

# A catenane consisting of a large ring threaded through both cyclic units of a handcuff-like compound†

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The template effect of copper(I) allowed the preparation of a new catenane constructed around a bis-macrocyclic unit; a double ring-closing metathesis reaction afforded the central ring which is threaded through both rings of the bis-macrocycle.

The synthesis of new catenanes, rotaxanes and knots continues to attract much attention, either for the synthetic challenge that the preparation of such compounds represents<sup>1</sup> or in relation to their novel properties (electron transfer, controlled motions, mechanical properties, *etc.*). Catenanes containing two rings connected by a chemical bond are not common. Examples of such systems are schematically represented in Fig. 1.

A molecular “pretzelane” with a topology such as (A) has been prepared by Vögtle and coworkers.<sup>2</sup> (A) has a planar molecular graph, which does not prevent it from being a chemically attractive compound even if its topology is trivial.<sup>3</sup> (B) is topologically non-trivial since it is a [2]catenane dimer. Such a molecule was made long ago by Stoddart *et al.*<sup>4</sup> (C) is a [2]catenane polymer, obviously with a non-trivial topology, and a few examples of such polymers and oligomers have been reported in the literature.<sup>5,6</sup>

As far as we are aware, topology (D) represented in Fig. 1 has been described only once by the group of Becher in 1996.<sup>7</sup> It consists of two connected rings, similar to (A) and (B) of the figure. Both rings are now threaded through the same large ring, contrary to (B). Compound (D) can also be regarded as a linear [3]catenane,

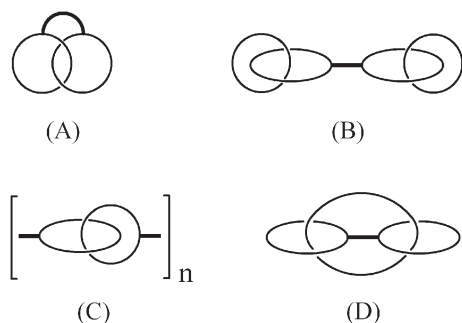


Fig. 1 A few catenanes containing covalently linked rings. (D) is the target catenane.

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† Electronic supplementary information (ESI) available: A numbered figure of the molecules **3**, **5**<sup>2+</sup> and **1**<sup>2+</sup> for the <sup>1</sup>H NMR assignment. See <http://dx.doi.org/10.1039/b509745b>

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for which the two peripheral rings have been linked by a chemical bond.

The synthetic strategy leading to catenane (D) is indicated in Fig. 2. It starts with the preparation of a bis-macrocycle, with coordinating fragments located at the right positions. A transition metal-directed threading process will lead to the desired precursor and a cyclisation reaction will complete the synthesis. Essential to the success of the strategy described here is the back-to-back arrangement of the chelates in the bis-ring. In addition, the mutual arrangement of the two threaded fragments in the precursor favours the formation of the large central ring.

The chemical structure of the precursors and the various reactions leading to the bis-macrocyclic catenane **1**<sup>2+</sup> are depicted in Fig. 3.

The macrocyclic dione **2** was obtained in 9 steps from 1,10-phenanthroline (phen) in 10% overall yield.<sup>8</sup> By homocondensation of **2** in melted ammonium acetate (180 °C),<sup>9</sup> the bis-macrocycle **3** was obtained as an ochre solid in 70–80% yield after work-up and chromatography. It was characterised<sup>10</sup> by <sup>1</sup>H NMR and ES-mass spectrometry (ES-MS). The subsequent threading reaction took advantage of the template effect of copper(I) and led to the quantitative formation of the precatenane **5**<sup>2+</sup>.<sup>10</sup> It was achieved by mixing first the bis-macrocycle **3** with [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) under argon, and subsequent addition of a stoichiometric amount of the di-butenylic derivative **4**. Cyclisation of the precursor complex by ring-closing metathesis (RCM)<sup>11</sup> of its terminal olefins was performed in dichloromethane at room temperature in the presence of Grubbs' first generation catalyst (0.5 equiv.). The double ring-closure could be easily monitored by

