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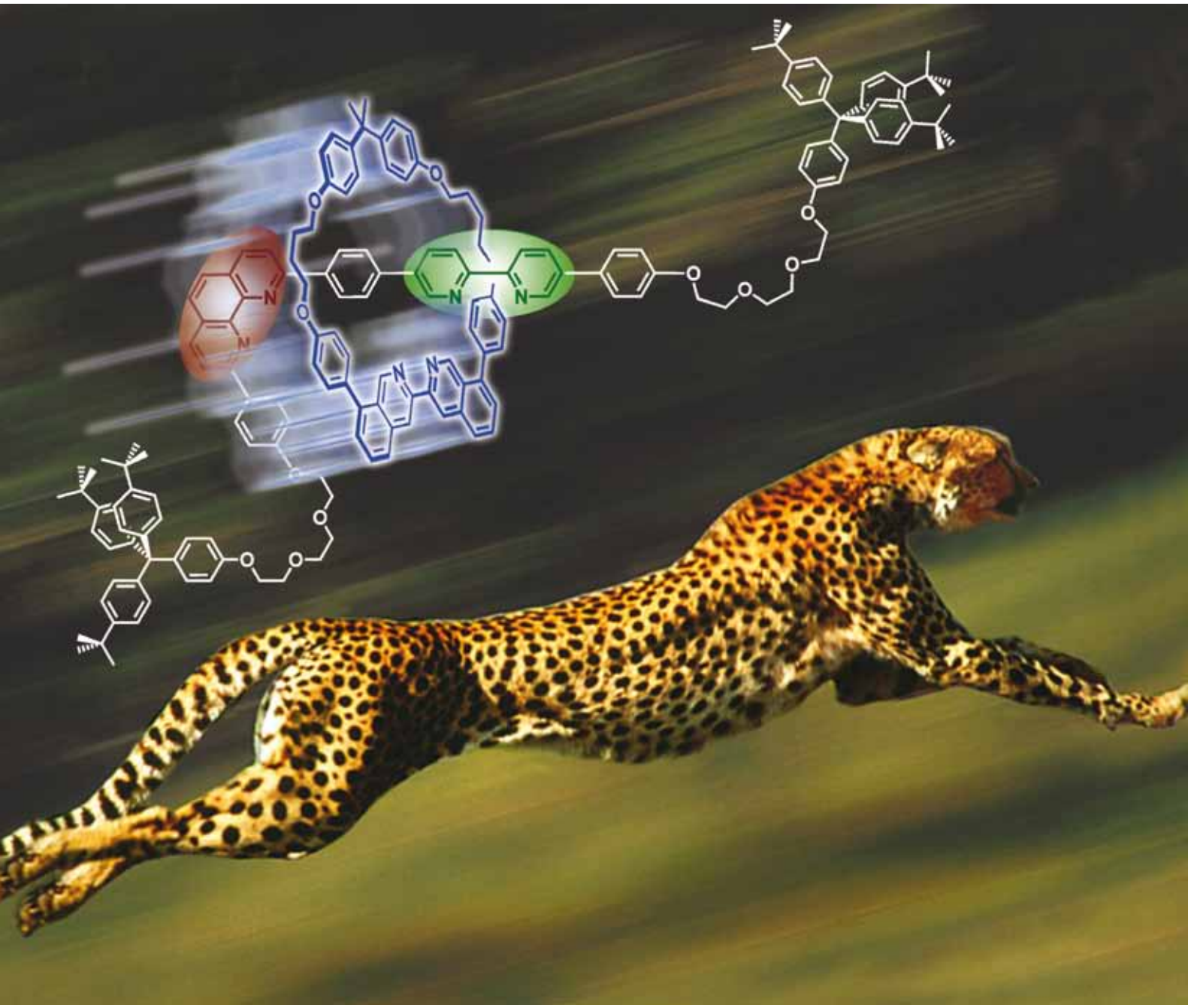

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PAPER

Jean-Pierre Sauvage *et al.*
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A copper-based shuttling [2]rotaxane with two bidentate chelates in the axis: steric control of the motion†

Jean-Paul Collin, Fabien Durola, Jacques Lux and Jean-Pierre Sauvage*

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Contrary to most of the other molecular machines based on copper-complexed catenanes or rotaxanes made and investigated in Strasbourg, the present report is dealing with a molecular shuttle for which the copper centre is complexed to two bidentate chelates, regardless of the state of the shuttle. In other words, the axis contains a sterically hindering bidentate chelate, namely a 2,9-diphenyl-1,10-phenanthroline (dpp) derivative, and another but less hindering bidentate chelate, 2,2′-bipyridine (bipy). The synthesis of the [2]rotaxane involves 15 individual chemical steps, excluding the preparation of the macrocyclic component of the [2]rotaxane. The threaded macrocycle is a 39-membered ring which incorporates an endocyclic but non sterically hindering chelate of the 8,8′-diphenyl-3,3′-biisoquinoline family (dpbiiq). The electrochemically-induced gliding motion of the copper-complexed ring from the dpp "station" to the bipy "station" and *vice versa* is fast on the cyclic voltammetry timescale (milliseconds). The copper(I) state is preferably located on the dpp unit whereas, by oxidising the copper(I) centre to its divalent state, the translation motion takes place to afford the thermodynamically most stable state now involving the bipy chelate.

Results and discussion

In the field of molecular machines,[1–7] catenanes and rotaxanes constitute an important class of such compounds.[8–15] Among them, [2]rotaxanes behaving as molecular shuttles are at the same type the prototypes of these controlled dynamic systems[16–24] and essential components in the fabrication of molecular electronic memories.[25–28] A wide family of molecular machines based on copper-complexed catenanes and rotaxanes has been synthesised and studied in our group since the report of an electrochemically "swinging" catenane.[29–34] Most of the copper-based dynamic catenanes or rotaxanes investigated were relatively slow to undergo electrochemically-driven rearrangement. A real breakthrough came with the use of the endocyclic but non sterically hindering dpbiiq chelate and its incorporation in the mobile ring.[35,36] The gliding motions of the copper-complexed ring in a new two-station shuttle based on this ligand were shown to be 10^4 to 10^5 times faster than when the sterically hindering dpp chelate was used as ring-incorporated chelate instead of dpbiiq.[35,36] As for the previous molecular copper-complexed machines described by our group, the two stable states of the systems were a 4-coordinate copper(I) complex (Cu_4^+) and a 5-coordinate divalent copper complex (Cu_5^{2+}). In order to verify whether the use of both a bidentate ligand and a tridentate one in the axis was important, we made a new molecular shuttle whose threads contained two bidentate ligands: a dpp unit and a bipy fragment. In this case, both states should be 4-coordinate, at least as far as the nitrogen atoms of the chelates are concerned, knowing that solvent molecules or counter ions could be coordinated to the copper. The two forms of the [2]rotaxane are represented in Fig. 1.

The difference between the two forms of the shuttle holds mainly to the steric properties of the axis-contained chelates: dpp is highly shielding and prevents the copper centre from strongly interacting with additional ligands whereas bipy is a non hindering chelate. Another important difference with the previous shuttling [2]rotaxanes is of thermodynamic origin. When the two stable states are a 4-coordinate complex similar to $[Cu(dpbiiq)(dpp)]^+$ for the monovalent copper and a 5-coordinate compound such as $[Cu(dpbiiq)(terpy)]^{2+}$ for Cu(II), the relatively large difference between the Cu(II)/Cu(I) redox potentials of the two forms (~0.46 V and ~0.07 V *vs.* SCE in CH_3CN, respectively) originates in a reasonably high driving force ($\Delta G^\circ \sim 0.39$ eV) for the motion between the two forms once the electrochemical perturbation has been introduced. For a molecular shuttle with two bidentate ligands in the axis, the corresponding driving force is expected to be more limited. In spite of this seemingly serious drawback, the present report demonstrates that a shuttle based on two 4-coordinate stable forms can be set in motion efficiently and undergo fast motion. The general principle of the shuttling motion is depicted in a schematic fashion in Fig. 2. Each chelate is represented by a different symbol related to its steric properties.

