Fast redox-triggered shuttling motions in a copper rotaxane based on a phenanthroline/terpyridine conjugate

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Fast shuttling motions in solution have been observed by cyclic voltammetry in a $Cu^{I/II}$-based [2] rotaxane. In the reported system, the different coordination preferences of both copper oxidation states are exploited to promote the electrochemically-triggered gliding of the ring from a tetra to a pentacoordinated site and vice versa. The thread of this rotaxane consists of a tridentate 2,2':6',2''-terpyridine chelating unit directly bonded through its 5-position to the 8- position of the bidentate 1,10-phenanthroline unit. This distribution reduces to a minimum the distance between the two coordination sites and lessens the congestion around the tetrahedral environment. These two factors have demonstrated to highly increase the kinetics of the switching process. In addition, the electrochemical experiments carried out in different solvent mixtures evidenced the influence of the solvent in the shuttling mechanism.

Introduction

The insight into the functioning of living organisms has demonstrated that highly efficient macroscopic mechanical motions can be achieved by the cooperative work of molecular based actuators.[1, 2] Such inspiration encouraged the chemical research towards the controlled realization of molecular level motions.[3, 4] One of the main approaches in this field has been focused on the development of stimuli-responsive mechanically interlocked molecules.[5, 6] In these molecules, the external alteration of the binding affinities established between the different subcomponents causes the isomerization of the system.[7] Particularly appealing is the case of molecular shuttles,[8] in which linear motions have been achieved either in solution[9-12] or in the solid state[13] by placing two different recognition sites along the axle of a stimuli-responsive rotaxane.

Metal-coordination bonds are one of the interactions that have been successfully exploited for the construction of rotaxanes.[14-16] Among them, copper-complexed rotaxanes constitute one of the most remarkable examples.[17-20] These molecules have demonstrated to undergo appreciable conformational changes upon the alteration of their redox state: whereas Cu^{I} ions prefer tetracoordinated environments, Cu^{II} tend to be penta or hexacoordinate. On that basis, the group led by Prof. Sauvage developed two decades ago the first bistable copper interlocked complexes.[21-23] In these pioneering works, that settled the grounds of the area, controlled shuttling motions were achieved by changing the oxidation state of the metal ion in threaded systems based on 1,10-phenanthrolines (phen) as bidentate and 2,2':6',2''-terpyridines (terpy) as tridentate ligands.

The motion cycle in these systems starts with the oxidation of the initial Cu^{I} at the tetracoordinated bis-bidentate site. Since the earliest examples of shuttling rotaxanes, such reorganization of the unstable Cu^{II} tetracoordinated species has demonstrated to be the limiting step of the cycle, the rearrangement of the pentacoordinated Cu^{I} being orders of magnitude faster.[17, 21, 24] Nevertheless, the thermodynamic and kinetic features of these threaded molecules could be accelerated by changing the nature and substitution of the chelating units involved.[24, 25] The presence of aryl groups in the 2,9- positions of the bidentate units (either phen or bipy) hampers the adoption of the more planar arrangements preferred by Cu^{II},[26] and greatly enhances the stability of the cuprous state.[27, 28] At the same time, it shields very effectively the copper center from the approach of nucleophiles, lowering the rate constant of the gliding process.[25, 29] On the other hand, the length and flexibility of the linker between the phen and terpy chelates have also demonstrated to have a main influence on the shuttling rate.[19, 20]

In order to get further insights into the structural factors determining the kinetics of copper-based molecular shuttles we have prepared switchable rotaxane $\mathbf{1}^{+}$, whose structure is shown in Figure 1, and studied its electrochemically-induced shuttling motion in solution by cyclic voltammetry. In this molecule, the

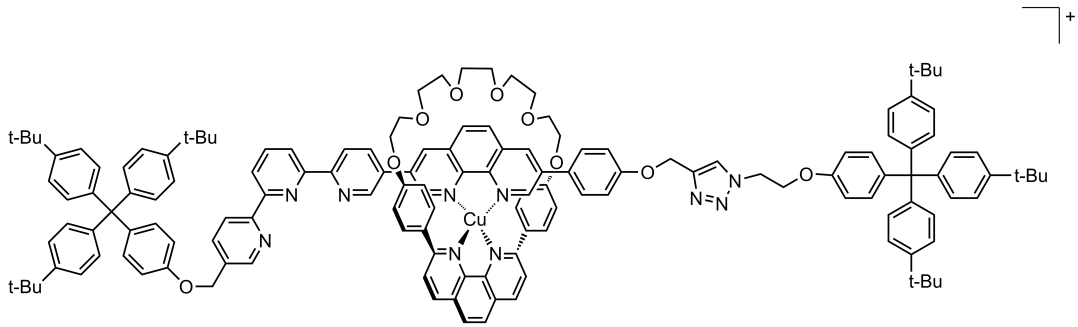


Figure 1 Chemical structure of rotaxane $\mathbf{1}^{+}$.

tridentate chelating unit, consisting of a terpy moiety, has been directly bonded through its 5- position to the 3- position of a bidentate phen unit. This distribution reduces to a minimum the distance between the two coordination sites to accelerate the gliding motion of the ring along the thread.[30] Moreover, in order to further increase the lability of the tetracoordinated site, we have lowered the steric hindrance around the copper ion by the functionalization of the axle phen through its 3- and 8- positions.[31] On the other hand, we have maintained a 2,9-diphenyl-1,10-phenanthroline moiety (dpp) in the macrocycle[21] to stabilize the Cu^{I} oxidation state.