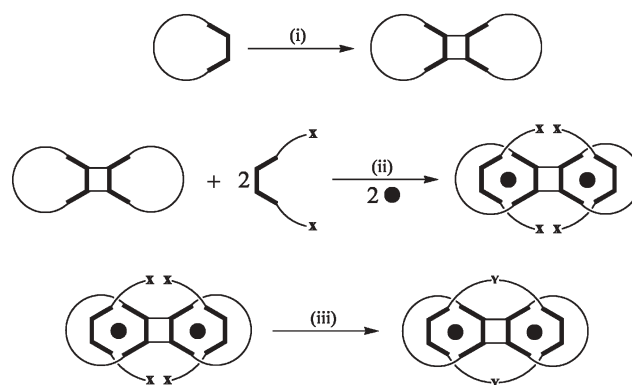


Fig. 2 Synthetic strategy leading to the target compound. (i) Formation of a bis-macrocycle, (ii) transition metal-directed threading step, and (iii) cyclisation reaction. The terminal functions X react with each other to afford the connectors Y.

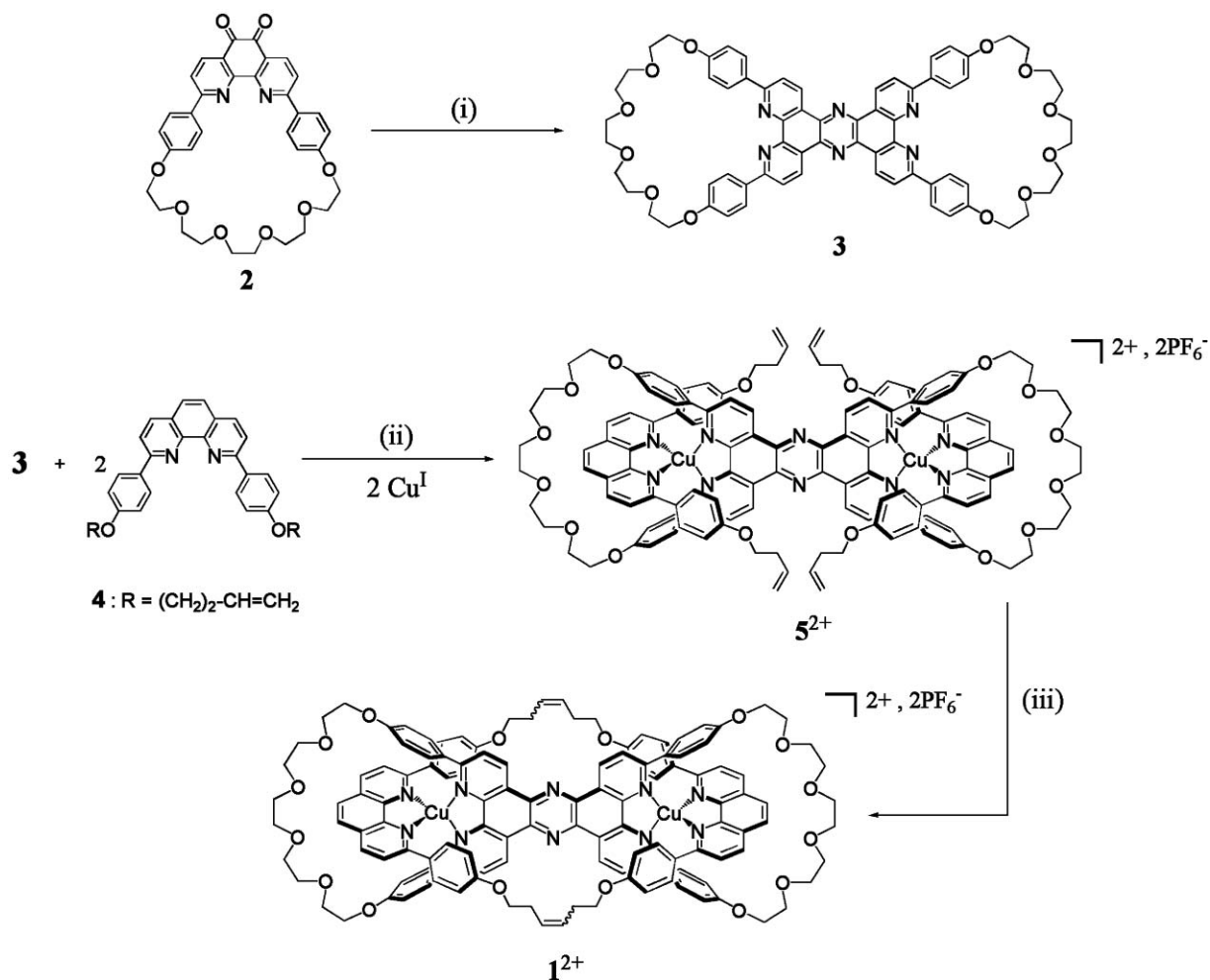


Fig. 3 Synthesis of  $1^{2+}$ . (i)  $\text{NH}_4\text{OAc}$ ,  $180^\circ\text{C}$ , 2 h; (ii)  $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$ ,  $\text{CH}_2\text{Cl}_2/\text{MeCN}$  2 : 1, 5 d; (iii)  $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$ ,  $\text{CH}_2\text{Cl}_2$ , 10 d.

$^1\text{H}$  NMR and was complete after 10 days. The crude product was purified by column chromatography after anion exchange by treatment with  $\text{KPF}_6$ , affording  $1^{2+}$  as a brown solid in 80% yield.<sup>10</sup>

The resulting molecule consists of a 44-membered ring which is threaded through both 30-membered rings of the bis-macrocycle **3**. The high-resolution ES-MS spectrum shows one peak at  $m/z$  1086.342 corresponding to  $[1]^{2+}$  (calcd 1086.342). The interlocked nature of  $1^{2+}$  is unambiguously supported by 2D-ROESY NMR. The  $^1\text{H}$  NMR spectrum clearly indicates a pseudo  $D_2$ -symmetry and is very similar to that of the open form of the precursor  $5^{2+}$ , except that there are modifications of the olefinic signals and broadening of the aromatic ones. This splitting is assigned to the three possible isomers *E-E*, *E-Z* and *Z-Z*, of the catenane that are formed during the RCM reaction.

$1^{2+}$  is a dicopper complex with phen-type ligands; these substituted derivatives lead to entwined complexes in which the metals are in a tetrahedral environment and thus strongly stabilise  $\text{Cu}(\text{I})$ . The electronic properties of the catenane are in perfect agreement with its structure. Relatively intense MLCT bands are observed in the visible ( $\lambda_{\text{max}} \sim 411 \text{ nm}$ ,  $\epsilon \sim 4300 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), but no significant intervalence bands are noticed. Cyclic voltammetry shows that the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple has a redox potential  $E^0 = 0.65 \text{ V}$  ( $\Delta E_p \sim 92 \text{ mV}$ ) vs. SCE in acetonitrile, in accordance

with previously reported values for similar systems.<sup>12</sup> Each reversible oxidation occurs at the same potential confirming the absence of strong interaction between the two metal centres.

In conclusion, the use of a bis-macrocylic unit containing a back-to-back bis-phen central motif appears particularly promising for making new topologies. It will also be utilized to elaborate and study controlled two-dimensional dynamic systems.