Synthesis of the [2]rotaxane $\mathbf{1}_{(dpp)}^+$ and of reference complexes containing $[Cu(dpbiiq)(dpp)]^+$ or $[Cu(dpbiiq)(bipy)]^+$ cores

[2]Rotaxane $\mathbf{1}_{dpp}^+$ was prepared in 15 individual chemical steps, excluding the preparation of the macrocyclic component

Laboratoire de Chimie Organo-Minérale, Institut de Chimie, LC3 UMR 7177 du CNRS, Université de Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France. E-mail: sauvage@chimie.u-strasbg.fr; Fax: (+33) 390-241-368; Web: http://www-chimie.u-strasbg.fr/~lcom/

† Electronic supplementary information (ESI) available: Mass spectra of $[\mathbf{1}_{dpp}^+][PF_6^-]$, $[\mathbf{18}^+][PF_6^-]$ and $[\mathbf{19}^+][PF_6^-]$. See DOI: 10.1039/b9nj00296k

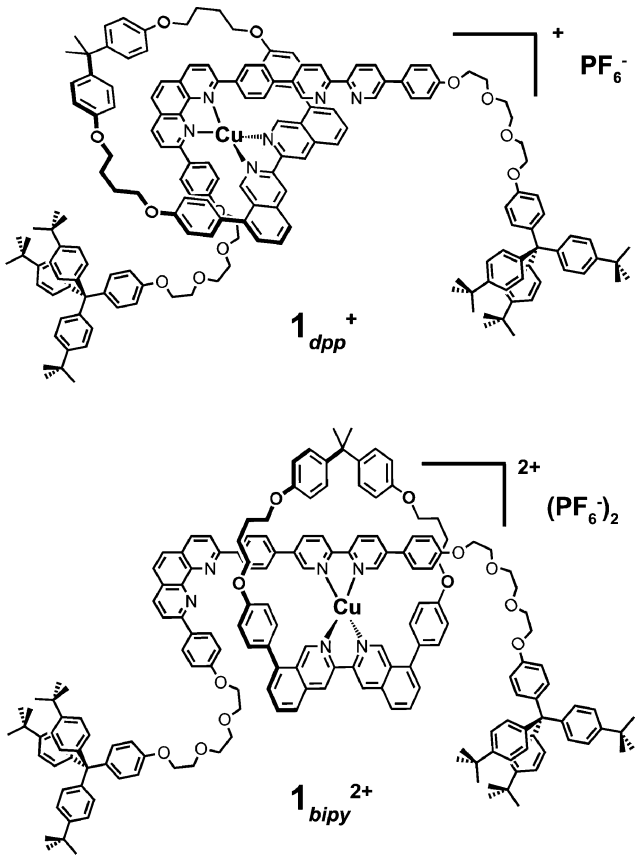


Fig. 1 The two forms of the rotaxane $\mathbf{1}_{\mathbf{dpp}}{}^{+}$ or $\mathbf{1}_{\mathbf{bipy}}{}^{2+}$; the subscripts dpp and bipy indicate the position of the mobile ring on the axis.

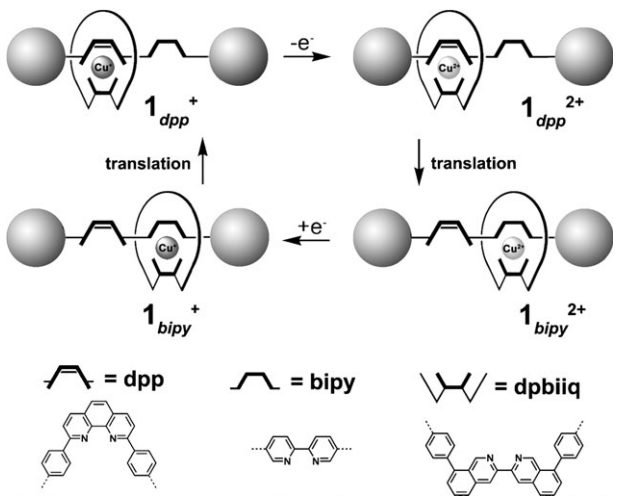


Fig. 2 Principle of the movement of the copper-based molecular shuttle. The structures of the coordinating groups are shown in addition to their schematic representations.

of the [2]rotaxane. This ring has already been described in the literature.[37] The synthesis of the [2]rotaxane $\mathbf{1}_{\mathbf{dpp}}{}^{+}$ consists in (i) the synthesis of a singly-stoppered axis, (ii) the copper(I)-driven threading process of this axis through the macrocycle (iii) and the stoppering reaction leading to [2]rotaxane $\mathbf{1}_{\mathbf{dpp}}{}^{+}$. The first sequence of reactions is represented in Fig. 3. The threading and stoppering steps are described in Fig. 4.

Synthesis of the axis

The axis **15** is composed of three parts: the stopper-precursor fragment, the dpp unit and the bipy fragment. The synthesis of the axis follows a convergent strategy.

First the stopper with iodo-ended chain **4** is synthesized in two steps from the usual stopper molecule **2**.[38] The first step is a Williamson reaction under classical conditions with 2-(2-(2-chloroethoxy)ethoxy)ethanol (commercially available) to afford compound **3** with 90% yield. The second step consists first in a mesylation reaction with a strict control of temperature in order to activate the alcohol function. A substitution reaction is subsequently performed with an excess of sodium iodide leading to the stopper-precursor **4** with 95% yield. The dpp unit **7** is synthesized in three steps from 1,10-phenanthroline. First, two different functionalisation reactions are performed in the α positions to the nitrogen atoms of the phenanthroline, by using the conditions developed years ago by Dietrich-Buchecker *et al.*[39] For both reactions, a solution of the appropriate aryl lithium compound is first prepared with a strict control of the temperature, by reaction of *tert*-butyl lithium or *n*-butyl lithium with 2-(4-bromophenoxy)-tetra-hydro-2*H*-pyran or 1,4-dibromobenzene, respectively. This solution is then added to a solution of the substrate, namely 1,10-phenanthroline and mono-substituted phenanthroline **5**, respectively, hydrolyzed, and finally re-aromatized with MnO_2. After treatment and purification, the corresponding substituted 1,10-phenanthroline is obtained: 2-(4-(OTHP)phenyl)-phenanthroline **5** (67% yield) and the 2-(4-(OTHP)phenyl)-9-(4-bromophenyl)-phenanthroline **6** (80% yield). The last step is a deprotection of the THP protective group to afford the 2,9-diaryl-1,10-phenanthroline fragment **7** (90% yield). A Williamson reaction is then performed between **4** and difunctionalised phenanthroline **7** under classical conditions to give the bromo-ended singly stoppered fragment **8** (46% yield). The bromide is then transformed into a boronic ester using bis(neopentyl glycolato)diboron and $Pd(dppf)Cl_2$ as catalyst. The boronic ester **9** can not be purified and is used in the next step without further purification. On the other side the boronic acid **10** is synthesized from the 4-(tetrahydro-2*H*-pyran-2-yloxy)bromobenzene to give the aryl lithium compound. Triisopropyl borate is then added and the boronate compound obtained in this way was hydrolysed to give the boronic acid **10** (81% yield). The 5-bromo-2-trimethylstannyl pyridine **11** is made from commercially available 5-bromo-2-iodopyridine with a slight excess of *n*BuLi and by addition of a solution of $ClSnMe_3$ (97% yield). The next step is a Stille coupling reaction between the 5-bromo-2-iodopyridine and its previously made stannyl derivative. 5,5′-dibromo-2,2′-bipyridine **12** is obtained with 68% yield. The latter is then reacted with the boronic acid **10** in a Suzuki coupling reaction. This statistical reaction leads to the 5-bromo-5′-(4-(OTHP)phenyl)-2,2′-bipyridine **13** (38% yield). The next step consists in a Suzuki coupling reaction between the asymmetric bipyridine **13** and the boronic ester-ended thread **9** under the same conditions as usual. The OTHP-ended two-station

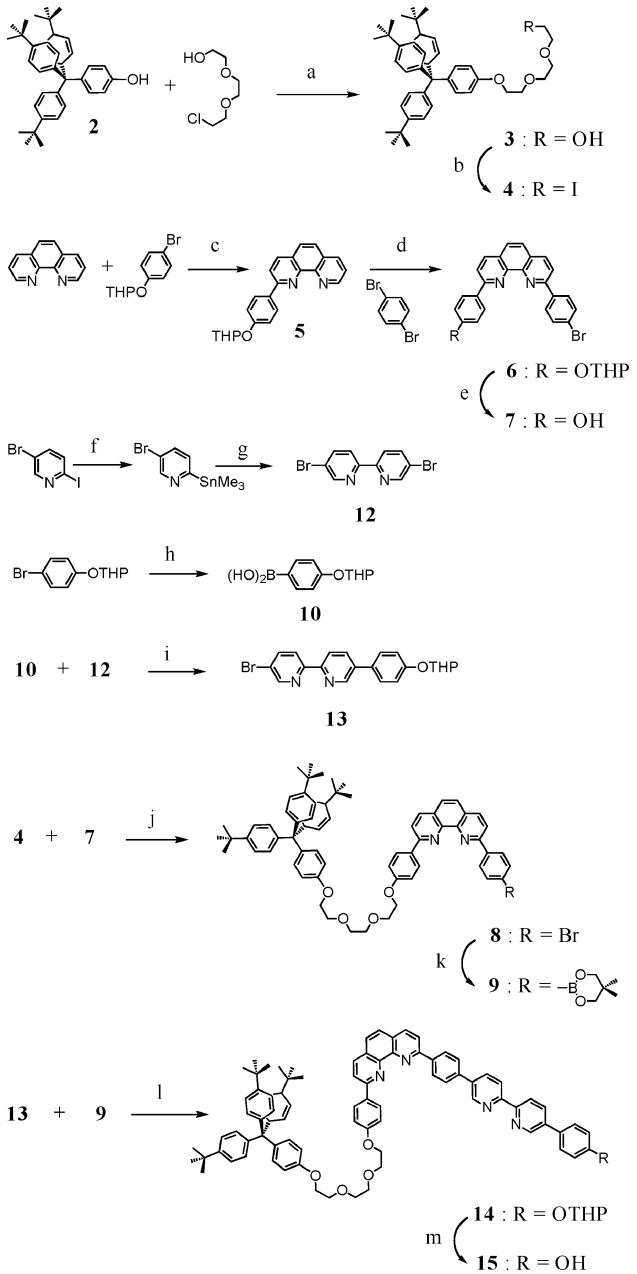


Fig. 3 Synthesis of the mono-stoppered axis. (a) Cs_2CO_3 in DMF, 90 °C, 48 h, 90%. (b) MsCl, NEt_3 in CH_2Cl_2, 0 °C, 4 h; then NaI in Me_2CO, reflux, 16 h, 95%. (c) ^{t}BuLi in THF, −78 °C, 30 min; then 0 °C, 2 h; then MnO_2, 25 °C, 16 h, 67%. (d) BuLi in Et_2O, 0 °C, 3 h; then MnO_2, 25 °C, 16 h, 80%. (e) HCl in MeOH, reflux, 16 h, 90%. (f) *n*BuLi in toluene, −20 °C; then −78 °C, 2 h; then $ClSnMe_3$, −78 °C, 1 h, 97%. (g) 5-Bromo-2-iodopyridine, $Pd(PPh_3)_4$ in toluene, reflux, 20 h, 68%. (h) *n*BuLi in THF, −78 °C, 20 min; then $B(O^iPr)_3$, 0 °C, 1 h; then 0.1 M HCl, 25 °C, 81%. (i) $Pd(PPh_3)_4$, Na_2CO_3 in toluene–H_2O–EtOH, 90 °C, 2.5 h, 38%. (j) Cs_2CO_3 in DMF, 50 °C, 16 h, 46%. (k) $PdCl_2$dppf, bis(neopentyl glycolato)diboron, KOAc in dioxane, 80 °C, 16 h. (l) $Pd(PPh_3)_4$, Na_2CO_3 in toluene–H_2O–EtOH, 90 °C, 16 h, 90%. (m) 37% HCl cat., CH_2Cl_2, MeOH, reflux, 4 h.

