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"Click" Methodology for Synthesis of Functionalized [3]Catenanes: Toward Higher Interlocked Structures

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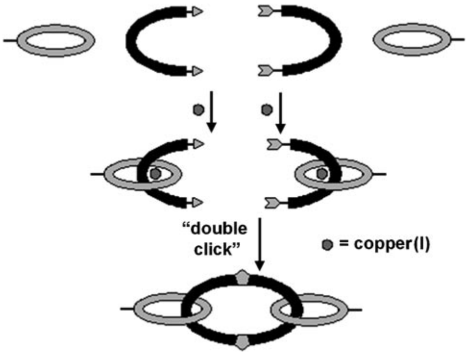
Synthesis of higher interlocked molecules, such as [3]catenanes, has been a synthetic challenge in chemistry for decades.[1] Systems containing several interlocked rings are interesting from a photochemical and photophysical point of view because of the properties deriving from electronic interactions between the various subunits. These features have been explored in principle for construction of nanomachines and molecular storage information devices.[2]

The copper(I) template approach developed by Sauvage and co-workers[3] is a general and highly effective strategy for the preparation of catenanes, rotaxanes, knots and interlocked oligomers. This methodology is based on tetrahedral coordination of a copper(I) atom to a pair of bidentate ligands which are held in a specific orientation that directs subsequent macrocyclization and/or "stoppering" reactions, affording interlocked structures.

The templated synthesis of [3]catenanes, consisting of three interlocked rings and two copper(I) centers, has been reported by Sauvage et al. following classical methodology, such as the Williamson reaction[1c] and oxidative acetylenic coupling (Glasser reaction).[1d,e] However, there are two major drawbacks to these approaches. First, cyclization yields are very poor using the Williamson reaction,[1c] and second, although acetylenic coupling affords reasonable cyclization yields, the product mixture obtained usually includes higher interlocked structures in addition to the target [3]catenane.[1d,e,4] Moreover, to the best of our knowledge, all [3]catenanes obtained previously lack functional groups for further structural elaboration.

The copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azides to alkynes ("click" chemistry or CuAAC),[5a,b] has emerged as a powerful and robust synthetic tool for construction of complex materials due to its unusual tolerance towards functional groups, and the fact that the reaction is both regioselective and virtually quantitative.[5c] Synthesis of elaborate structures such as dendrimers,[5d] macrocycles,[5e] and polymers,[5f] of donor- acceptor materials,[5g] as well as derivatization of biological substrates (e.g., virus particles,[5h] enzymes[5i] and proteins[5j]), has been accomplished very nicely using CuAAC reactions. In the field of interlocked structures, "click" chemistry has been used in the synthesis of rotaxanes[6a–e] and [2]catenanes.[6f–h] The mild conditions normally employed in CuAAC reactions seem to be well adapted to the ultimate stoppering or cyclization step, affording final products without rupture of the interlocked structures in precursors.

Our strategy (Scheme 1) is based on the separate threading of two phenanthroline string-like fragments, containing terminal azido groups and alkynyl moieties, respectively, through a functionalized coordinating macrocycle, using the copper(I) template approach.[3] Subsequent "double-click" reaction and demetalation[3b] affords bis-functionalized



Scheme 1. Principle of the copper(I) template effect leading to bis-functionalized catenanes. The complementary arrows represent terminal azide and alkynyl groups, respectively, while the pentagon represents triazole rings. The final molecular architecture after demetalation consists of two functionalized rings interlocked with a larger central ring constructed using " double-click" chemistry.

