3$. The filtrate was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using DCM–EtOAc (90 : 10, v/v) as eluent, affording **7** (0.100 g, 70%) as a light yellow solid. δ_H (400 MHz; $CDCl_3$) 9.86 (1H, s, CHO), 8.34 (4H, d, J = 9.0, H_o), 8.26 (2H, d, J = 8.8, $H_{4,7}$), 8.08 (2H, d, J = 8.8, $H_{3,8}$), 7.73 (2H, s, $H_{5,6}$), 7.11 (4H, d, J = 9.0, H_m), 6.95 (2H, d, J = 8.4, *ortho* Ar-*H*), 6.62 (1H, m, J = 8.4, *para* Ar-*H*), 4.10 (4H, s, Ar-O-CH_2), 4.05–3.50 (20H, m, O-CH_2-CH_2-O). δ_c (400 MHz; $CDCl_3$) benzaldehyde ring: 192.1, 145.6, 136.7, 107.5, 106.3; phenanthroline nuclei: 159.5, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8; trioxoethyl linker: 72.7, 69.7, 69.5, 67.6, 66.0, 61.6; m/z (LC-MSD) found 731.56 ($[M + H]^+$), $C_{43}H_{42}N_2O_9$ requires 730.29.

3,5-Dibromostyrene (9). Methyltriphenylphosphonium bromide (1.430 g, 4.00 mmol) was dissolved in 15 mL of dry THF under an N_2 atmosphere. The solution was cooled to 0 °C (ice bath) and potassium *tert*-butoxide (0.450 g, 4.00 mmol) was added portionwise (3 × 0.150 g over 10 min). The resulting red mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was then cooled to −78 °C (ethanol–liquid N_2 bath) and a solution of 3,5-dibromobenzaldehyde (1.00 g, 3.780 mmol) in 10 mL of dry THF was added dropwise. The reaction mixture was warmed to room temperature, stirred for 2 h and carefully quenched with 5% aqueous HCl solution. The solvent was evaporated and DCM (100 mL) was added. The organic layer was separated and the aqueous phase was extracted with DCM (3 × 150 mL). The combined organic layers were washed with water (3 × 250 mL), dried over Na_2SO_4, filtered through paper and evaporated to dryness. Final purification was achieved by column chromatography (SiO_2) using hexanes as eluent to afford 3,5-dibromostyrene **9** (0.450 g, 45%) as a colorless oil. δ_H (400 MHz; $CDCl_3$) 7.45 (1H, t, J = 1.8, Ar-*para-H*), 7.40 (2H, d, J = 1.8, Ar-*ortho-H*), 6.46 (1H, m, $CH{=}CH_2$), 5.19 (1H, d, J = 17.4, $CH{=}CH_2$) and 5.26 (1H, d, J = 10.8, $CH{=}CH_2$); δ_c (400 MHz; $CDCl_3$) 139.6 (C_1), 135.5 ($CH{=}CH_2$), 134.2 (C_4), 128.5 ($C_{2,6}$), 123.7 ($C_{3,5}$), 112.1 ($CH{=}CH_2$); m/z (GC-MS) found 260.42 ($[M + H]^+$), $C_8H_6Br_2$ requires 259.88.

3,5-Diazidostyrene (10). Compound **10** was synthesized from **9** following the same procedure described for compound **2**. After workup, the crude product was purified by column chromatography (SiO_2) using DCM as eluent to afford compound **10** (0.250 g, 55%) as a gold oil. ν_{max} (KBr)/cm^{-1} 2094 (N=N stretch); δ_H (400 MHz; $CDCl_3$) 6.55 (1H, m, $CH = CH_2$), 6.48 (2H, d, J = 2.0, *ortho* Ar-*H*), 6.21 (1H, t, J = 2.0, *para* Ar-*H*), 5.19 (1H, d, J = 17.4, $CH{=}CH_2$) and 5.26 (1H, d, J = 10.8, $CH{=}CH_2$); δ_c (400 MHz; $CDCl_3$) 143.1 ($C_{3,5}$), 137.0 ($CH{=}CH_2$), 135.9 (C_1), 129.4 (C_4), 125.0 ($C_{2,6}$), 112.2 ($CH{=}CH_2$).