thread **14** was isolated with a 90% yield. The last step is the deprotection of the THP protective group in presence of a catalytic amount of HCl. The desired OH-ended

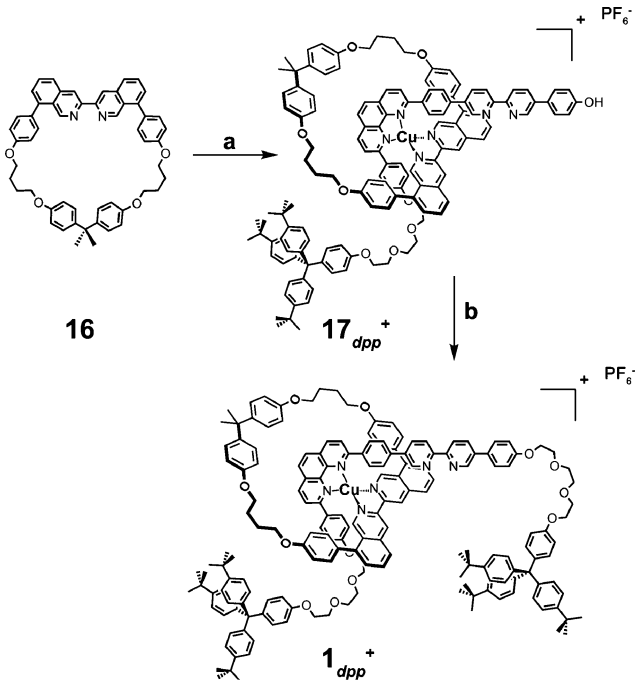


Fig. 4 Synthesis of rotaxane $\mathbf{1_{dpp}}^+$. (a) $[Cu(MeCN)_4][PF_6]$ in $CHCl_3$–MeCN, 25 °C, 30 min; then **15** in $CHCl_3$, 25 °C, 16 h. (b) Stopper precursor **4**, Cs_2CO_3, sodium ascorbate in DMF, 50 °C, 20 h, 14%.

compound **15** is obtained as a crude product. It is subsequently used without further purification because of its low solubility.

Synthesis of the rotaxane

The copper(I)-based molecular shuttle $\mathbf{1_{dpp}}^+$ is synthesized from the two-station thread **15** and the chelating ring **16**.[37] The synthesis follows a threading-and-stoppering strategy. First the macrocycle **16** is dissolved in chloroform and a solution of $[Cu(MeCN)_4][PF_6]$ in acetonitrile is added to form a bright orange complex consisting of one ring and one metal centre. A solution of the mono-stoppered thread **15** in chloroform is then added to give a brown–red complex corresponding to the pseudo-rotaxane $\mathbf{17_{dpp}}^+$. The final step is a stoppering reaction under classical Williamson conditions, with the stopper precursor **4**. After purification, the desired rotaxane $\mathbf{[1_{dpp}}^+\mathbf{][PF_6}^-\mathbf{]}$ is obtained with a low yield of 14%, which can be explained by the relative sensitivity of copper(I)-based complexes to basic conditions.

In the case of rotaxane $\mathbf{1_{dpp}}^+$ the dpp and the bipyridine stations could be in competition but the most thermodynamically stable complex is clearly the one involving the dpp chelate, as demonstrated both by ^{1}H NMR spectroscopy and cyclic voltammetry (*vide infra*). On the spectrum of $\mathbf{1_{dpp}}^+$ (Fig. 5), all the protons localised around the dpp of the thread and around the coordination site of the macrocycle are highly upfield-shifted. This can easily be understood by considering the strong ring-current effect created by the 3,3′-biisoquinoline (biiq) nucleus. Since the phenyl rings borne by the 1,10-phenanthroline unit are located above and below the biiq plane,

they are strongly exposed to this effect and the corresponding protons m, o, m′ and o′ are thus strongly shielded. To a lesser extent, the same holds true for the H atoms of the dpbiiq unit, and especially bi1, which are now in the shielding region of the 1,10-phenanthroline nucleus. On the other hand, the protons bp5 and bp6 which are distant from the coordination site of the dpp unit are not shifted and bp3 and bp4 which are closer are slightly upfield-shifted. This also confirms that the macrocycle is coordinated to the dpp station and not the bipy station.

Synthesis of the reference complexes

Following the synthesis of [2]rotaxane $\mathbf{1_{dpp}}^{+}$, a detailed electrochemical study was undertaken. In order to understand the behaviour of the shuttle, it was necessary to prepare simple model complexes (Fig. 6) whose electrochemical properties were assumed to be very close to those of either of the two forms of the [2]rotaxane, $\mathbf{1_{dpp}}^{+}$ and $\mathbf{1_{bipy}}^{+}$.

The experimental procedures for making the two reference complexes are identical. First the 39-membered macrocycle **16** is dissolved in dichloromethane, and a solution of $[Cu(MeCN)_4][PF_6]$ in acetonitrile is added. A bright orange solution corresponding to a complex composed of one ring and one metal centre was rapidly obtained. The reaction is stirred for 30 min and a solution of the appropriate ligand: dap (2,9-dianisylphenanthroline)[40] or dabipy (4,4′-dianisyl-2,2′-bipyridine) is then added to furnish, after evaporation of the solvents the corresponding complex (namely $\mathbf{[18^+][PF_6^-]}$ and $\mathbf{[19^+][PF_6^-]}$) quantitatively.

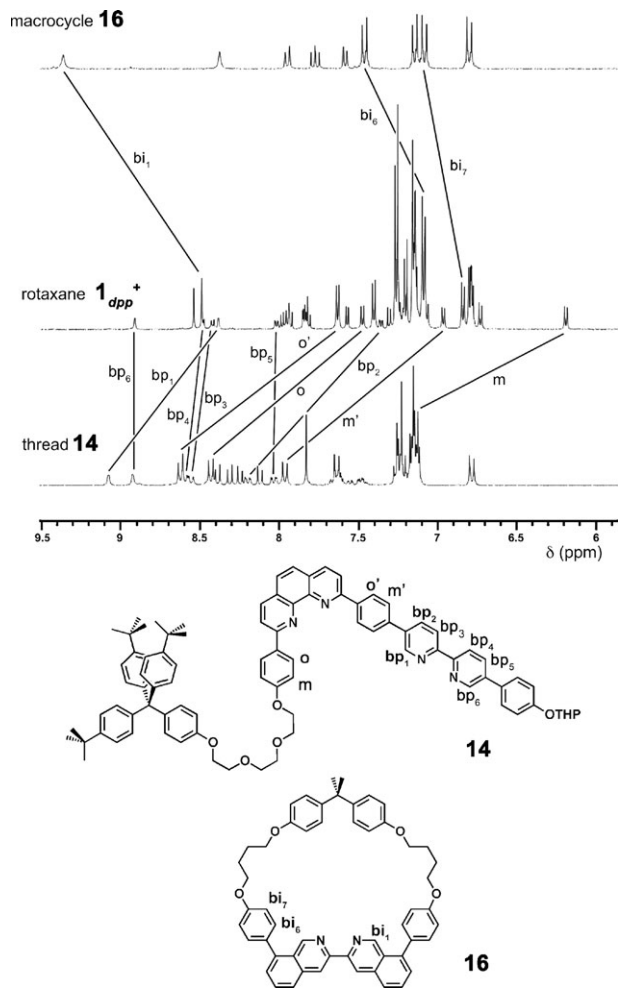


Fig. 5 ^{1}H NMR spectra of $\mathbf{1}^+$ and its organic precursors **14** and **16**.

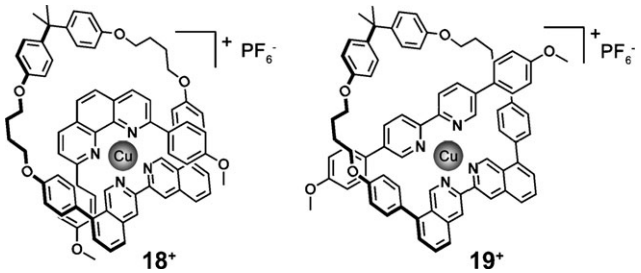


Fig. 6 Reference complexes $\mathbf{[18^+][PF_6^-]}$, $\mathbf{[19^+][PF_6^-]}$.