Results and discussion

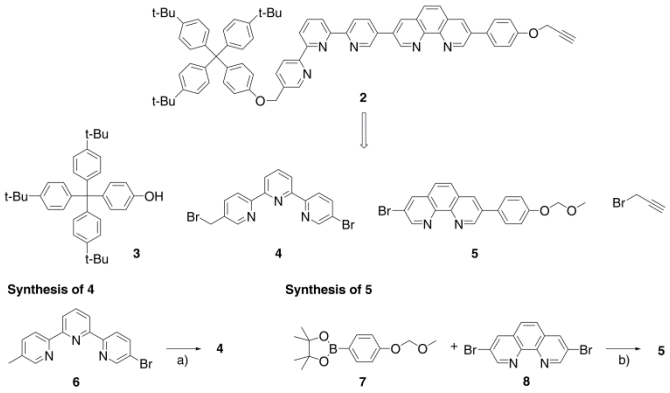
Synthesis

Synthesis of rotaxane $\mathbf{1}^{+}$ was carried out using the threading followed by stoppering approach.[32] We decided to use CuAAC (Copper-Catalyzed Azide-Alkyne Cycloadition) methodology for the final capping of the [2] pseudorotaxane since these reactions are carried out under very mild conditions and CuAAC has already proven successful in the synthesis of other copper-interlocked systems.[33-35] In order to enhance the yield of the process, only one single blocking group was incorporated in the final capping step, the other stopper being already present in the terpy extreme of the axle precursor.[35] Hence, the monostoppered thread **2** was provided with a terminal alkyne, whereas the second stopper was functionalized with an azide derivative.

SYNTHESIS OF THE THREAD

The structure of linear ethynyl-terminated thread **2** is depicted in Scheme 1. It is composed by a terpy unit directly bonded through its 5- position to the 3- position of a phen moiety. Attached to the other terpy end there is also a tetraphenyl methane stoppering group. The synthesis of **2** was accomplished by the convergent assembly of its various constituent fragments: stopper **3**, terpy derivative **4** and bromophenanthroline **5**.

Synthesis of phenolic blocking group **3** was carried out in two steps from 1-bromo-4-*tert*-butylbenzene, p-*tert*-butylbenzoate and phenol, according to a reported literature procedure.[36] Preparation of the terpy and phen fragments, **4** and **5,** is depicted in Scheme 1. We decided to prepare unsymmetrically substituted derivatives of both terpyridine and phenanthroline ligands in order to increase the bonding selectivity during the assembly of **2**. Thereby, both extremes of **4** were functionalized with groups of very different reactivity: an aryl bromide, to be reacted in palladium-catalyzed cross-coupling reactions, and a benzylic bromide, which is very reactive in nucleophilic substitution reactions. For the same reason, phen **5** was functionalized in its 3- and 8- positions with a bromide and a protected phenol substituent.



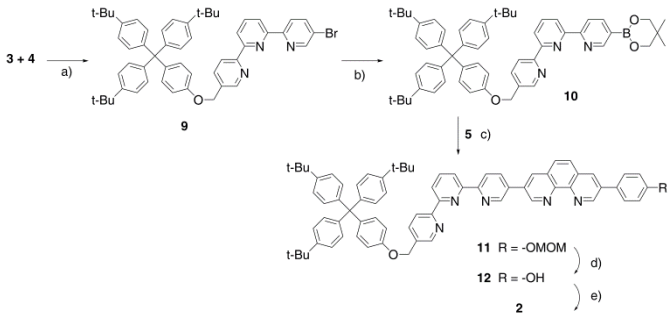
Scheme 1 Retrosynthesis of axle precursor **2**. Synthesis of building blocks **4** and **5**: **a)** NBS, CH_2Cl_2, H_2O, light (77%); **b)** $Pd(PPh_3)_4$, DMF, K_2CO_3, H_2O (33%).

Unsymmetrically substituted terpy derivative **4** was prepared in good yield (77 %) by photobromination of the benzylic position of **6** with NBS in a dichloromethane/water biphasic media. The synthesis of **6** was carried out in 42% overall yield from 2,6-dibromopyridine and the corresponding stannyl pyridines using two consecutive Stille cross-coupling reactions, as described in a prior communication.[37]

Unsymmetrically substituted phen derivative **5** was prepared by the cross-coupling of 3,8-dibromophenanthroline **8**[38] with one equivalent of aryl boronic ester **7**. This reactant was prepared from commercially available 4-hydroxyphenylboronic acid pinacol ester and chloromethyl methyl ether. Although there are several examples in the literature describing Suzuki cross-couplings performed in the presence of free phenol groups, in our case, the protection of the phenol group as a methoxymethyl (MOM) ether resulted convenient in order to increase the yield of the coupling reaction and to increase the solubility of the resulting product. The MOM ether group is

resistant to the basic cross-coupling media used in a later synthetic stage and can be cleaved under very mild conditions.[39]

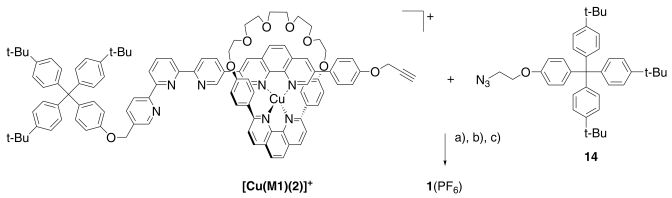
Molecular thread **2** was assembled by first attaching the bulky group **3** to terpy derivative **4**, next coupling with phen fragment **5** and final reaction with propargyl bromide. This synthetic route is described in Scheme 2 and involves: a) the initial nucleophilic attack of **3** to the benzylic bromide group in **4** under typical Williamson conditions to afford intermediate **9**; b) the conversion of **9** to its neopentyl boronic ester under Miyaura conditions using neo_2B_2 and $Pd(ddpf)Cl_2$ as catalyst;[40, 41] c) the Suzuki cross-coupling between **10** and **5** to afford **11** in reasonable yield (28 %); d) the cleavage of the MOM-protecting group in **11** to yield phenol **12** under the mild acidic media resulting from the visible-light irradiation of catalytic amounts of carbon tetrabromide in 2-propanol,[39] and e) the final nucleophilic substitution reaction between **12** and propargyl bromide under Williamson conditions to afford axle **2** in 80% yield.



Scheme 2 **a)** K_2CO_3, DMF 80 ^{0}C (55%); **b)** neo_2B_2, [$PdCl_2$(dppf)ferrocene], DMSO 80 ^{0}C (49%); **c)** $Pd(PPh_3)_4$, DMF, K_2CO_3, H_2O (28%); **d)** CBr_4, 2-propanol, light (81%); **e)** NaH, propargyl bromide, THF 45 ^{0}C (80%).