3,5-Diethynylstyrene (15). In a round-bottomed flask covered by aluminium foil, triethylamine (12 mL), dibromostyrene **9** (0.380 g, 1.45 mmol), $Pd(Ph_3P)_2Cl_2$ (0.203 g, 0.29 mmol) and trimethylsilylacetylene (0.653 g, 6.70 mmol) were added under inert atmosphere and the reaction mixture was heated to 50 °C. After 10 min, CuI (0.041 g, 0.22 mmol) was added to the reaction flask and the mixture was stirred at 50 °C for 18 h under an N_2 atmosphere. The black crude suspension was then filtered through celite using DCM as eluent and the solvents were evaporated. The product was redissolved in THF and tetrabutylammonium fluoride (5 mL) was added and the solution was stirred for 30 min at room temperature. THF was evaporated under reduced pressure, DCM (150 mL) was added and the crude product was washed with water, dried over Na_2SO_4, filtered through paper and concentrated. Final purification was achieved by column chromatography (SiO_2) using hexanes as eluent to afford 3,5-diethynylstyrene **15** (0.154 g, 70%) as a colorless oil. δ_H (400 MHz; $CDCl_3$) 7.43 (3H, m, Ar-*H*), 6.50 (1H, m, $CH{=}CH_2$), 5.70 (1H, d, J = 17.4, $CH{=}CH_2$), 5.24 (1H, d, J = 10.8, $CH{=}CH_2$), 2.98 (2H, s, $C{\equiv}CH$); δ_c (400 MHz; $CDCl_3$) 136.3 ($CH{=}CH_2$), 135.4 (C_4), 134.2 (C_1), 129.9 ($C_{2,6}$), 123.4 ($C_{3,5}$), 114.2 ($CH{=}CH_2$), 82.4 ($CH{\equiv}CH$), 81.1 ($CH{\equiv}CH$); m/z (GC-MS) found 152.9 ($[M + H]^+$), $C_{12}H_8$ requires 152.06.

Synthesis of Cu(I)-catenate 17. In flask A, macrocycle **7** (0.050 g, 0.068 mmol) was dissolved in 2.0 mL of degassed DCM–CH_3CN (7 : 3, v/v) to which $[Cu(CH_3CN)_4][PF_6]$ (0.026 g, 0.068 mmol) was added under N_2 and the solution was stirred at rt for 30 min. The azidophenanthroline ligand **14** (0.046 g, 0.068 mmol) was then added as a solid to flask A and the deep red solution was stirred under N_2 at rt for 3 h to generate precursor **16**. Meanwhile, in the reaction flask, CuI (0.026 g, 0.137 mmol), sodium ascorbate (0.110 g, 0.548 mmol) and SBP (0.161 g, 0.274 mmol) were dissolved in 20 mL of degassed aqueous ethanol (1 : 1, v/v). The pink suspension was heated at reflux for 2 min and cooled back to rt. The deep red solution in the flask A containing **16** was then diluted to 8 mL with degassed DCM and added by syringe to the reaction flask. Finally, **15** (0.013 g, 0.068 mmol), dissolved in 10 mL of degassed DCM, and DBU (0.031 g, 0.205 mmol) were added and the resulting purple mixture was stirred under nitrogen for 12 h at rt. The crude mixture was neutralized by adding 5 mL of 10% HCl_{aq} solution and extracted with DCM (3 × 50 mL). The organic phase was washed with water (3 × 100 mL), concentrated to a volume of 10 mL and then stirred for 3 h with a saturated methanolic solution of KPF_6 to effect the anion exchange. The solvents were evaporated under reduced pressure; the remaining insoluble light red solid was extracted with DCM (3 × 100 mL) and filtered through paper. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2) using DCM–CH_3OH (99/1 v/v) as eluent, affording **17** (0.070 g, 75%) as a red solid. δ_H (400 MHz; $CDCl_3$) 9.73 (1H, s, CHO), 8.50 (1H, s, $CH_2{=}CH$-Ar-*H* at *para* position), 8.43 (2H, s, $CH_2{=}CH$-Ar-*H* at *ortho* position), 8.34 (2H, d, J = 8.4 Hz, $H_{4,7}$), 8.23 (2H, d, J = 8.4 Hz, $H_{4',7'}$), 8.03 (2H, s, *H*-triazole ring), 7.92 (2H, s, $H_{5,6}$), 7.76 (2H, s, $H_{5',6'}$), 7.72 (2H, d, J = 8.4, $H_{3,8}$), 7.64 (2H, d, $J = 8.4$, $H_{3',8'}$), 7.26 (4H, d, $J = 9.0$, H_o), 7.21 (4H, d, $J = 9.0$, $H_{o'}$), 6.96 (2H, s, CHO-Ar-*H* at *ortho* position), 6.71 (1H, s, CHO-Ar-*H* at *para* position), 6.45 (1H, m, $CH{=}CH_2$), 5.96 (4H, d, $J = 9.0$, H_m), 5.88 (4H, d, $J = 9.0$, $H_{m'}$), 5.59 (1H, d, $CH{=}CH_2$), 4.98 (1H, d, $CH{=}CH_2$), 4.65 (4H, s, O-CH_2-triazole ring), 4.20–3.00 (44H, m, O-CH_2-CH_2-O); *m*/*z* (MALDI-TOF) found 1623.12 ($[M]^+$), $C_{91}H_{88}N_{10}O_{15}Cu$ requires 1623.57.