Electrochemical study

According to previous works on similar shuttling and pirouetting systems[29,30,32,36] the cyclic voltammetry method is well adapted to study square scheme involving electron transfers and chemical reactions as displayed in Fig. 2. The cyclic voltammograms (CV) of $\mathbf{1_{dpp}}^{+}$ and of the references complexes $\mathbf{18}^+$ and $\mathbf{19}^+$ have been obtained in CH_2Cl_2–CH_3CN mixture (1 : 9) with 0.1 M Bu_4NPF_6 on platinum electrodes and are shown on Fig. 7. An Ag wire was used as pseudo-reference electrode. Since the potential of the redox couple ferricinium$^+$/ferrocene was in the range of the various examined copper redox couples, we choose to add the complex $Os(tterpy)_2(PF_6)_2$ in the electrochemical cell as internal reference (tterpy = 4′-*p*-tolyl-2,2′,6′,2″-terpyridine). All the potentials are reported *versus* SCE (E^0 ($Os^{III/II}$) = 0.9 V *vs*. SCE in this electrolyte).

The CV of the reference complex $\mathbf{19}^+$ displays a quasi-reversible redox couple at 0.18 V (ΔE_p = 170 mV). This low redox potential reflects the large stabilization of the Cu(II) oxidation state. Such a stabilization is the consequence of the coordination of the Cu(II) cation by two 2,2′-bipyridine type ligands allowing a square planar or an octahedral geometry. The CV of the complex $\mathbf{18}^+$ shows also a quasi-reversible redox couple at 0.34 V (ΔE_p = 160 mV). An additional reversible redox couple at 0.63 V (ΔE_p = 100 mV) is assigned without ambiguity[29] to the complex $Cu(dap)_2^+$ which is formed, because its very high stability, during the synthesis of $\mathbf{18}^+$. The CV of $\mathbf{1_{dpp}}^{+}$, performed at a scan rate of 100 mV s^{-1}, displays a partially reversible redox couple at 0.41 V (ΔE_p = 100 mV) and an irreversible redox couple characterized by a peak potential at 0.16 V. These values are in accordance with the values of the redox potentials for $\mathbf{18}^+$ and $\mathbf{19}^+$ considering the close similitude between the structural feature of $\mathbf{18}^+$ and $\mathbf{19}^+$ and those of the two forms of the [2]rotaxane ($\mathbf{1_{dpp}}^{+}$ and $\mathbf{1_{bipy}}^{2+}$, Fig. 1). These experiments suggest that the general pattern described for copper-containing catenanes and rotaxanes[32] is also operative in this case, *i.e.* the unstable four-coordinate copper(II) complex ($\mathbf{1_{bipy}}^{2+}$) moves much faster than the other unstable complex ($\mathbf{1_{dpp}}^{2+}$)

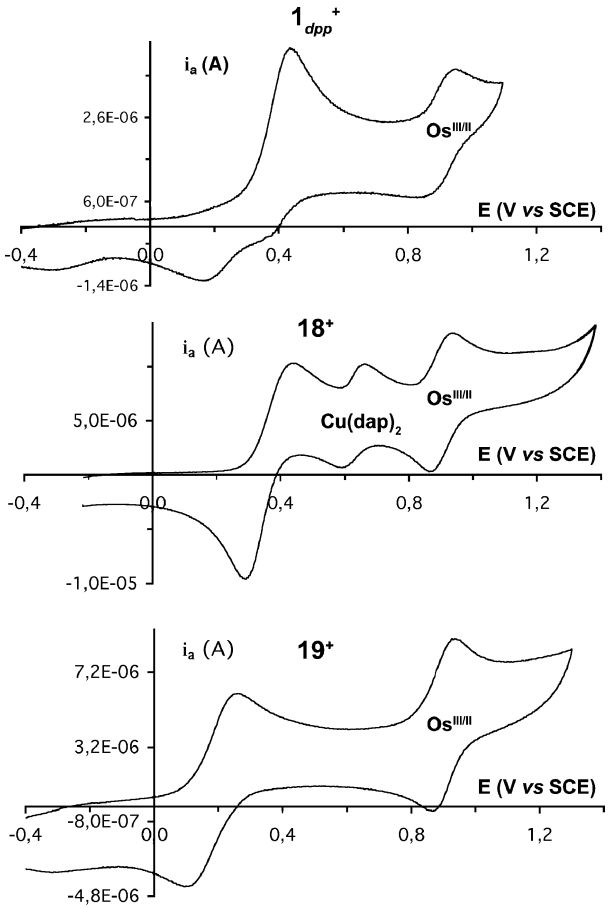


Fig. 7 Cyclic voltammograms of complexes $\mathbf{1_{dpp}}^{+}$, $\mathbf{18}^{+}$ and $\mathbf{19}^{+}$ recorded on a Pt working electrode at 100 mV s^{-1} in CH_2Cl_2–CH_3CN (1 : 9) with 0.1M Bu_4NPF_6 and the complex $Os(tterpy)_2(PF_6)_2$ as internal reference (E^0 ($Os^{III/II}$) = 0.9 V *vs.* SCE).

(See Fig. 2). By varying the potential scan rate, this behaviour can be also illustrated.

Fig. 8 shows the cyclic voltammograms of $\mathbf{1_{dpp}}^{+}$ recorded at various scan rates. As already observed with pirouetting and shuttling rotaxanes,[29,30,32,36] as the scan rate is increased the four-coordinate copper(II/I) redox couple become more reversible. This is especially true for a scan rate of 1600 mV s^{-1}. Conversely, by scanning at lower scan rate, the motion of the macrocycle **16** along the axis becomes more and more discernable, as evidenced by the emergence of an irreversible peak at lower voltage (reduction peak of $\mathbf{1_{bipy}}^{2+}$) and the parallel decreasing intensity of the reduction peak of $\mathbf{1_{dpp}}^{2+}$. The rate constant for the rearrangement of the four-coordinate $\mathbf{1_{dpp}}^{2+}$, *i.e.* the translation of the macrocycle **16** from the dpp site to the bipy site, can be estimated to 0.8 s^{-1} using the procedure reported by Nicholson and Shain.[41,42] The incertitude on the value of the rate constant can be estimated to 10%. An upper value of 50 s^{-1} is deduced for the conversion of the four-coordinate $\mathbf{1_{bipy}}^{+}$ to the four coordinate $\mathbf{1_{dpp}}^{+}$. These two high rate constants demonstrated that the low thermodynamic driving force between the two stable complexes $\mathbf{1_{dpp}}^{+}$ and $\mathbf{1_{bipy}}^{2+}$ (the difference between the redox potentials of $\mathbf{1_{dpp}}^{2+/+}$ and $\mathbf{1_{bipy}}^{2+/+}$ being 0.25 V, which corresponds to a free energy of 0.25 eV) is not a critical disadvantage for a shuttle in which the stations on the axis are two bidentate chelates.

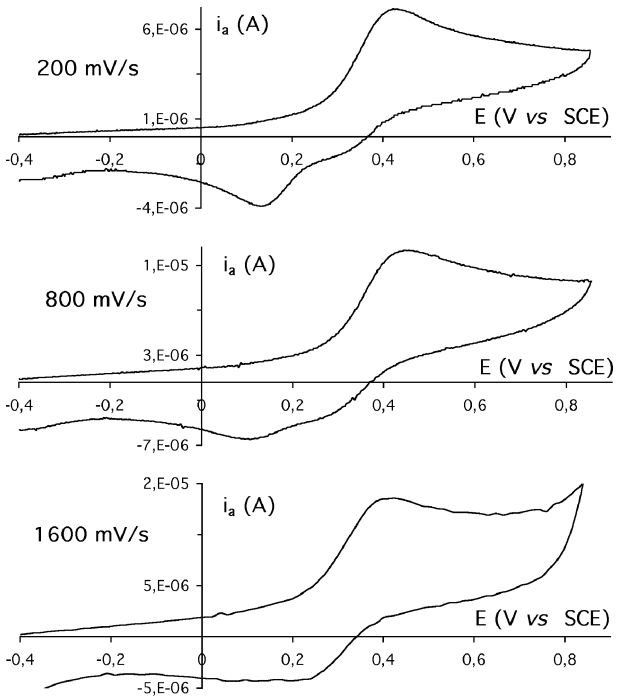


Fig. 8 Cyclic voltammograms of complexes $\mathbf{1_{dpp}}^{+}$, recorded at various scan rate (200, 800, 1600 mV s^{-1}) in CH_2Cl_2 CH_3CN (1 : 9) with 0.1M Bu_4NPF_6.

Conclusions

In conclusion, a new dynamic copper-complexed [2]rotaxane has been prepared which behaves as a molecular shuttle. In spite of the large number of chemical steps involved, the synthesis of the copper(I)-complexed [2]rotaxane is relatively efficient and gives access to several tens of milligrams of the desired compound. The threaded fragments incorporates two different "stations": a highly shielding dpp chelate and a non sterically hindering bipy unit. Contrary to the previously reported electrochemically-driven molecular machines made in our group, which traditionally contained a bidentate and a tridentate station, the denticity of the ring-contained chelates is the same: both stations are bidentate ligands. The copper(I) state is stabilised by the shielding chelate whereas copper(II) is preferably associated to the non hindering bipy chelate. As far as we are aware, this is the first example of bistable transition metal-based molecular machines where the selection between the two stable situations is due to steric factors only. The shuttling motion of the copper-complexed ring between the dpp and bipy stations takes place very cleanly under the action of an electrochemical signal. Remarkably, although the driving force for the electrochemically-induced rearrangement process of the [2]rotaxane is small ($\Delta G^{\circ} = -0.25$ eV), the movement is relatively fast ($k \sim 0.8$ s^{-1} for the $\mathbf{1_{dpp}}^{2+}$ and $k > 50$ s^{-1} for the $\mathbf{1_{bipy}}^{+}$ state). The present systems paves the way to multi-state molecular machines incorporating several different bidentate and tridentate chelates.