THREADING AND STOPPERING REACTION

Threading and stoppering of linear fragment **2** was carried out in one pot, as illustrated in Scheme 3. Azide-functionalized stopper **14** was synthesized in 69 % yield in only two steps from previously described 2-(4-(tris(4-*tert*-butylphenyl)methyl)phenoxy)ethan-1-ol,[17] which was prepared from the reaction of **3** with 2-bromo-ethanol.[31]



Scheme 3 Capping reaction: **a)** $Cu(Me_6Tren)Br$, Na_2CO_3, Sodium ascorbate, CH_3CN, CH_2Cl_2.; **b)** KCN aq.; **c)** $[Cu(CH_3CN)_4](PF_6)$, CH_3CN, CH_2Cl_2 (11%).

For the threading step, equimolecular amounts of mono-stoppered axle **2** and the previously reported dpp-based macrocycle **M1** and $[Cu(CH_3CN)_4](PF_6)$ were stirred in dichloromethane/acetonitrile under an inert atmosphere. The mixture rapidly turned dark-red, indicating the formation of the [2]pseudorotaxane [Cu(**M1**)(**2**)]$^+$. The ensuing addition of the azide-functionalized stopper **14**, Na_2CO_3, sodium ascorbate and a copper catalyst promoted the CuAAC reaction described in Scheme 3. The election of the Cu^I catalyst for the CuAAC capping was an important issue. Although $[Cu(CH_3CN)_4](PF_6)$ can be used as catalyst in CuAAC reactions, some reports found recommended the use of coordinatively saturated Cu^I catalysts for the coupling of metal-chelating substrates.[42-44] In our case, we opted for the complex $[Cu(Me_6tren)]Br$ which has been described as an efficient catalyst in CuAAC[45] and can be easily prepared by mixing equimolecular amounts of CuBr with commercial Me_6Tren ligand in degassed acetonitrile. After the CuAAC capping reaction, treatment of the reaction crude with aqueous KCN afforded a mixture containing demetallated rotaxane **15** and 13% of unthreaded stoppered axle **16** as a by-product after column chromatography. Copper-complexed rotaxane **1**$^+$ could be finally obtained in overall 11% yield by the remetallation of the mixture with one equivalent of $[Cu(CH_3CN)_4](PF_6)$ and further purification by column chromatography. Despite the use of a coordinatively saturated copper catalyst, click chemistry afforded poor yields (ca. 10 %). This is most probably due to the presence of an unoccupied chelating terpy site in [Cu(**M1**)(**2**)]$^+$.[42]

Spectroscopic characterization

The structure of rotaxane **1**$^+$ was confirmed by High Resolution Mass Spectrometry and ^{1}H NMR spectroscopy. Assignment of the signals in Figure 2 could be done by the combined use of 1D and 2D ^{1}H NMR spectroscopy (COSY, NOE) and comparison with the spectra of precursors **2** and **M1**. The precise coordination of copper to the axle and to the macrocycle phens was evidenced in the NMR spectrum of **1**$^+$ by the appearance of a doublet below 6.0 ppm, corresponding to Mm-protons under the effect of the aromatic ring current of the phen moiety of the axle.[17] The location of the ring on the phen station of the axle was further evidenced by the noticeable shift experienced by P2, P5, P6 and P9 protons. The identity of P2 and P9 protons was confirmed by NOE experiments (see Supporting Info.). By contrast, all the protons coming from the terpy moiety appeared at similar chemical shifts than in the uncoordinated axle with the exception of T6, which is the closest to the macrocycle. Thereby, ^{1}H NMR confirms that the terpy site remains uncoordinated.

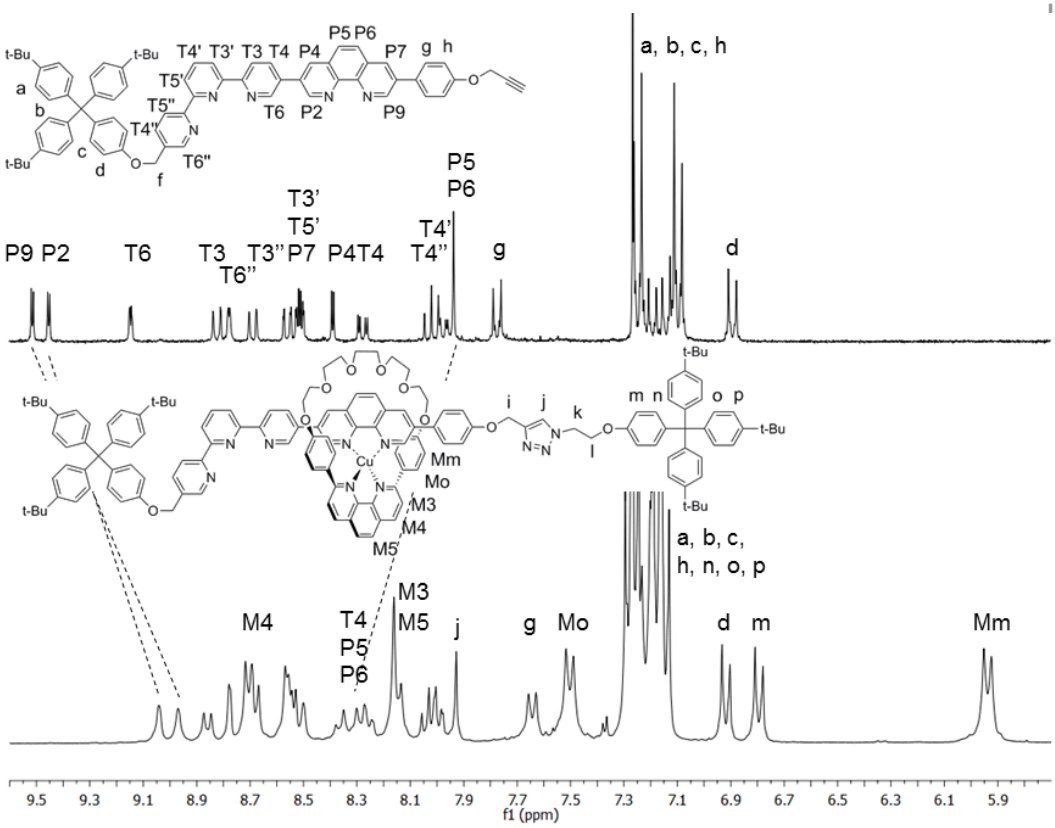


Figure 2 ^{1}H NMR spectra of axle precursor **2** (in $CDCl_3$) and rotaxane **1**(PF_6) (in CD_2Cl_2).