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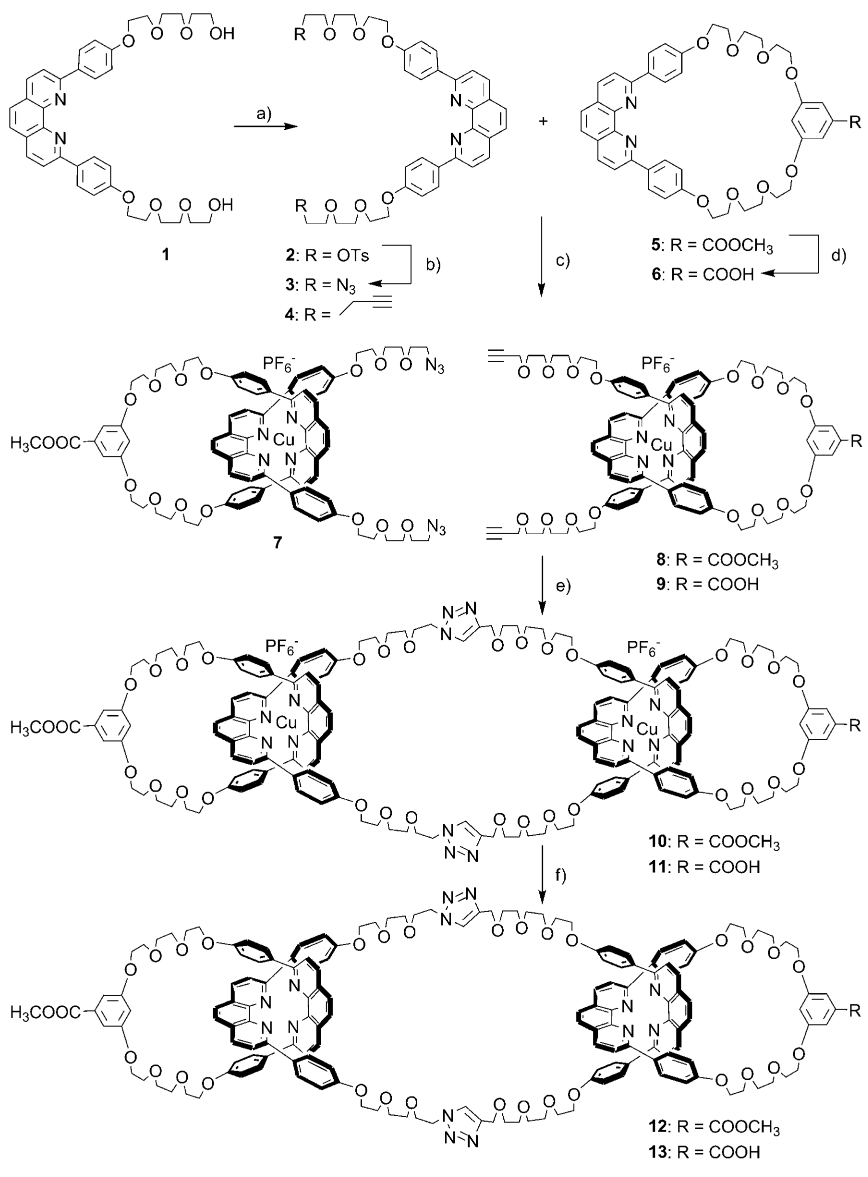
[3]catenanes. The main difficulty with this strategy resides in the fact that the non-stoppered diazido and dialkynyl copper(I) precursors are not stable and easily dissociate from the metal core at high temperatures in the presence of coordinating solvents or strong bases.[3c] To prevent this detrimental unthreading process, the connecting reactions must be done quickly and, if possible, simultaneously. With this in mind, it seemed reasonable that a good strategy to overcome these challenges would involve adjusting the reaction medium to stabilize the precursors while simultaneously accelerating the "click" cycloaddition. To overcome the precursor stability problem, we used a heterogeneous medium, composed of CH_2Cl_2 and H_2O/EtOH. The copper(I)–(phen)$_2$ complexes are less susceptible to unthreading in the CH_2Cl_2 phase, while the other CuAAC reagents remain mainly in the aqueous phase; the reaction to connect the pieces then takes place at the interface. To enhance the reaction kinetics and prevent dissociation, we used "click additives", namely sulfonated bathophenanthroline (SBP) and 1,8-diaza[5.4.0]bicycloundec-7-ane (DBU).[5g–i,7]



Scheme 2. Building blocks used in the synthesis of the triazole-linked [3]catenanes: a) p-TsCl, Et_3N, CH_2Cl_2, 0 °C, 1 d; for synthesis of **4**, see ref. [7]; b) NaN_3, DMF, 80 °C, 1 d; c) $[Cu(CH_3CN)_4PF_6]$, CH_2Cl_2/CH_3CN, 3 h, RT; d) NaOH, dioxane/H_2O, 6 h, reflux; e) CuI, SA, SBP, DBU H_2O/EtOH, 12 h, RT; f) CH_2Cl_2/MeOH, KCN, 3 h, RT.