Experimental section

General

Solvents were dried in the laboratory by distillation under argon, over the appropriate drying agent: tetrahydrofuran and diethyl ether over sodium and benzophenone, dichloromethane over calcium hydride and triethylamine over potassium hydroxide. Other anhydrous solvents used (DMF and dioxane) are commercially available. Thin-layer chromatography was performed using glass sheets coated with silica or neutral alumina. Column chromatographies were carried out on silica gel (Kieselgel 60, 0.063–0.200 mm or 0.040–0.063 mm, Merck) or alumina (Aluminium oxide 90 standardized or acid, 0.063–0.200 mm, Merck). ^{1}H NMR spectra were acquired on either a Bruker AVANCE 300 (300 MHz) or a Bruker AVANCE 500 (500 MHz) spectrometer. The spectra were referenced to residual proton–solvent references. ^{1}H: [D$_6$]DMSO: 2.50 ppm, CD_2Cl_2: 5.32 ppm, $CDCl_3$: 7.26 ppm. Mass spectra† were obtained by using a Bruker MicroTOF spectrometer (ES-MS) or a Bruker Daltonics autoflex II TOF/TOF spectrometer with dithranol as a matrix (MALDI).

Stopper with hydroxy-ended chain 3

4-(Tris(4-*tert*-butylphenyl)methyl)phenol **2** (2.00 g, 3.96 mmol), caesium carbonate (2.50 g, 7.67 mmol) and 2-(2-(2-chloroethoxy)ethoxy)ethanol (1.2 mL, 1.4 g, 8.26 mmol) were mixed in dry DMF (150 mL) and stirred at 90 °C for 24 h. More 2-(2-(2-chloroethoxy)ethoxy)ethanol (1.2 mL, 1.4 g, 8.26 mmol) was added and the reaction mixture stirred for 24 hours. The solvent was removed and the residue was taken up with CH_2Cl_2–H_2O. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were washed first with brine, then with distilled water. The solvent was removed and the residue purified by chromatography on silica gel by using CH_2Cl_2 as the eluent to give the title compound **3** (white solid, 2.26 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.22 (d, 6H, J = 8.7 Hz), 7.07 (d, 8H, J = 8.7 Hz), 6.77 (d, 2H, J = 9.0 Hz), 4.11 (t, 2H, J = 4.8 Hz), 3.85 (t, 2H, J = 4.8 Hz), 3.71 (m, 6H), 3.61 (t, 2H, J = 4.4 Hz), 2.38 (bs, 1H), 1.30 (s, 27H).

Stopper with iodo-ended chain 4

Compound **3** (2.36 g, 3.7 mmol) was dissolved in dry CH_2Cl_2 (250 mL). The solution was cooled to about −2 °C in an ice–salt mixture, then triethylamine (8 mL) was added. The subsequent addition of methylsulfonyl chloride (0.7 g, 0.5 mL, 6.1 mmol) in CH_2Cl_2 (60 mL) was made dropwise over a period of 1 h, under an argon atmosphere. The solution was then allowed to stir at 0 °C for 3 h. Distilled water (50 mL) was then added dropwise and the mixture was allowed to warm to room temperature. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were washed with distilled water. The solvent was evaporated and the residue purified by chromatography on silica gel by using CH_2Cl_2 as the eluent to give the mesylated compound (white solid, 2.52 g, 95%). It was then dissolved in 200 mL of acetone with sodium iodide (10 g, 67 mmol) and heated to reflux overnight, under an argon atmosphere. A white precipitate of sodium mesylate appeared. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (100 mL) and distilled water (100 mL). The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were washed with distilled water. The solvent was evaporated and the residue purified by chromatography on silica gel by using CH_2Cl_2 as the eluent to give the title compound **4** (white solid, 2.50 g, 95%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.26 (d, 6H, J = 8.7 Hz), 7.14 (d, 6H, J = 8.7 Hz), 7.13 (d, 2H, J = 8.7 Hz), 6.78 (d, 2H, J = 9.0 Hz), 4.08 (t, 2H, J = 4.7 Hz), 3.80 (t, 2H, J = 4.8 Hz), 3.73 (t, 2H, J = 6.6 Hz), 3.65 (m, 6H), 3.25 (t, 2H, J = 6.6 Hz), 1.29 (s, 27H). ES-MS m/z = 769.3035 (calculated 769.3088 for $C_{43}H_{55}IO_3 + Na^+$).

2-(4-(OTHP)phenyl)-phenanthroline 5

2-(4-Lithiophenoxy)-tetrahydro-2*H*-pyran was prepared by interconversion of commercially available 2-(4-bromophenoxy)-tetrahydro-2*H*-pyran with two equivalents of ^{t}BuLi; a THF solution (50 mL) of 2-(4-lithiophenoxy)-tetrahydro-2*H*-pyran (17 mmol) was obtained by slow addition of ^{t}BuLi (35 mmol) to a THF solution (25 mL) of 2-(4-bromophenoxy)-tetrahydro-2*H*-pyran (4,37 g, 17.0 mmol) at −78 °C under argon. After being stirred for 30 min at −78 °C, this solution was slowly added to a degassed THF solution (70 mL) of 1,10-phenanthroline (3.0 g, 16.6 mmol) maintained at −2 °C. The phenanthroline solution turned dark red instantaneously and was stirred under argon at 0 °C for 2 h. Thereafter the reaction was quenched by addition of water (30 mL) and the resulting mixture was evaporated to dryness. The residue thus obtained was taken up in a mixture of CH_2Cl_2 and water and decanted. The aqueous layer was washed and extracted with more CH_2Cl_2. The organic phase was then re-aromatized by successive additions of batches of MnO_2 (25 g). The re-aromatization was monitored by TLC (compound **5** can be recognized by a blue luminescence under UV light). The solution was then dried by addition of $MgSO_4$ and the black MnO_2/$MgSO_4$ slurry was filtered through sintered glass with Celite. After evaporation of the solvent, the crude product was purified by column chromatography over silica gel, with CH_2Cl_2 as the eluent, to give the title compound **5** (pale yellow glassy solid, 3.98 g, 67%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): δ = 9.22 (dd, 1H, J = 4.2, 1.8 Hz), 8.34 (d, 1H, J = 8.4 Hz), 8.32 (dd, 1H, J = 8.1, 1.8 Hz), 8.31 (d, 2H, J = 9.0 Hz), 8.12 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.7 Hz), 7.82 (d, 1H, J = 8.7 Hz), 7.69 (dd, 1H, J = 8.1, 4.2 Hz), 7.26 (d, 2H, J = 9.0 Hz), 5.57 (t, 1H, J = 3.3 Hz), 3.96 (m, 1H), 3.67 (m, 1H), 2.07 (m, 2H), 1.94 (m, 2H), 1.74 (m, 2H). ES-MS m/z = 357.1631 (calculated 357.1603 for $C_{23}H_{20}N_2O_2 + H^+$).

2-(4-(OTHP)phenyl)-9-(4-bromophenyl)-phenanthroline 6

A 6.9 mL portion (11 mmol) of a 1.6 M *n*BuLi solution in hexane was rapidly added to a degassed solution of *p*-dibromobenzene (2.9 g, 12 mmol) in distilled diethyl ether (20 mL) at 0 °C and allowed to warm at room temperature. The *p*-bromophenyl lithium solution thus obtained were slowly added, by the mean of a double-ended needle, to a degassed suspension of phenanthroline compound **5**

(2.14 g, 6 mmol) in 70 mL of distilled diethyl ether kept at 0 °C. After the resulting dark red solution was stirred for 3 h under argon at 0 °C, it was hydrolyzed with water (25 mL) at 0 °C. The ether layer was decanted and the aqueous layer extracted three times with CH_2Cl_2. The combined organic layers were thereafter re-aromatized by addition of MnO_2 (15 g, 170 mmol) under effective stirring overnight. The re-aromatization was monitored by TLC (compound **6** can be recognized by a blue luminescence under UV light). After the mixture was dried over Na_2SO_4, the black slurry could easily be filtered on a sintered glass with Celite, washed with CH_2Cl_2, and the filtrate evaporated to dryness. The crude product was purified by column chromatography over silica gel, with CH_2Cl_2 as the eluent, to give the title compound **6** (pale yellow glassy solid, 2.44 g, 80%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): δ = 8.38 (d, 2H, J = 9.0 Hz), 8.34 (d, 2H, J = 9.0 Hz), 8.32 (d, 1H, J = 8.4 Hz), 8.29 (d, 1H, J = 8.4 Hz), 8.11 (d, 1H, J = 8.4 Hz), 8.10 (d, 1H, J = 8.4 Hz), 7.80 (d, 1H, J = 8.7 Hz), 7.77 (d, 1H, J = 8.7 Hz), 7.74 (d, 2H, J = 8.7 Hz), 7.25 (d, 2H, J = 8.7 Hz), 5.55 (t, 1H, J = 3.2 Hz), 3.95 (m, 1H), 3.65 (m, 1H), 2.03 (m, 2H), 1.92 (m, 2H), 1.69 (m, 2H). ES-MS m/z = 511.0992 (calculated 511.1021 for $C_{29}H_{23}BrN_2O_2 + H^+$).