The UV-Vis spectra of stoppered axle **16** and the Cu^I and Cu^{II} forms of rotaxane **1** recorded in $1\cdot10^{-5}$ M dichloromethane solution are shown in Figure 3.

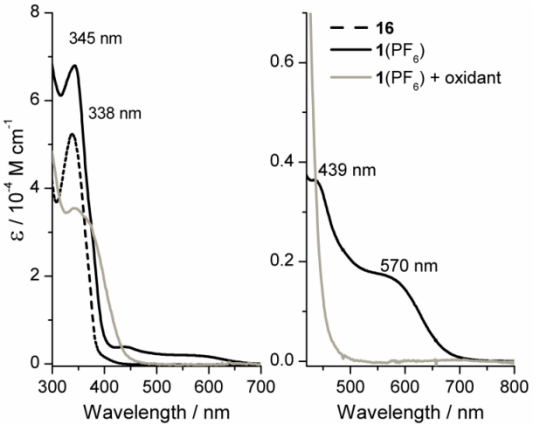


Figure 3 UV-Visible spectra of molecular axle **16**, rotaxane **1**(PF_6) and its oxidized Cu^{II} form (left). Visible region absorption spectra of rotaxane **1**(PF_6) and its oxidized form (right). Data recorded in dichloromethane $1\cdot10^{-5}$ M (oxidant: $NOBF_4$).

The absorption UV-Vis spectra of axle **16** presented an intense absorption band (343 nm, 68000 $M^{-1}cm^{-1}$) in the UV region associated to π-π* ligand-centered (LC) transitions.[46] The spectrum of rotaxane **1**(PF_6) showed red-shifted LC transitions due to the coordination of copper and low-intensity overlapping Metal-to-Ligand Charge Transfer (MLCT) bands extending from 420 to 650 nm with absorption maxima at 439 nm (3900 $M^{-1}cm^{-1}$) and 570 nm (1700 $M^{-1}cm^{-1}$).[47] These MLCT bands responsible of the characteristic red color of tetrahedral $[Cu(phen)_2]^+$ complexes disappeared upon the oxidation of **1**(PF_6) with $NO(BF_4)$ turning the colour of the solution into yellow. The original red colour could be recovered by the addition of hydrazine. These facts were ascribed to the oxidation/reduction of the copper centre and subsequent reorganization of its coordination sphere.

Electrochemical studies

Cyclic and differential pulse voltammetry studies were carried out in order to evaluate the electrochemical response of shuttling rotaxane **1**(PF_6). The cyclic voltammograms in dichloromethane/acetonitrile (1:9) solution at different scan rates are shown in Figure 4.

The different waves observed in the cyclic voltammograms resulted from the electrochemically induced gliding of the ring along the axis. On scanning from 0 V to positive potentials a redox process associated with the oxidation of Cu^I in a tetrahedral environment appeared at $E_{1/2}$ = 0.53 V. This value is below that of $Cu(dpp)_2$,[48] and is close to that reported[29] for other 2,9/3,8-substituted copper complexes like heteroleptic Cu(dpp)(dpbiiq) (dpbiiq = 8,8'-diphenyl-3,3'-bisisoquinoline). As expected, the reduction of the steric hindrance around the tetracoordinated site is reflected in the destabilization of the cuprous state. In agreement with the electrochemical potential of other Cu(terpy)(dpp)$^+$ like complexes,[17, 48] the irreversible wave appearing below 0.00 V was associated to the reduction of Cu^{II} in the pentacoordinated environment. When the scan direction was inverted, this last wave was absent in the first scan. This fact evidences the quantitative coordination of the Cu^I ion in the tetrahedral environment and confirms that the

peak below 0 V is the result of the gliding motion of the Cu^{II} ion to the pentacoordinated site.

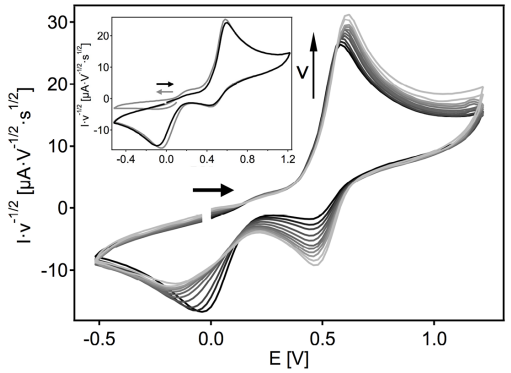


Figure 4 Cyclic voltammograms at 100, 150, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mV s^{-1} scan rates of rotaxane **1**(PF_6) ($1 \cdot 10^{-3}$ M) in dichloromethane/acetonitrile (1:9) using TBA(PF_6) 0.1 M as supporting electrolyte. The inset shows the cyclic voltammograms of rotaxane **1**(PF_6) at 100 mV s^{-1} using the same experimental conditions but in the two opposite scan directions. Horizontal arrows denote the scan direction. Current intensities have been divided by the square root of the scan rate for comparison.