The synthetic route to afford the building blocks and precursors in the synthesis of the triazole-linked [3]catenanes is presented in Scheme 2. The conversion of the 2,9-diaryl-1,10-phenanthroline diol **1**[3c] into ditosylate derivative **2**,[8] followed by treatment of the ditosylate with NaN_3 in DMF, afforded the diazide **3** in 70% overall yield. The dialkyne terminated phenanthroline derivative **4** was prepared as in our previous report.[7] For synthesis of the *symmetric* [3]catenane, the threading of **3** and **4** through the previously synthesized carboxymethyl-functionalized macrocycle **5**,[3e, 8,9] using the copper(I)-template approach,[3] afforded the pseudorotaxane precursors **7** and **8**, respectively, bearing ester substituents. The final "double-click" macrocyclization reaction was carried out as follows: the CH_2Cl_2/CH_3CN solutions containing **7** (1 equiv) and **8** (1 equiv) were each diluted to 10 mL with degassed CH_2Cl_2. Meanwhile, in the reaction flask, CuI (2 equiv), sodium ascorbate (SA) (8 equiv) and SBP (4 equiv) were added to 20 mL of an oxygen-free mixture of H_2O/EtOH (1:1). The pink suspension was heated at reflux for 5 min with magnetic stirring in an N_2 atmosphere. After cooling to RT, DBU (4 equiv) and the dilute deep red solutions containing **7** and **8** were added to the reaction flask. The resulting red mixture was stirred under N_2 for 12 h at room temperature. After workup, the crude product was purified by column chromatography (SiO_2) using CH_2Cl_2/CH_3OH (99:1 *v*/*v*) as eluent, affording triazole-linked bis-copper–[3]catenane **10** bearing two peripheral carboxymethyl groups as a red solid in 65% yield.[10] Formation of higher catenanes was not observed and two minor byproducts (MALDI-TOF *m*/*z* 2980, yield 18% and *m*/*z* 1865, yield 8%) were isolated but not identified.[9]

Evidence supporting the structure assignment of the isolated product as *symmetric* metalated ester-functionalized [3]catenane **10** came from the comparison of the ^{1}H NMR data for the product and the macrocyclic precursor **5**. The ^{1}H NMR spectrum of the isolated product (Figure 1b) corresponds to a molecule containing 1) two diphenylphenanthroline fragments (dpp) entwined around a copper(I) center (the phenyl protons, identified as *o* and *m*, Figure 1), show shielding effects similar to those found in other metallo-catenanes,[3,11] 2) a polyoxoethylene link bearing a triazole ring (the CH_2 groups adjacent to the triazole moieties are assigned at δ 4.46 and 4.21 ppm) and 3) the triazole ring itself (proton on the triazole ring appears at 7.8 ppm). Confirmation of the interlocked structure **10** with a central 74-membered ring bearing two triazole moeties was obtained from MALDI-TOF analysis.[9–11] The spectrum of the isolated product[9,10] exhibits peaks at *m*/*z* 3174 $[M-PF_6]^+$, 2205 $[M-2PF_6-823]^+$, corresponding to ring opening and loss of one of the peripheral esterified macrocycles and one Cu ion, 1514 $[M-2PF_6]^{2+}$, 823 [*M* for one esterified macrocycle + Cu]$^+$ and 761 [Cu-free esterified macrocycle + H]$^+$.

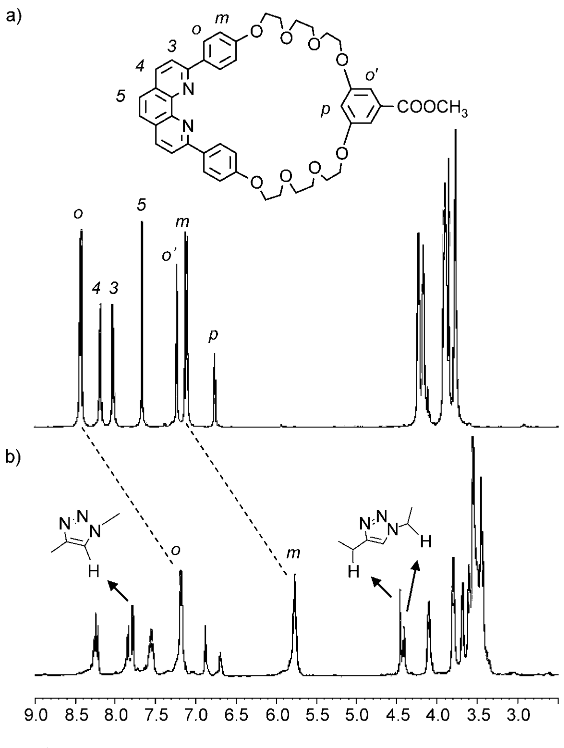


Figure 1. ^{1}H NMR spectra (400 MHz, CD_3CN, 300 K) of a) free macrocycle **5**; b) copper(I) triazole-linked carboxymethyl-functionalized [3]catenane **10**.