2-(4-Hydroxyphenyl)-9-(4-bromophenyl)-phenanthroline 7

Phenanthroline compound **6** (2.44 g, 4,77 mmol) was dissolved in methanol (200 mL) in the presence of a catalytic amount of a 37% solution of HCl (10 drops). The mixture was heated to reflux overnight (~18 h). The solvent was removed and the product was dispersed in distilled water (100 mL) and CH_2Cl_2 (200 mL). The aqueous layer was neutralized with a 1 M solution of NaOH and the two layers were separated (a precipitate was in suspension in CH_2Cl_2). Pentane (200 mL) was then added to the organic phase and the precipitate was filtered to give the title product **7**. This product was not soluble enough to be more purified and was therefore used without further purification (yellow solid, 1.84 g, 90%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 8.55 (d, 1H, J = 8.7 Hz), 8.53 (d, 1H, J = 9.3 Hz), 8.41 (d, 2H, J = 8.4 Hz), 8.34 (d, 1H, J = 8.7 Hz), 8.30 (d, 2H, J = 8.4 Hz), 8.27 (d, 1H, J = 9.3 Hz), 7.96 (s, 2H), 7.81 (d, 2H, J = 8.4 Hz), 7.00 (d, 2H, J = 8.7 Hz). ES-MS m/z = 429.0344 (calculated 429.0423 for $C_{24}H_{15}BrN_2O + H^+$).

Mono-stoppered and bromo-ended phenanthroline fragment 8

Phenanthroline compound **7** (550 mg, 1.29 mmol), caesium carbonate (840 mg, 2.58 mmol) and stopper with iodo-ended chain **8** (1.93 g, 2.58 mmol) were mixed in dry DMF (150 mL) and stirred at 50 °C for 5h. More stopper with iodo-ended chain **8** (960 mg, 0.65 mmol) was added and the reaction mixture stirred at 50 °C overnight. The solvent was removed and the residue was taken up with CH_2Cl_2–H_2O. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The solvent was removed and the residue purified by chromatography on silica gel by using CH_2Cl_2–MeOH (0.5%) as the eluent to give the title compound **8** (yellowish glassy solid, 620 mg, 46%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): δ = 8.39 (d, 2H, J = 8.7 Hz), 8.35 (d, 1H, J = 8.1 Hz), 8.34 (d, 2H, J = 8.7 Hz), 8.29 (d, 1H, J = 8.4 Hz), 8.13 (d, 1H, J = 8.4 Hz), 8.10 (d, 1H, J = 8.4 Hz), 7.82 (d, 1H, J = 8.7 Hz), 7.79 (d, 1H, J = 8.7 Hz), 7.74 (d, 2H, J = 8.7 Hz), 7.25 (d, 6H, J = 8.8 Hz), 7.14 (d, 6H, J = 8.8 Hz), 7.13 (d, 4H, J = 9.0 Hz), 6.78 (d, 2H, J = 9.0 Hz), 4.24 (dd, 2H, J = 4.6, 6.0 Hz), 4.09 (dd, 2H, J = 4.6, 6.0 Hz), 3.90 (dd, 2H, J = 3.3, 4.8 Hz), 3.82 (dd, 2H, J = 3.4, 4.9 Hz), 3.73 (s, 4H), 1.28 (s, 27H). MALDI-MS m/z = 1047.375 (calculated 1047.450 for $C_{67}H_{69}BrN_2O_4 + H^+$).

Mono-stoppered and boronic ester-ended phenanthroline fragment 9

Brominated phenanthroline fragment **8** (660 mg, 0.63 mmol), bis(neopentyl glycolato)diboron (157 mg, 0.70 mmol), potassium acetate (186 mg, 1.90 mmol) and Pd(dppf)Cl_2,CH_2Cl_2 (16 mg, 0.02 mmol) were dissolved in dry dioxane. The mixture was stirred under Ar at 80 °C overnight. After the solution was cooled down at room temperature, 50 mL of water and 100 mL of CH_2Cl_2 were added. The organic layer was then decanted and the aqueous layer was extracted 2 times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The title product **9** such obtained was used without further purification (dark brown solid, 681 mg, 100%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): δ = 8.43 (d, 2H, J = 8.4 Hz), 8.40 (d, 2H, J = 8.9 Hz), 8.34 (d, 1H, J = 8.4 Hz), 8.29 (d, 1H, J = 8.5 Hz), 8.19 (d, 1H, J = 8.5 Hz), 8.10 (d, 1H, J = 8.5 Hz), 8.00 (d, 2H, J = 8.4 Hz), 7.80 (s, 2H), 7.26 (d, 2H, J = 8.8 Hz), 7.24 (d, 6H, J = 8.8 Hz), 7.14 (d, 6H, J = 8.8 Hz), 7.12 (d, 2H, J = 9.0 Hz), 4.24 (m, 2H), 4.09 (m, 2H), 3.89 (m, 2H), 3.82 (m, 2H), 3.82 (s, 4H), 3.74 (s, 4H), 1.28 (s, 27H), 1.05 (s, 6H).

4-(Tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid 10

4-(Tetrahydro-2*H*-pyran-2-yloxy)bromobenzene (4.33 g, 16.8 mmol) was dissolved in freshly distilled THF (100 mL). After cooling to −78 °C a solution of *n*BuLi in hexane (1.6 M, 11.6 mL, 18.5 mmol) was added dropwise and the reaction mixture and was stirred at −78 °C for 20 min under Ar. After addition of triisopropyl borate (4.3 mL, 18.5 mmol), the solution stirred at −78 °C for another 1 h and was allowed to warm to room temperature. Diethyl ether (500 mL) and water (500 mL) were then added and the mixture was slowly neutralized with an aqueous 0.1 M HCl solution. The organic layer was then decanted, the aqueous layer was extracted 2 times with diethyl ether and the combined organic layer evaporated to dryness. The crude product was purified by chromatography on silica gel by using toluene–acetone (4 : 1) as the eluent to give the title compound **10** (white solid, 3.04 g, 81%). ^{1}H NMR (acetone d^6–D_2O (3 : 1), 300 MHz): δ = 7.71 (d, 2H, J = 8.7 Hz), 6.93 (d, 2H, J = 8.7 Hz), 5.42 (t, 1H, J = 3.2 Hz), 3.75 (m, 1H), 3.52 (m, 1H), 1.78 (m, 2H), 1.57 (m, 2H), 1.26 (m, 2H).

5-Bromo-2-trimethylstannylpyridine 11

5-Bromo-2-iodopyridine (5.85 g, 20.5 mmol) was dissolved in 200 mL of toluene. *n*BuLi (16.2 mL, 1.4 M in hexane, 22.5 mmol) was added dropwise onto the solution maintained at −20 °C during the beginning of the addition. The mixture turned immediately red and the temperature was lowered to

−78 °C. The solution was then stirred at −78 °C for 2 h after which a solution of $ClSnMe_3$ (4.92 g, 24.6 mmol) in toluene (50 mL) was carefully added. At the end of the addition, the yellow solution was stirred for one additional hour at −78 °C and then allowed to warm up to room temperature. Toluene was evaporated and the crude product taken up in CH_2Cl_2. Insoluble salts were filtered off on a sintered glass. The filtrate was evaporated to dryness and the resulting yellow oil was submitted to a very fast chromatography on alumina with diethyl ether as the eluent to afford the title stannyl compound **11** (yellow oil, 6.39 g, 97%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 8.82 (d, 1H, J = 2.5 Hz), 7.68 (dd, 1H, J = 8.1, 2.5 Hz), 7.35 (d, 1H, J = 8.1 Hz), 0.32 (s, 9H). EI-MS m/z = 305.9 (calculated 305.8 for $C_8H_{12}BrNSn - CH_3^+$).

5,5′-Dibromo-2,2′-bipyridine 12

5-Bromo-2-trimethylstannylpyridine **11** (5.6 g, 17.5 mmol) and 5-bromo-2-iodopyridine (5.45 g, 19.2 mmol) were dissolved in dry toluene (200 mL). The solution was degassed three times, $Pd(PPh_3)_4$ (582 mg, 0.50 mmol) was added under an Ar stream and the mixture was degassed three times again. The solution was heated at reflux for 20 h. Pd black was filtered off and the solvent was evaporated. Recrystallisation of the resulting solid in $CHCl_3$ afforded the title bipyridine **12** (light brown solid, 3.72 g, 68%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 8.70 (d, 2H, J = 2.3 Hz), 8.29 (d, 2H, J = 8.5 Hz), 7.93 (dd, 2H, J = 8.5, 2.3 Hz). ES-MS m/z = 336.8826 (calculated 336.8770 for $C_{10}H_6Br_2N_2 + Na^+$).