On decreasing the scan rate from 1000 to 100 mV s^{-1}, the electrochemically induced gliding of the ring was further evidenced by a decrease in the intensity of the reduction wave corresponding to the Cu^{II} in the tetracoordinated environment (see Figure 4). As observed in previous copper dynamic interlocked molecules, whereas the translational movement of the unstable Cu^{I} pentacoordinated specie is very fast in the measurement timescale, the rearrangement of tetracoordinated Cu^{II} occurs at lower rates.[17, 24, 49] Making use of the working curve reported by Nicholson and Shain,[50] a value for the rate constant, associated to the limiting tetracoordinated Cu^{II} reorganization, of k = 2 s^{-1} could be calculated from the peak intensity ratios of the waves associated to the Cu centre in the tetracoordinated environment. This shuttling rate is comparable to that of the fastest copper shuttling rotaxane reported to date.[19] Using the same procedure, the evaluation of the rate constant in different dichlorometane/acetronitrile mixtures afforded values of k = 1 and 0.6 s^{-1} for 1:1 and 9:1 dichloromethane/acetonitrile mixtures, respectively. From these data it is evident that increasing the proportion of the more coordinating solvent (acetonitrile) leads to higher kinetic rates. This observation seems to indicate that acetonitrile molecules stabilize more effectively the coordinatively unsaturated Cu^{II} intermediate formed during the gliding of the macrocycle to the pentacoordinated site, thus enhancing the kinetics of the process.[51] The ^{1}H NMR spectra of rotaxane **1**(PF_6) also reflects the higher lability of the Cu^{I} complex in 1:9 dichloromethane/acetonitrile mixtures in comparison with pure dichloromethane (see Supporting Info.). Despite proton signals coming from the terpy moiety retain their position in acetonitrile mixtures, phen signals appear broadened due to the establishment of a fast ligand exchange with acetonitrile molecules.

The influence of the spacer connecting the phen and terpy units, on the motion of copper-complexed molecular shuttles, has been studied before by comparing analogue rotaxane molecules with spacers of aliphatic and aromatic nature.[17, 52] In that case, the aliphatic spacer gave rise to a faster shuttling rate than the aromatic one. This fact was ascribed to the flexibility of the aliphatic chain, since it affords shorter distances between coordination environments. Herein, the rate constant of rotaxane $\mathbf{1}^+$, is more than three orders of magnitude above that reported in the same solvent mixture for a shuttling rotaxane where the dpp and terpy units are linked by an aliphatic spacer. Considering that in previous studies the change on the substitution in one of the bidentate chelates from 2,9-[29] to 3,8-bipy[25] resulted in an approximately 5-fold increase of the rearrangement rate of the tetracoordinated Cu^{II} species, the high rate observed in the shuttling motion of $\mathbf{1}^+$ can be mainly ascribed to the proximity of both coordination sites.

Conclusions

The synthesis and characterization of a shuttling copper-complexed rotaxane $\mathbf{1}^+$ has been reported. In this rotaxane, the axle contains a 3,8-disubstituted 1,10-phenanthroline bidentate chelate directly connected through its 3-position to the 5-position of a 2,2',6',2"-terpyridine unit, whereas the threaded ring contains a 2,9-disubstituted phenanthroline. Threading of the mono-stoppered axle into the ring and capping of the resulting [2]semirotaxane was carried out in one pot by Cu^{I}-templated self-assembly followed by CuAAC-mediated stoppering.

Cyclic voltammetry experiments performed on rotaxane $\mathbf{1}^+$ at different scan rates confirmed the reversible electrochemically-triggered shuttling motion of the ring along the axle. The substitution of the phen in its 3,8- positions and the direct attachment of the phen and terpy coordination sites makes rotaxane $\mathbf{1}^+$ one of the fastest copper-based molecular shuttles. This result evidences the large enhancing effect of the direct attachment of the bidentate and terdentate ligands on the gliding motion of copper-based molecular shuttles. In addition, the evaluation of the kinetic rates in solvent mixtures with different polarity put some evidence on the accelerating effect of acetonitrile molecules on the motion cycle.

Experimental

Materials

All chemicals used were purchased from commercial sources and used without further purification, unless specially mentioned. Anhydrous dichloromethane, acetonitrile and tetrahydrofuran solvents were freshly distilled under argon over the appropriate drying agent (calcium chloride, calcium hydroxide and sodium respectively). Column chromatographies were carried out on silica or alumina gel (60 Å, 230-400 mesh). A lamp equipped with two incandescent bulbs (General Electric, 220 V, 100 W) was used in benzylic bromination reactions.

Measurements

^{1}H NMR spectra were acquired on a Bruker AVANCE DRX 300 spectrometer. The spectra were referred to residual proton-solvent references. Electrospray mass spectra MS(ES) were obtained with a Waters Micromass ZQ spectrometer in the positive ion mode. High-resolution mass spectra HRMS (MALDI) were recorded in a 5800 MALDI TOFTOF (ABSciex) in positive reflector mode. Absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer using quartz 1 cm path length cuvettes.

Electrochemical measurements were performed in a nitrogen glove box using an Autolab PGSTAT 128N potentiostat in a three-electrode electrochemical cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and a silver wire quasi-reference electrode. Supporting electrolytes were prepared from anhydrous dichloromethane and acetonitrile and tetrabutylammonium hexafluorophosphate.

Synthesis and characterization

Macrocycle **M1** was prepared from commercial 1,10-phenanthroline and pentaethylene glycol as described in previous reports.[21] tris(p-*tert*-butylphenyl)-(4-hydroxyphenyl)methane (**3**),[36] 2-(4-(tris(4-*tert*-butylphenyl)methyl)phenoxy)ethan-1-ol[17] and asymmetric bromoterpyridine **6**[37] were prepared as described elsewhere.

5-BROMO-5''-BROMOMETHYL-2,2':6',2''-TERPYRIDINE (4). A mixture of 5-bromo-5''-methyl-2,2':6',2''-terpyridine (**6**) (0.16 g, 0.50 mmol), NBS (0.11 g, 0.60 mmol), dichloromethane (35 mL) and water (35 ml) was irradiated at reflux for 1 day using 100W light bulbs. Then, the solution was basified with Na_2CO_3 0.05 M and the aqueous phase was extracted with dichloromethane (4 x 20 mL). The combined organic phases were washed with aqueous $Na_2S_2O_3$ 15% (2 x 30 mL) and water (60 mL). After drying over Na_2SO_4, the solvent was eliminated under rotary evaporation to yield **4** as a brown solid (0.20 g, 77 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (d, *J*= 2.2 Hz, 1H), 8.70 (d, *J*= 2.2 Hz, 1H), 8.57 (d, *J*= 8.2 Hz, 1H), 8.51 (d, *J*= 8.5 Hz, 1H), 8.46 (d, *J*= 7.9 Hz, 1H), 8.43 (d, *J*= 7.9 Hz, 1H), 7.98 (dd, *J*= 8.5 and 2.2 Hz, 1H), 7.96 (t, *J*= 7.9 Hz, 1H), 7.89 (dd, *J*= 8.2 and 2.2 Hz, 1H), 4.56 (s, 2H).