Synthesis of Cu-free catenand 18. Catenane **17** (0.050 g, 0.028 mmol) was dissolved in 5 mL of DCM to which was added a solution of KCN (0.020 g, 0.30 mmol) dissolved in 5 mL of H_2O, and the mixture was stirred at room temperature for 30 min. The deep red solution became colorless and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL), dried over Na_2SO_4, filtered through paper and evaporated to dryness. Final purification was achieved by column chromatography (SiO_2) using DCM–CH_3OH (99/1 v/v) as eluent, affording **17** as a waxy solid in quantitative yield. δ_H (400 MHz; $CDCl_3$) 9.75 (1H, s, C*H*O), 8.44 (4H, d, $J = 9.0$, H_o), 8.32 (4H, d, $J = 9.0$, $H_{o'}$), 8.25 (2H, d, $J = 8.4$ Hz, $H_{4,7}$), 8.19 (2H, d, $J = 8.4$ Hz, $H_{4',7'}$), 8.16 (2H, d, $CH_2{=}CH$-Ar-*H* at *ortho* position), 8.09 (2H, d, $J = 8.4$, $H_{3,8}$), 8.02 (2H, s, *H*-triazole ring), 8.00 (2H, d, $J = 8.4$, $H_{3',8'}$), 7.93 (1H, s, $CH_2{=}CH$-Ar-*H* at *para* position), 7.73 (2H, s, $H_{5,6}$), 7.71 (2H, s, $H_{5',6'}$), 7.03 (4H, d, $J = 9.0$, H_m), 6.94 (4H, d, $J = 9.0$, $H_{m'}$), 6.89 (1H, m, $CH{=}CH_2$), 6.90 (2H, s, CHO-Ar-*H* at *ortho* position), 6.63 (1H, s, CHO-Ar-*H* at *para* position), 5.92 (1H, d, $CH{=}CH_2$), 5.35 (4H, s, O-CH_2-triazole ring), 5.30 (1H, d, $CH{=}CH_2$), 5.20–3.00 (44H, m, all O-CH_2-CH_2-O); *m*/*z* (MALDI-TOF) found 1600.15 ($[M + K]^+$), $C_{91}H_{88}N_{10}O_{15}$ requires 1560.64.

Acknowledgements

The authors are deeply grateful to the National Science Foundation (Grant CHE-0647334) for financial support. This investigation was conducted in part in a facility constructed with support from Research Facilities Improvement Grant Number C06 RR-16572-01 from the National Center for Research Resources, National Institutes of Health.

References

1 For some examples, see: (*a*) J. D. Crowley, S. M. Goldup, A. L. Lee, D. A. Leigh and R. T. McBurney, *Chem. Soc. Rev.*, 2009, **38**, 1530–1541; (*b*) R. Jäger and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 930–944; (*c*) V. Balzani, M. Gomez-Lopez and J. F. Stoddart, *Acc. Chem. Res.*, 1998, **31**, 405–414; (*d*) K. Yamashita, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2007, **129**, 1850–1851; (*e*) C. O. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 189–192; (*f*) J. F. Stoddart, *Chem. Soc. Rev.*, 2009, **38**, 1802–1820.