5-Bromo-5′-(4-(OTHP)phenyl)-2,2′-bipyridine 13

5,5′-Dibromo-2,2′-bipyridine **12** (1.0 g, 3.18 mmol), Na_2CO_3 (3.36 g, 31.8 mmol) and boronic acid **10** (730 mg, 3.29 mmol) were dissolved in toluene (150 mL), water (50 mL) and ethanol (25 mL). The solution was degassed three times, $Pd(PPh_3)_4$ (187 mg, 0.16 mmol) was added under an Ar stream and the mixture was degassed three times again. The solution was heated at 90 °C for 2.5 h. The organic layer was then decanted and the aqueous layer was extracted 3 times with CH_2Cl_2. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on aluminium oxide by using pentane–ethyl acetate (5%) as the eluent to give the title bipyridine **13** (white solid, 478 mg, 36%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 8.86 (d, 1H, J = 2.3 Hz), 8.71 (d, 1H, J = 2.3 Hz), 8.43 (d, 1H, J = 8.3 Hz), 8.37 (d, 1H, J = 8.5 Hz), 7.99 (dd, 1H, J = 8.3, 2.4 Hz), 7.85 (dd, 1H, J = 8.5, 2.4 Hz), 7.60 (d, 2H, J = 8.8 Hz), 7.17 (d, 2H, J = 8.8 Hz), 5.47 (t, 1H, J = 3.2 Hz), 3.89 (m, 1H), 3.62 (m, 1H), 2.00 (m, 2H), 1.88 (m, 2H), 1.66 (m, 2H). ES-MS m/z = 411.0654 (calculated 411.0703 for $C_{21}H_{19}BrN_2O_2 + H^+$).

OTHP-ended thread with phen and bipy ligands 14

Boronic ester phenanthroline fragment **9** (340 mg, ~0.315 mmol), asymmetrical bipyridine **13** (130 mg, 0.316 mmol) and Na_2CO_3 (334 mg, 3.15 mmol) were dissolved in toluene (30 mL), water (10 mL) and ethanol (5 mL). The solution was degassed three times, $Pd(PPh_3)_4$ (16 mg, 0.013 mmol) was added under an Ar stream and the mixture was degassed three times again. The solution was heated at 90 °C overnight. The organic layer was then decanted and the aqueous layer was extracted 3 times with CH_2Cl_2. The combine organic layer was washed with water and evaporated. The crude product was purified by chromatography on aluminium oxide by using CH_2Cl_2–pentane (3 : 1) as the eluent to give the title compound **14** (colourless glassy solid, 367 mg, 90%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 9.07 (d, 1H, J = 2.0 Hz), 8.91 (d, 1H, J = 1.9 Hz), 8.61 (d, 2H, J = 8.5 Hz), 8.59 (d, 1H, J = 8.4 Hz), 8.55 (d, 1H, J = 8.4 Hz), 8.43 (d, 2H, J = 8.9 Hz), 8.38 (d, 1H, J = 8.5 Hz), 8.31 (d, 1H, J = 8.5 Hz), 8.24 (d, 1H, J = 8.5 Hz), 8.19 (dd, 1H, J = 8.3, 2.3 Hz), 8.11 (d, 1H, J = 8.5 Hz), 8.03 (dd, 1H, J = 8.3, 2.3 Hz), 7.96 (d, 2H, J = 8.5 Hz), 7.83 (s, 2H), 7.63 (d, 2H, J = 8.8 Hz), 7.26 (d, 2H, J = 8.7 Hz), 7.24 (d, 6H, J = 8.7 Hz), 7.18 (d, 2H, J = 8.9 Hz), 7.13 (d, 6H, J = 8.8 Hz), 7.12 (d, 2H, J = 9.0 Hz), 6.78 (d, 2H, J = 9.0 Hz), 5.49 (t, 1H, J = 3.3 Hz), 4.25 (dd, 2H, J = 6.1, 4.6 Hz), 4.09 (dd, 2H, J = 6.0, 4.6 Hz), 3.91 (m, 1H), 3.90 (dd, 2H, J = 4.6, 3.3 Hz), 3.83 (dd, 2H, J = 4.8, 3.4 Hz), 3.73 (s, 4H), 3.64 (m, 1H), 2.02 (m, 2H), 1.88 (m, 2H), 1.66 (m, 2H), 1.27 (s, 27H). MALDI-MS m/z = 1297.681 (calculated 1297.678 for $C_{88}H_{88}N_4O_6 + H^+$).

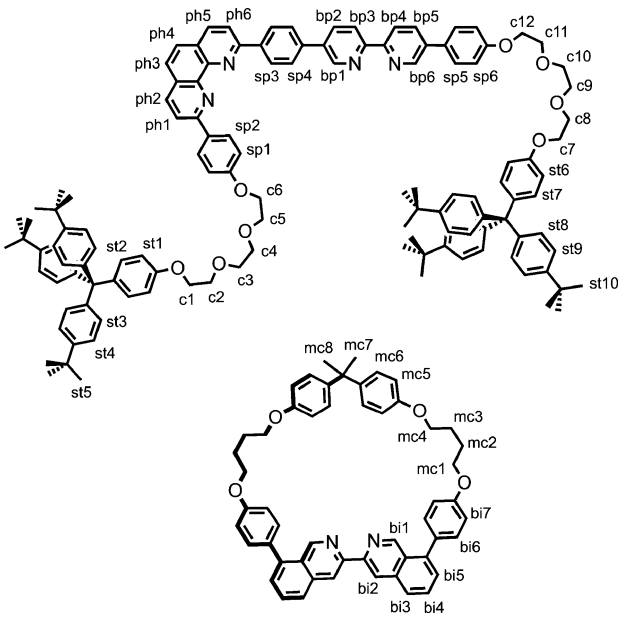
OH-ended thread with phen and bipy ligands 15

OTHP-ended thread **14** (365 mg, 0.281 mmol) was dissolved in CH_2Cl_2 (20 mL) and methanol (20 mL) in the presence of a catalytic amount of a 37% solution of HCl (5 drops). The mixture was heated to reflux for 4 h. The solvent was removed and the product was dispersed in distilled water (100 mL) and CH_2Cl_2 (200 mL). The aqueous layer was neutralized with a 1 M solution of NaOH. The organic layer was then decanted and the aqueous layer was extracted 4 times with more CH_2Cl_2. The combined organic phases were washed with distilled water. The solvent was evaporated and the title product **15** such obtained (yellow solid, 345 mg, supposed quantitative) was used without further purification because of its low solubility. MALDI-MS m/z = 1213.624 (calculated 1213.621 for $C_{83}H_{80}N_4O_5 + H^+$).

Two-station copper-based [2]rotaxane [1_{dpp}^+][PF_6^-] (*via* 17^+)

A solution of $Cu(MeCN)_4PF_6$ (24.5 mg, 0.066 mmol) in degassed MeCN (3 mL) was transferred *via* a cannula to a stirred solution of 39-membered macrocycle **16** (51.2 mg, 0.066 mmol) in $CHCl_3$ (5 mL) under Ar, and the resulting orange solution was stirred at room temperature for 30 min. This mixture is then transferred to a degassed solution of OH-ended two-station thread **15** (80 mg, 0.066 mmol) in $CHCl_3$ (15 mL) *via* a cannula, resulting in the immediate formation of a brown–red solution, which was stirred under Ar at room temperature overnight. Solvents were evaporated to give the pseudo-rotaxane $\mathbf{17}^+$ (PF_6^-) (brown–red solid). It was then dissolved in dry and degassed DMF (6 mL) with Cs_2CO_3 (43 mg, 0.132 mmol), stopper with iodo-ended chain **4** (147.7 mg, 0.198 mmol) and sodium ascorbate (2.6 mg, 0.013 mmol). This mixture was stirred under Ar at 50 °C for 20 h. DMF was evaporated and the resulting crude product taken up in $CHCl_3$ and washed with water. After evaporation of the solvent and two successive column chromatographies on aluminium oxide active acidic (CH_2Cl_2 containing 1% MeOH

and 1% MeCN) the title product $\mathbf{1}^+$ (PF_6^-) was obtained (brown–red solid, 25 mg, 14%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 8.91 (d, 1H, J = 1.5 Hz, bp6), 8.54 (s, 2H, bi2), 8.49 (s, 2H, bi1), 8.48 (d, 1H, J = 6.6 Hz, bp4), 8.42 (d, 1H, J = 8.3 Hz, bp3), 8.38 (d, 1H, J = 1.5 Hz, bp1), 8.01 (dd, 1H, J = 8.3, 2.4 Hz, bp5), 7.98 (d, 1H, J = 8.4 Hz, ph2), 7.96 (d, 2H, J = 8.4 Hz, bi3), 7.92 (d, 1H, J = 8.4 Hz, ph5), 7.84 (d, 1H, J = 7.3 Hz, ph6), 7.82 (t, 2H, J = 8.3 Hz, bi4), 7.80 (d, 1H, J = 8.3 Hz, ph1), 7.62 (d, 4H, J = 8.4 Hz, sp3–sp5), 7.57 (dd, 2H, J = 6.4, 0.7 Hz, bi5), 7.47 (d, 2H, J = 8.6 Hz, sp2), 7.40 (d, 4H, J = 8.8 Hz, mc6), 7.35 (dd, 1H, J = 8.3, 2.2 Hz, bp2), 7.31 (d, 1H, J = 8.6 Hz, ph3), 7.26 (d, 6H, J = 8.4 Hz, st9), 7.22 (d, 1H, J = 8.8 Hz, ph4), 7.19 (d, 6H, J = 8.6 Hz, st4), 7.15 (d, 6H, J = 8.6 Hz, st8), 7.15 (d, 2H, J = 8.6 Hz, st2), 7.14 (d, 2H, J = 8.6 Hz, st7), 7.09 (d, 4H, J = 8.8 Hz, bi6), 7.09 (d, 6H, J = 8.8 Hz, st3), 7.08 (d, 2H, J = 9.5 Hz, sp6), 6.96 (d, 2H, J = 8.1 Hz, sp4), 6.84 (d, 4H, J = 8.6 Hz, bi7), 6.79 (d, 4H, J = 8.8 Hz, mc5), 6.78 (d, 2H, J = 9 Hz, st1), 6.73 (d, 2H, J = 9 Hz, st6), 6.18 (d, 2H, J = 8.6 Hz, sp1), 4.19 (t, 2H, J = 4.4 Hz, c12), 4.16 (t, 4H, J = 6.2 Hz, mc1), 4.11 (t, 2H, J = 5 Hz, c7), 3.87 (t, 2H, J = 4.6 Hz, c1), 3.85 (t, 2H, J = 4.4 Hz, c11), 3.83 (t, 2H, J = 4.6 Hz, c8), 3.82 (t, 2H, J = 4.6 Hz, c2), 3.80 (t, 2H, J = 5.7 Hz, mc4), 3.73 (s, 8H, c3–c4–c9–c10), 3.67 (t, 2H, J = 5.3 Hz, c5), 3.59 (d, 2H, J = 5.3 Hz, c6), 1.85 (m, 8H, mc2-mc3), 1.77 (s, 6H, mc7–mc8), 1.30 (s, 27H, st10), 3.73 (s, 27H, st5). ES-MS m/z = 2672.2933 (calculated 2672.3157 for $C_{179}H_{182}CuN_6O_{12}^+$).†