HRMS (MALDI): *m/z* (%) calcd. for $[C_{16}H_{12}Br_2N_3]^+$: 405.938; found: 405.852 (35) $[MH]^+$.

MOM-PROTECTED (P-HYDROXYPHENYL) BORONIC ACID PINACOL ESTER (7). Chloromethyl methyl ether (0.30 g, 3.6 mmol) was added dropwise over a 0 ^{0}C anhydrous THF solution (5 mL) containing 4-hydroxyphenyl boronic acid pinacol ester (0.50 g, 2.3 mmol) and sodium hydride (60% in mineral oil, 0.12 g, 2.9 mmol). The mixture was stirred at room temperature for 2 h. After this time, addition of water (40 mL) afforded two phases. The aqueous phase was separated and extracted with dichloromethane (4 x 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was eliminated under reduced pressure to yield the pure product as brown oil (0.57 g, 94%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J*= 8.4 Hz, 2H), 7.02 (d, *J*= 8.4, 2H), 5.20 (s, 2H), 3.45 (s, 3H), 1.33 (s, 12H).

MOM-PROTECTED 3-BROMO-8-(P-HIDROXYPHENYL)-1,10-PHENANTHROLINE (5). A toluene (120 mL) solution containing 3,8-dibromo-1,10-phenanthroline (**8**) (2.10 g, 6.2 mmol), MOM-protected boronic ester derivative **7** (1.90 g, 7.4 mmol) and $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol) was added to a degassed aqueous solution of Na_2CO_3 2 M (36 mL) and refluxed under argon at 120 ^{0}C for 3 days. After the addition of water (100 mL), the organic layer was separated and the aqueous layer extracted with dichloromethane (4 x 40 mL). The combined organic phases were washed once again with water, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was chromatographed in a silica column using CH_2Cl_2/MeOH as eluent affording the desired monosubstituted product **5** as a yellow solid (0.82 g, 33%) and followed by the disubstituted derivative as a secondary product.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.40 (d, *J*= 2.2 Hz, 1H), 9.19 (d, *J*= 2.2 Hz, 1H), 8.42 (d, *J*=2.2 Hz, 1H), 8.35 (d, *J*= 2.2 Hz, 1H), 7.89 (d, *J*= 8.6 Hz, 1H), 7.74 (d, *J*= 8.6 Hz, 1H), 7.72 (d, *J*= 8.5 Hz, 2H), 7.23 (d, *J*= 8.5 Hz, 2H), 5.27 (s, 2H), 3.53 (s, 3H).

MS (ES): *m/z* (%): calcd for $[C_{20}H_{15}BrN_2O_2H]^+$: 395.0; found: 395.3 (100) $[MH]^+$.

Elemental Analysis calcd for $C_{20}H_{15}BrN_2O_2$: C, 60.78; H, 3.83; N, 7.09; found: C, 61.20; H, 4.14; N, 6.74.

MOM-protected 3,8-bis(*p*-methoxyphenyl)-1,10-phenanthroline (disubstituted derivative)

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.40 (d, *J*= 2.3 Hz, 2H), 8.35 (d, *J*= 2.3 Hz, 2H), 7.87 (s, 2H), 7.73 (d, *J*= 8.7 Hz, 4H), 7.23 (d, *J*= 8.7 Hz, 4H), 5.27 (s, 4H), 3.53 (s, *6*H).

STOPPERED BROMO TERPYRIDINE DERIVATIVE 9. A mixture of tris(p-*tert*-butylphenyl)-(4-hydroxyphenyl)methane (**3**) (0.76 g, 1.5 mmol), 5-bromo-5''-bromomethyl-2,2':6',2''-terpyridine (**4**) (0.59 g, 1.45 mmol), anhydrous K_2CO_3 (2.1 g, 15.0 mmol) and anhydrous DMF (40 mL) was heated at 80 ^{0}C for 20 h. The warm mixture was filtered to remove the excess of K_2CO_3 and the DMF was evaporated under reduced pressure to afford a solid which was redissolved in dichloromethane (60 mL). The organic layer was washed with water (4 x 15 mL) and dried over Na_2SO_4. Evaporation of the solvent yielded a solid which was chromatographed over silica gel using CH_2Cl_2/MeOH as eluent (White solid. 0.98 g, 55%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (d, *J*= 1.9 Hz, 1H), 8.75 (d, *J*= 1.9 Hz, 1H), 8.62 (d, *J*= 8.2 Hz, 1H), 8.57 (d, *J*= 8.4 Hz, 1H), 8.51 (d, *J*= 7.5 Hz, 1H), 8.45 (d, *J*= 7.5 Hz, 1H), 8.03-7.95 (m, 3H), 7.24 (d, *J*= 8.6 Hz, 6H), 7.13 (d, *J*= 8.9 Hz, 2H), 7.08 (d, *J*= 8.6 Hz, 6H), 6.87 (d, *J*= 8.9 Hz, 2H), 5.15 (s, 2H), 1.30 (s, 27H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 150.3, 148.5, 144.2, 140.7, 139.7, 138.3, 132.6, 130.9, 124.2, 122.7, 121.7, 121.4, 113.5, 67.4, 63.2, 34.5, 31.5.

HRMS (MALDI): *m/z* (%) calcd. for $[C_{35}H_{55}BrN_4O]^+$: 828.353; found: 828.364 (65) $[MH]^+$.