Demetalation using saturated aqueous KCN[3] followed by flash chromatography (SiO_2, CH_2Cl_2/CH_3OH 99:1 *v*/*v*) afforded the colorless *symmetric* Cu-free [3]catenane **12** in quantitative yield. The MALDI-TOF spectrum of **12** (Figure 2) features a molecular ion peak at 2904 $[M+H]^+$ and also the characteristic pattern for catenated species, namely, the absence of peaks between the molecular ion peak and the peaks corresponding to [2]catenane and the individual macrocycle fragments.[11]

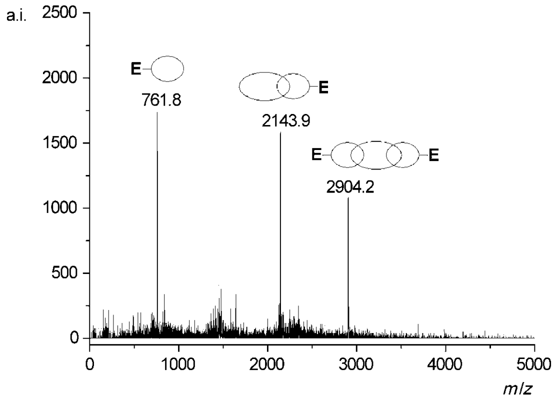


Figure 2. MALDI-TOF mass-spectrum of triazole-linked Cu-free symmetric functionalized [3]catenane **12**. a.i. = arbitrary intensity; E= methyl ester groups.[9]

These promising results prompted us to explore the possibility of synthesizing a *nonsymmetric* [3]catenane molecule, in which the peripheral rings bear different functional groups. This approach was attempted first using carboxylic acid and ester moieties, and is also shown in Scheme 2. Carboxy-functionalized macrocycle **6** was obtained from **5** by basic hydrolysis.[9] The threading of **3** through **5** and of **4** through **6** afforded the carboxy- and carbomethoxy-substituted pseudorotaxanes **7** and **9**, respectively. The final “double-click” macrocyclization carried out using the same conditions as reported above for **10**, followed by column chromatography (SiO_2, using CH_2Cl_2/CH_3OH, 99:1 *v*/*v*, as eluent), afforded the triazole-linked bis-copper–[3]catenane **11** bearing different peripheral functional groups (red solid, yield 70%). The ^{1}H NMR spectrum of the isolated product is quite similar to that of the analogous metalated **10**. However, the MALDI-TOF analysis confirmed the postulated *nonsymmetric* metalated [3]catenane **11** with peripheral carboxy and carboxymethyl substituents.[9–11]

Demetalation using saturated aqueous KCN afforded quantitatively the *nonsymmetric* functionalized [3]catenane **13**, as a yellow solid. The MALDI-TOF spectrum (Figure 3) clearly supports the assigned structure **13**. The mass spectrum of **13** displays a peak at *m*/*z* 2890, which corresponds to [3]catenane **13** $[M+H]^+$, and four additional fragments: two peaks at 2144 $[M-746+H]^+$ and 2130 $[M-760+H]^+$, correspond to the [2]catenane fragments formed by the large central macrocycle and a smaller macrocycle bearing peripheral carboxymethyl or carboxy groups, respectively, while peaks at *m*/*z* 761 and 747 correspond to the two protonated macrocycles.