Copper-based reference complexes [18^+][PF_6^-], [19^+][PF_6^-]

A solution of $Cu(MeCN)_4PF_6$ (5.8 mg, 0.015 mmol) in degassed MeCN (2 mL) was added to a stirred solution of 39-membered macrocycle **16** (12 mg, 0.015 mmol) in dichloromethane (2 mL) under Ar, and the resulting bright orange solution was stirred at room temperature for 30 min. Then the corresponding chelate, namely dap (6.1 mg, 0.015 mmol) or dabipy (5,7 mg, 0.015 mmol) is added to the solution to form the corresponding copper-based complex, respectively **[18^+][PF_6^-]** and **[19^+][PF_6^-]**, with a quantitative yield. The electrochemical studies were performed without any further purification, due to the relative air- and base- sensitivity of these copper-based complexes.

^{1}H NMR of **[18^+][PF_6^-]** (CD_2Cl_2, 300 MHz): δ = 8.6 (s, 2H), 8.51 (s, 2H), 8.06 (d, 2H, J = 8.3 Hz), 7.94 (d, 2H, J = 8.5 Hz), 7.93 (t, 2H, J = 8.2, 7 Hz), 7.89 (d, 2H, J = 8.5 Hz), 7.80 (d, 2H, J = 8.3 Hz), 7.65 (d, 2H, J = 7 Hz), 7.51 (d, 4H, J = 8.7 Hz), 7.41 (d, 4H, J = 8.7 Hz), 7.26 (s, 2H), 7.15 (d, 4H, J = 8.5 Hz), 6.87 (d, 4H, J = 8.7 Hz), 6.81 (d, 4H, J = 8.5 Hz), 6.22 (d, 4H, J = 8.7 Hz), 4.18 (t, 4H, J = 6, 5.7 Hz), 3.81 (t, 4H, J = 6 Hz), 3.4 (s, 6H), 1.83 (m, 8H), 1.3 (s, 6H). ES-MS m/z = 1231.4810 (calculated 1231.4429 for $C_{79}H_{68}CuN_4O_6^+$).†

^{1}H NMR of **[19^+][PF_6^-]** (CD_2Cl_2, 300 MHz): δ = 9.06 (s, 2H), 9.0 (s, 2H), 8.76 (d, 2H), 8.15 (d, 2H, J = 8.3 Hz), 7.96 (t, 2H, J = 7.9, 7.5 Hz), 7.69 (d, 2H, J = 8.3 Hz), 7.65 (d, 2H, J = 7.5 Hz), 7.57 (d, 4H, J = 8.5 Hz), 7.38 (d, 2H, J = 8.3Hz), 7.36 (d, 4H, J = 8.3 Hz), 7.20 (d, 4H, J = 8.2 Hz), 7.08 (d, 4H, J = 8.2 Hz), 6.89 (d, 4H, J = 8.3 Hz), 6.61 (d, 4H, J = 8.2 Hz), 4.01 (m, 4H), 3.86 (m, 4H), 3.86 (s, 6H), 1.87 (m, 8H), 1.7 (s, 6H). ES-MS m/z = 1207.4818 (calculated 1207.4429 for $C_{77}H_{68}CuN_4O_6^+$).†

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References

1 D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.
2 A. Harada, *Acc. Chem. Res.*, 2001, **34**, 456.
3 K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
4 A. Kocer, M. Walko, W. Meijberg and B. L. Feringa, *Science*, 2005, **309**, 755.
5 B. Champin, P. Mobian and J.-P. Sauvage, *Chem. Soc. Rev.*, 2007, **36**, 358.
6 E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72.
7 V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines—Concepts and Perspectives for the Nanoworld*, Wiley-VCH, Weinheim, 2008.
8 G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York and London, 1971.
9 J.-P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611.
10 J.-P. Sauvage and C. O. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, 1999.
11 G. W. H. Wurpel, A. M. Brouwer, I. H. M. van Stokkum, A. Farran and D. A. Leigh, *J. Am. Chem. Soc.*, 2001, **123**, 11327.
12 M. Cavallini, F. Biscarini, S. Leon, F. Zerbetto, G. Bottari and D. A. Leigh, *Science*, 2003, **299**, 531.
13 V. Balzani, A. Credi, S. Silvi and M. Venturi, *Chem. Soc. Rev.*, 2006, **35**, 1135.
14 R. E. Dawson, S. F. Lincoln and C. J. Easton, *Chem. Commun.*, 2008, 3980.
15 C. Chuang, W.-S. Li, C.-C. Lai, Y.-H. Liu, S.-M. Peng, I. Chao and S.-H. Chiu, *Org. Lett.*, 2009, **11**(2), 385.
16 R. A. Bissell, E. Córdova, A. E. Kaifer and J. F. Stoddart, *Nature*, 1994, **369**, 133.
17 H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake and N. Nakashima, *J. Am. Chem. Soc.*, 1997, **119**, 7605.
18 G. W. H. Wurpel, A. M. Brouwer, I. H. M. van Stokkum, A. Farran and D. A. Leigh, *J. Am. Chem. Soc.*, 2001, **123**, 11327.
19 C. A. Stanier, S. J. Alderman, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2002, **41**, 1769.
20 C. M. Keaveney and D. A Leigh, *Angew. Chem., Int. Ed.*, 2004, **43**, 1222.

21 E. M. Pérez, D. T. F. Dryden, D. A. Leigh, G. Teobaldi and F. Zerbetto, *J. Am. Chem. Soc.*, 2004, **126**, 12210.
22 Q.-C. Wang, D.-H. Qu, J. Ren, K. Chen and H. Tian, *Angew. Chem., Int. Ed.*, 2004, **43**, 2661.
23 V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood and J. F. Stoddart, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 1178.
24 G. Fioravanti, N. Haraszkiewicz, E. R. Kay, S. M. Mendoza, C. Bruno, M. Marcaccio, P. G. Wiering, F. Paolucci, P. Rudolf, A. M. Brouwer and D. A. Leigh, *J. Am. Chem. Soc.*, 2008, **130**, 2593.
25 C. P. Collier, E. W. Wong, M. Belohradsky, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams and J. R. Heath, *Science*, 1999, **285**, 391.
26 A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier and J. R. Heath, *Acc. Chem. Res.*, 2001, **34**, 433.
27 J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. DeIonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart and J. R. Heath, *Nature*, 2007, **445**, 414.
28 T. D. Nguyen, Y. Liu, S. Saha, K. C.-F. Leung, J. F. Stoddart and J. I. Zink, *J. Am. Chem. Soc.*, 2007, **129**, 626.
29 A. Livoreil, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 9399.
30 D. J. Cárdenas, A. Livoreil and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1996, **118**, 11980.
31 N. Solladié, J.-C. Chambron, C. O. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 906.
32 J.-P. Collin, P. Gaviña and J.-P. Sauvage, *New J. Chem.*, 1997, **21**, 525.
33 B. Colasson, C. O. Dietrich-Buchecker, M. C. Jimenez-Molero and J.-P. Sauvage, *J. Phys. Org. Chem.*, 2002, **15**, 476.
34 J. Frey, T. Kraus, V. Heitz and J.-P. Sauvage, *Chem.–Eur. J.*, 2007, **13**, 7584.
35 F. Durola and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2007, **46**, 3537.
36 F. Durola, J. Lux and J.-P. Sauvage, *Chem.–Eur. J.*, 2009, **15**, 4124.
37 F. Durola, O. S. Wenger and J.-P. Sauvage, *Helv. Chim. Acta*, 2007, **90**, 1439.
38 H. W. Gibson, S.-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen and M. Bheda, *J. Org. Chem.*, 1993, **58**, 3748.
39 B. X. Colasson, C. Dietrich-Buchecker and J.-P. Sauvage, *Synlett*, 2002, 271.
40 C. O. Dietrich-Buchecker, J.-P. Sauvage and J.-P. Kintzinger, *Tetrahedron Lett.*, 1983, **24**, 5095.
41 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
42 L. Raehm, J.-M. Kern and J.-P. Sauvage, *Chem.–Eur. J.*, 1999, **5**, 3310.