2 (*a*) V. Serreli, C.-F. Lee, E. R. Kay and D. A. Leigh, *Nature*, 2007, **445**, 523–527; (*b*) J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. Delonno, Y. Luo, B. A. Scheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart and J. R. Heath, *Nature*, 2007, **445**, 414–417; (*c*) A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni and B. Ventura, *J. Am. Chem. Soc.*, 1997, **119**, 12114–12124; (*d*) V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines-A Journey into the Nano World*, Wiley-VCH, Weinheim, Germany, 2003; (*e*) A. Credi, M. Montalli, V. Balzani, S. J. Langford, F. M. Raymo and J. F. Stoddart, *New J. Chem.*, 1998, **22**, 1061–1065.

3 (*a*) D. J. Cárdenas, J.-P. Collin, P. Gaviña, J.-P. Sauvage, A. De Cian, J. Fischer, N. Armaroli, L. Flamigni, V. Vicinelli and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 5481–5488; (*b*) H. Sasabe, N. Kihara, Y. Furusho, K. Mizuno, A. Ogawa and T. Takata, *Org. Lett.*, 2004, **6**, 3957–3960; (*c*) S. Saha, A. H. Flood, J. F. Stoddart, S. Impellizzeri, S. Silvi, M. Venturi and A. Credi, *J. Am. Chem. Soc.*, 2007, **129**, 12159–12171; (*d*) A. S. D. Sandanayaka, N. Watanabe, K.-I. Ikeshita, Y. Araki, N. Kihara, Y. Furusho, O. Ito and T. Takata, *J. Phys. Chem. B*, 2005, **109**, 2516–2525; (*e*) L. Flamigni, N. Amaroli, F. Barigelletti, J.-C. Chambron, J.-P. Sauvage and N. Solladie, *New J. Chem.*, 1999, **23**, 1151–1158.

4 (*a*) M. J. Chmielewski, J. J. Davis and P. D. Beer, *Org. Biomol. Chem.*, 2009, **7**, 415–424; (*b*) P. Thordarson, J. A. Bijsterveld, A. E. Rowan and R. J. M. Nolte, *Nature*, 2003, **424**, 915–918.

5 K. Patel, S. Angelos, W. R. Dichtel, A. Coskun, Y.-W. Yang, J. I. Zink and J. F. Stoddart, *J. Am. Chem. Soc.*, 2008, **130**, 2382–2383.

6 (*a*) W. R. Dichtel, O. S. Miljanic, W. Zhang, J. M. Pruell, K. Patel, I. Aprahamian, J. R. Heath and J. F. Stoddart, *Acc. Chem. Res.*, 2008, **41**, 1750–1761; (*b*) J.-P. Sauvage and C. O. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, Germany, 1999; (*c*) D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725–2828; (*d*) J. A. G. Williams, *Chem. Soc. Rev.*, 2009, **38**, 1783.

7 (*a*) B. Mohr, M. Weck, J.-P. Sauvage and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1308–1310; (*b*) V. Aucagne, K. D. Hanni, D. A. Leigh, P. J. Lusby and D. B. Walker, *J. Am. Chem. Soc.*, 2006, **128**, 2186–2187; (*c*) P. Mobian, J.-P. Collin and J.-P. Sauvage, *Tetrahedron Lett.*, 2006, **47**, 4907–4909; (*d*) A. I. Prikhod'ko, F. Durola and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2008, **130**, 448–449; (*e*) S. Durot, P. Mobian, J.-P. Collin and J.-P. Sauvage, *Tetrahedron*, 2008, **64**, 8496–8506; (*f*) V. Aucagne, J. Bernà, J. D. Crowley, S. M. Goldup, K. D. Hanni, D. A. Leigh, P. J. Lusby, V. E. Ronaldson, A. M. Z. Slawin, A. Viterisi and D. B. Walker, *J. Am. Chem. Soc.*, 2007, **129**, 11950–11963; (*g*) W. R. Dichtel, O. S. Miljanic, J. M. Spruell, J. R. Heath and J. F. Stoddart, *J. Am. Chem. Soc.*, 2006, **128**, 10388–10390; (*h*) M. Hutin, C. A. Schalley, G. Bernardinelli and J. R. Nitschke, *Chem.–Eur. J.*, 2006, **12**, 4069–4076; (*i*) Y. Sato, R. Yamasaki and S. Saito, *Angew. Chem., Int. Ed.*, 2009, **48**, 504–508.