STOPPERED BORYL TERPYRIDINE DERIVATIVE 10. A degassed mixture of **9** (0.41 g, 0.49 mmol), bis(neopentyl glycolato)diboron (0.12 g, 0.55 mmol), [$PdCl_2$(dppf)ferrocene]

(12 mg, 0.015 mmol) and anhydrous DMSO (15 mL) was stirred under argon at 80 ^{0}C during 5 h. The insoluble precipitate was removed by filtration. Dichloromethane (100 mL) was added and the organic layers were washed with water (4 x 25 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting red solid was recrystallized from a CH_2Cl_2/EtOH mixture to yield **10** as a white solid (0.21 g, 49%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.03 (d, *J*=1.7 Hz, 1H), 8.74 (d, *J*=1.7 Hz, 1H), 8.66 (d, *J*= 8.2 Hz, 1H), 8.57 (dd, *J*= 7.9 and 0.8 Hz, 1H), 8.50 (dd, *J*= 7.9 and 0.8 Hz, 1H), 8.45 (dd, *J*=7.9 and 0.8 Hz, 1H), 8.21 (dd, *J*=7.9 and 1.7 Hz, 1H), 7.98-7.94 (m, 2H), 7.24 (d, *J*= 8.7 Hz, 6H), 7.11 (d, *J*= 9.0 Hz, 2H), 7.08 (d, *J*= 8.7 Hz, 6H), 6.87 (d, *J*= 9.0 Hz, 2H), 5.14 (s, 2H), 3.82 (s, 4H), 1.30 (s, 27H); 1.06 (s, 6H).

HRMS (MALDI): *m/z* (%) calcd. for $[C_{58}H_{65}BN_3O_3]^+$: 862.512; found: 862.519 (100) $[MH]^+$.

MOM-PROTECTED THREAD 11. A degassed mixture of MOM-protected phenanthroline **5** (65 mg, 0.17 mmol), terpyridine derivative **10** (15 mg, 0.17 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), K_2CO_3 (230 mg, 1.6 mmol), water (0.4 mL) and DMF (8 mL) was heated under argon at 80 ^{0}C for 20 h. After evaporation of the solvents, 30 mL of water were added and the mixture was submerged in an ultrasound bath for at least 2 h. The suspended solid was filtered, washed with water (20 mL), dried and further purified by silica gel column chromatography using CH_2Cl_2/ MeOH as eluent to obtain the pure product as a pale yellow solid (0.049 g, 28%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.50 (d *J*= 2.1 Hz, 1H), 9.44 (d, *J*= 2.1 Hz, 1H), 9.13 (d, *J*= 1.7 Hz, 1H), 8.81 (d, *J*= 8.3 Hz, 1H), 8.78 (d, *J* = 1.7 Hz, 1H), 8.69 (d, *J* = 8.1 Hz, 1H), 8.57-8.45 (m, 3H), 8.37 (d, *J*= 2.1 Hz, 1H), 8.26 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.02 (t, J = 7.9 Hz, 1H), 7.97 (dd, *J*= 8.1 and 1.7 Hz, 1H), 7.94 (s, 2H), 7.75 (d, *J*= 8.9, 2H), 7.26 – 7.20 (m, 8H), 7.13 (d, *J* = 8.7, 2H), 7.09 (d, *J* =8.7 Hz, 6H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.27 (s, 2H), 5.15 (s, 2H), 3.53 (s, 3H), 1.30 (s, 27H).

HRMS (MALDI): *m/z* (%): calcd for $[C_{73}H_{71}N_5O_3]^+$: 1064.548; found: 1064.427 (50) $[MH]^+$.

DEPROTECTED THREAD 12. MOM-protected thread **11** (0.35 g, 0.33 mmol)**,** carbon tetrabromide (0.22 g, 0.66 mmol) and anhydrous 2-propanol (40 mL) were placed in a round-bottom flask and irradiated at reflux for 15 min using 100 W light bulbs. Then the reaction mixture was heated at reflux overnight. After that, addition of 10 mL of dichloromethane the mixture was washed with a *pH* 6 NH_4Cl buffer solution (2 x 20 mL) and water (2 x 20mL). Finally, evaporation of the solvents afforded the pure product as a yellow solid (0.28 g, 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (d, *J* = 2.2 Hz, 1H), 9.43 (d, *J* = 2.2 Hz, 1H), 9.14 (d, *J* = 1.6 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.77 (d, J = 1.6 Hz, 1H), 8.69 (d, *J* = 8.2 Hz, 1H), 8.58 – 8.47 (m, 3H), 8.38 (d, *J* = 2.2 Hz, 1H), 8.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.04-7.96 (m, *2*H), 7.93 (s, 2H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.26 – 7.20 (m, 8H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 6H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.16 (s, 2H), 1.30 (s, 27H).

ETHYNYL-TERMINATED THREAD 2. Sodium hydride (60 % dispersion in mineral oil, 0.26 g, 0.66 mmol) was added over a solution of **12** (0.34 g, 0.33 mmol) in anhydrous THF (20 ml). After stirring for 10 min, 20 equiv of propargyl bromide (80 wt. % solution in toluene, 0.70 mL, 0.66 mmol) were added. The mixture was stirred under argon at 45 ^{0}C for 5 days. Evaporation of the solvent afforded an orange solid that was suspended in water, filtered, washed with some more water, hexane and finally a 1:1 mixture of hexane/ diethyl ether. The resulting brownish solid was purified by alumina column chromatography using CH_2Cl_2/ MeOH as eluent affording a pale yellow solid (0.28 g, 80%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (d, *J* = 2.3 Hz, 1H), 9.45 (d, *J* = 2.3 Hz, 1H), 9.14 (d, *J* = 2.3 Hz, 1H), 8.82 (d, *J*= 8.3 Hz, 1H), 8.77 (d, *J* = 1.9 Hz, 1H), 8.68-8.49 (m, 3H), 8.39 (d, *J* = 2.3 Hz, 1H), 8.27 (dd, *J* = 8.3 and 2.3 Hz, 1H), 8.01 (t, *J*= 7.8 Hz, 1H), 7.97 (dd, *J*= 7.9 and 1.9 Hz, 1H), 7.93 (s, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 6H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 6H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.16 (s, 2H), 4.80 (d, *J* = 2.4 Hz, 2H), 2.58 (t, *J* = 2.4 Hz, 1H), 1.30 (s, 27H).