The modular and high yield synthetic strategy presented in this paper establishes an efficient and straightforward way to prepare functionalized [3]catenanes. Thanks to its

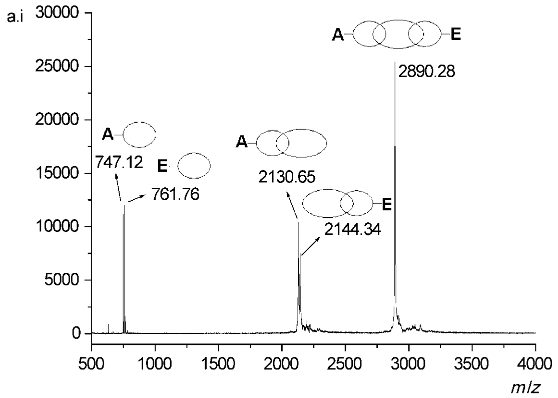


Figure 3. MALDI-TOF mass-spectrum of triazole-linked Cu-free non-symmetric acid-ester functionalized [3]catenane **13**. A = carboxyl group and E = carbomethoxy ester group.[9]

mild conditions, this methodology seems to be well adapted to the synthesis of large interlocked structures, whose precursors are relatively unstable or are sensitive to the final macrocyclization "click" reaction. The possibility of introducing different peripheral functional groups into the [3]catenane structures allows the preparation of structurally elaborated materials, such as nanoscale interlocked donor-acceptor systems. For example, we are currently converting [3]catenanes **11** and **13** into porphyrin–fullerene functionalized [3]catenanes for study of long-range photoinduced electron transfer reactions.[13] The easy access to such structures will facilitate photochemical and photophysical studies of even more extended interlocked electron donor-acceptor systems and other interesting concatenated materials.[14]

Experimental Section

Synthesis of 11: In flask A,[9] carboxymethyl-macrocycle **5** (0.047 g, 0.0618 mmol) was dissolved in degassed CH_2Cl_2/CH_3CN 7:3 (1 mL), to which $[Cu(CH_3CN)_4PF_6]$ (0.023 g, 0.0618 mmol) was added under N_2 at RT. In flask B, carboxy-macrocycle **6** (0.046 g, 0.0618 mmol) was dissolved in degassed CH_2Cl_2/CH_3CN 7:3 (1 mL), to which $[Cu(CH_3CN)_4PF_6]$ (0.023 g, 0.0618 mmol) was added under N_2 at RT. Both dark orange solutions were stirred for 30 min at RT. The azidophenanthroline ligand **3** (0.042 g, 0.0618 mmol) was then added to flask A, while the alkynylphenanthroline ligand **4** (0.044 g, 0.0618 mmol) was added to flask B. Both deep red solutions were stirred at RT for 3 h. Meanwhile, in the reaction flask C, CuI (0.024 g, 0.123 mmol), SA (0.195 g, 0.988 mmol) and SBP (0.146 g, 0.247 mmol) were dissolved in degassed H_2O/EtOH 1:1 (20 mL). The pink suspension was heated at reflux for 5 min and then cooled to RT. The deep red solutions in the flasks A and B were diluted to degassed CH_2Cl_2 (10 mL) and then added by cannula to flask C. Finally, DBU (0.146 g, 0.247 mmol) was added and the red mixture was stirred under N_2 for 12 h at RT. The crude mixture was neutralized by addition of 10% aqueous HCl (10 mL) and extracted with CH_2Cl_2 (3×50 mL). The organic phase was washed with water (2×100 mL) and stirred for 2 h with a saturated MeOH solution of KPF_6 to effect the anion exchange. The solvents were evaporated, the remaining insoluble white solid was extracted with CH_2Cl_2 (3×100 mL) and the solution was filtered through paper. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2) using CH_2Cl_2/CH_3OH 99:1 as eluent, affording metalated **11** as a red solid in 65–70% yield. Demetalation was carried out by vigorously stirring a solution of the copper complex (0.100 g, 0.033 mmol) **11** in CH_2Cl_2 (10 mL) with a large excess of KCN (~0.200 g, 3.0 mmol) in water (10 mL) at RT for 3 h. The reddish-brown color disappeared. The organic phase was separated, washed with water (5×10 mL), dried over Na_2SO_4, filtered through paper and finally concentrated to dryness. Final purification was achieved by flash chromatography (SiO_2) using CH_2Cl_2/CH_3OH 99:1, quantitatively affording **13** as a yellow solid.

Synthesis of 10: A similar procedure was used as in the case of **11**.[9]

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Keywords: click chemistry • catenanes • cyclization • supramolecular chemistry • template synthesis

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[13] Preliminary results have showed that the introduction of an amine Zn–porphyrin moiety into the acid group of the [3]catenane **11** is possible using classical coupling reagents. The synthesis of the complete porphyrin–fullerene [3]catenane dyad will be reported in a future paper.

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