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- 10 Characterisations of the new compounds. **3**:  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2/\text{F}_3\text{CCO}_2\text{D}$ , 300 MHz):  $\delta$  = 10.19 (d, 4H,  $^3J$  = 8.4 Hz;  $\text{H}_{4,7}$ ), 8.72 (d, 4H,  $^3J$  = 8.4 Hz;  $\text{H}_{3,8}$ ), 8.28 (d, 8H,  $^3J$  = 8.7 Hz;  $\text{H}_o$ ), 7.36 (d, 8H,  $^3J$  = 8.6 Hz;  $\text{H}_m$ ), 4.44 (t, 8H,  $^3J$  = 5.1 Hz;  $\text{H}_z$ ), 4.05 (t, 8H,  $^3J$  = 5.1 Hz;  $\text{H}_p$ ), 3.95–3.70 (m, 24H;  $\text{H}_y + \text{H}_8 + \text{H}_c$ ) ppm. ES-MS:  $m/z$  1157.4653 [ $\mathbf{3} + \text{H}$ ] $^+$  (calcd 1157.4661 for  $\text{C}_{68}\text{H}_{65}\text{N}_6\text{O}_{12}$ );  $5^{2+}$ :  $^1\text{H-NMR}$  ( $\text{d}^6$ -acetone, 300 MHz):  $\delta$  = 10.25 (d, 4H,  $^3J$  = 8.4 Hz;  $\text{H}_{4,7}$ ), 8.87 (d, 4H,  $^3J$  = 8.4 Hz;  $\text{H}_{4,7}$ ), 8.40 (s, 4H;  $\text{H}_{5,6}$ ), 8.41 (d, 4H,  $^3J$  = 8.4 Hz;  $\text{H}_{3,8}$ ), 8.12 (d, 4H,  $^3J$  = 8.4 Hz;  $\text{H}_{3,8}$ ), 7.74 (m, 8H,  $^3J$  = 8.7 Hz;  $\text{H}_o$ ), 7.59 (m, 8H,

- $^3J$  = 8.6 Hz;  $\text{H}_o$ ), 6.37 (m, 8H,  $^3J$  = 8.7 Hz;  $\text{H}_m$ ), 6.20 (m, 8H,  $^3J$  = 8.7 Hz;  $\text{H}_m$ ), 5.68–5.54 (m, 4H,  $^3J$  = 5.0, 10.2 and 17.3 Hz;  $\text{H}_c$ ), 4.93–4.78 (m, 8H,  $^3J$  = 10.2 and 17.3 Hz;  $\text{H}_d + \text{H}_e$ ), 3.88 (s, 8H;  $\text{H}_c$ ), 3.78–3.69 (m, 16H;  $\text{H}_8 + \text{H}_a$ ), 3.68–3.61 (m, 16H;  $\text{H}_8 + \text{H}_a$ ), 3.59–3.55 (m, 8H;  $\text{H}_z$ ), 2.41–2.34 (m, 8H;  $\text{H}_b$ ) ppm. ES-MS:  $m/z$  1114.3710 [ $\mathbf{5}^{2+}$ ] (calcd 1114.3746 for  $\text{C}_{132}\text{H}_{120}\text{N}_{10}\text{O}_{16}\text{Cu}_2$ );  $1^{2+}$ :  $^1\text{H-NMR}$  ( $\text{d}^6$ -acetone, 500 MHz, COSY-ROESY):  $\delta$  = 10.34–10.10 (m, 4H;  $\text{H}_{4,7}$ ), 8.91–8.80 (m, 4H;  $\text{H}_{4,7}$ ), 8.37–8.31 (m, 4H;  $\text{H}_{5,6}$ ), 8.16–8.07 (m, 4H;  $\text{H}_{3,8}$ ), 7.75–7.66 (m, 4H;  $\text{H}_{3,8}$ ), 7.99–7.76 (m, 8H;  $\text{H}_o$ ), 7.75–7.66 (m, 8H;  $\text{H}_o$ ), 6.55–6.35 (m, 8H;  $\text{H}_m$ ), 6.20–6.14 (m, 8H;  $\text{H}_m$ ), 5.74–5.16 (m, 4H;  $\text{H}_c$ ), 3.89 (s, 8H;  $\text{H}_c$ ), 3.85–3.70 (m, 16H;  $\text{H}_8 + \text{H}_a$ ), 3.68–3.65 (m, 8H;  $\text{H}_y$ ), 3.60–3.46 (m, 16H;  $\text{H}_z + \text{H}_p$ ), 2.40–2.18 (m, 8H;  $\text{H}_b$ ) ppm. ES-MS:  $m/z$  1086.3420 [ $\mathbf{1}^{2+}$ ] (calcd 1086.3425 for  $\text{C}_{128}\text{H}_{112}\text{N}_{10}\text{O}_{16}\text{Cu}_2$ ).
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