8 (*a*) C. O. Dietrich-Buchecker and J.-P. Sauvage, *Tetrahedron Lett.*, 1983, **24**, 5095–5098; (*b*) C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1984, **106**, 3043–3044; (*c*) C. O. Dietrich-Buchecker and J.-P. Sauvage, *Tetrahedron*, 1990, **46**, 503–512; (*d*) C. O. Dietrich-Buchecker and J.-P. Sauvage, *Chem. Rev.*, 1987, **87**, 795–810; (*e*) J.-P. Collin, J.-P. Sauvage, Y. Trolez and K. Rissanen, *New J. Chem.*, 2009, **33**, 2148–2154.

9 (*a*) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 321–328; (*b*) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021; (*c*) M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952–3015.

10 (*a*) C. Ornelas, J. R. Aranzaes, E. Cloutet, S. Alvez and D. Astruc, *Angew. Chem., Int. Ed.*, 2007, **46**, 872–877; (*b*) P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. Frèchet and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2004, **43**, 3028–3030; (*c*) V. O. Rodionov, V. V. Fokin and M. G. Finn, *Angew. Chem., Int. Ed.*, 2005, **44**, 2210–2215; (*d*) M. Meldal, *Macromol. Rapid Commun.*, 2008, **29**, 1016–1051; (*e*) P. D. Jarowski, Y. L. Wu, W. B. Schweitzer and F. Diederich, *Org. Lett.*, 2008, **10**, 3347–3350; (*f*) S. S. Gupta, J. Kuzelka, P. Singh, W. G. Lewis, M. Manchester and M. G. Finn, *Bioconjugate Chem.*, 2005, **16**, 1572–1579; (*g*) W. G. Lewis, F. G. Magallon, V. V. Fokin and M. G. Finn, *J. Am. Chem. Soc.*, 2004, **126**, 9152–9153; (*h*) P. Wu and V. V. Fokin, *Aldrichimica Acta*, 2007, **1**, 7–17.

11 (*a*) J. D. Megiatto, Jr. and D. I. Schuster, *J. Am. Chem. Soc.*, 2008, **130**, 12872–12873; (*b*) J. D. Megiatto, Jr. and D. I. Schuster, *Chem.–Eur. J.*, 2009, **15**, 5444–5448; (*c*) J. D. Megiatto, Jr., R. Spencer and D. I. Schuster, *Org. Lett.*, 2009, **11**, 4152–4155.

12 (*a*) R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446–452; (*b*) R. W. Hoffmann, *Angew. Chem., Int. Ed.*, 2001, **40**, 1411–1416; (*c*) C. D. Meyer, C. S. Joiner and J. F. Stoddart, *Chem. Soc. Rev.*, 2007, **36**, 1705–1723; (*d*) N. E. Borisova, M. D. Reshetova and Y. A. Ustynyuk, *Chem. Rev.*, 2007, **107**, 46–79.

13 J. Andersen, U. Madsen, F. Bjorkling and X. Liang, *Synlett*, 2005, 2209–2213.

14 D. B. Amabilino and J.-P. Sauvage, *New J. Chem.*, 1998, **22**, 395–409.

15 (*a*) K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467–4470; (*b*) M. A. Fazio, O. P. Lee and D. I. Schuster, *Org. Lett.*, 2008, **10**, 4979–4982.

16 For mass spectroscopic studies of catenanes, see: (*a*) W. Vetter and G. Schill, *Tetrahedron*, 1967, **23**, 3079–3093; (*b*) F. Bitsch, C. O. Dietrich-Buchecker, A. K. Khemiss, J.-P. Sauvage and A. V. Dorsselaer, *J. Am. Chem. Soc.*, 1991, **113**, 4023–4025.

17 E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless and S. Chang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1730–1733.

18 Similar electron-withdrawing effects induced by triazole rings attached to ferrocene moieties have also been observed electrochemically in dendrimers. See ref. 10*a*.

19 D. B. Amabilino, C. O. Dietrich-Buchecker, A. Livoreil, L. Perez-Garcia, J.-P. Sauvage and J. F. Stoddart, *J. Am. Chem. Soc.*, 1996, **118**, 3905–3913.