HRMS (MALDI): *m/z* (%): calcd for $[C_{74}H_{68}N_5O_3]^+$: 1058.537; found: 1058.525 (20) $[MH]^+$.

MESYLATE-FUNCTIONALIZED STOPPER 13. Triethylamine (13 mL) and methanesulfonyl chloride (0.62 mL, 8.0 mmol) were added dropwise to a stirred solution of 2-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)ethan-1-ol (1.13 g, 2.00 mmol) in dry dichloromethane (20 mL) at 0 ^{0}C. The mixture was stirred for 2 h at 0 ^{0}C, and then it was allowed to reach room temperature overnight. The resulting organic solution was washed with water (4 x 40mL), dried over Na_2SO_4, and concentrated under reduced pressure to obtain the pure product as a white solid (1.19 g, 93%) without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.5 Hz, 6H), 7.11 (d, J = 8.9 Hz, 2H), 7.07 (d, J = 8.5 Hz, 6H), 6.76 (d, J = 8.9 Hz, 2H), 4.59 – 4.53 (m, 2H), 4.25 – 4.19 (m, 2H), 3.08 (s, 3H), 1.30 (s, 27H).

Elemental Analysis calcd for $C_{40}H_{50}O_4S$: C, 76.64; H, 8.04; S, 5.11; found: C, 75.56; H, 8.36; S, 5.44.

AZIDE-FUNCTIONALIZED STOPPER 14. A mixture of **13** (0.38 g, 0.62 mmol) and NaN_3 (0.20 g, 3.10 mmol) was dissolved in 10 mL of DMF and stirred at 50 ^{0}C for 24 h. After evaporation of the solvent, the resulting solid was dissolved in dichloromethane. The organic layer was washed with water (3 x 30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure affording a white solid that was purified by silica gel column chromatography using hexane/CH_2Cl_2 to yield **14** as a white solid (0.27 g, 74%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 6H), 7.09 (m, 8H), 6.78 (d, *J* = 9.0 Hz, 2H), 4.13 (t, *J* = 6.0 Hz, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 1.30 (s, 27H).

MS (ES): *m/z* (%): calcd for $[MNH_4]^+$: 591.4; found: 591.4 (100) $[MNH_4]^+$.

Elemental Analysis calcd for $C_{39}H_{47}N_3O$: C, 81.63; H, 8.26; N, 7.32; found: C, 81.22; H, 8.04; N, 6.93.

SHUTTLING ROTAXANE, 1(PF_6). A solution of $[Cu(CH_3CN)_4](PF_6)$ (37 mg, 0.10 mmol) in dry degassed acetonitrile (5 mL) was added to a degassed solution of macrocycle **M1** (57 mg, 0.10 mmol) in dichloromethane (5 mL). After 30 minutes of stirring under argon, a degassed solution of ethynyl-terminated thread **2** (11 mg, 0.10 mmol) in dichloromethane (8 mL) was added via cannula. The mixture turned immediately into dark red and was left to react for another 30 minutes. After that time the solvents were removed under reduced pressure. Azide stopper **14** (0.072 g, 0.125 mmol), Na_2CO_3 (0.003 g, 0.025 mmol) and sodium ascorbate (0.020 g, 0.1 mmol) were added to the remaining solid and the mixture was dissolved in degassed dichloromethane (4 mL). In a separated flask, CuBr (3.7 mg 0.025 mmol) and Me_6Tren (7 µL, 0.025 mmol) were heated in degassed acetonitrile (2 mL) at 60 ^{0}C for 30 minutes. The resulting green solution was added via cannula to the reaction mixture. After 7 days of stirring under argon at room temperature the crude was treated with 5 mL of aqueous KCN (30 mg, 0.46 mmol) and some more dichloromethane (10 mL). After vigorous stirring for 4 hours, the phases were separated and the organic layer was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by silica column chromatography using CH_2Cl_2/ MeOH as eluent affording unthreaded axle **18** (57 mg, 13%) as a by-product. The rest of the material was remetallated in a degassed mixture of dichloromethane (2 mL) and acetonitrile (1 mL) with $[Cu(CH_3CN)_4](PF_6)$ (19 mg, 0.05 mmol). After 1 hour of stirring the solvents were evaporated under reduced pressure and the resulting solid was purified by silica gel column chromatography using CH_2Cl_2/ MeOH to afford pure rotaxane **1**(PF_6) as a brown solid (72 mg, 11%).

1(PF_6). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.04 (s, 1H), 8.97 (s, 1H), 8.86 (d, J = 8.1 Hz, 1H), 8.78 (s, 1H), 8.74 – 8.64 (m, 4H), 8.59 – 8.47 (m, 4H), 8.40-8.22 (m, 3H), 8.20-8.10 (m, 4H), 8.10-7.96 (m, 2H), 7.93 (s, 1H), 7.64 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.6 Hz, 4H), 7.32 – 7.10 (m, 30H), 6.92 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 5.94 (d, J = 8.6 Hz, 4H), 5.26 (s, 2H), 5.16 (s, 2H), 4.78 (t, J = 4.8 Hz, 2H), 4.37 (t, J = 4.9 Hz, 2H), 3.81 (s, 4H), 3.76-3.66 (m, 4H), 3.65-3.55 (m, 4H), 3.50-3.35 (m, 8H), 1.31 (s, 27H), 1.29 (s, 27H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.0, 159.5, 158.6, 156.3, 149.0, 145.0, 144.9, 144.0, 141.4, 141.1, 141.0, 136.8, 132.6, 131.0, 130.9, 129.4, 129.3, 124.9, 116.4, 114.1, 113.8, 71.7, 71.3, 71.2, 69.4, 67.7, 66.9, 63.7, 62.5, 50.5, 34.8, 31.6.

HRMS (MALDI): m/z (%) calcd. for $[CuC_{147}H_{148}N_{10}O_9]^+$: 2261.08; found: 2261.04 (15) $[M]^+$.

Molecular thread **16**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (d, J = 2.5 Hz, 1H), 9.44 (d, J = 2.2 Hz, 1H), 9.14 (d, J = 1.4 Hz, 1H), 8.81 (d, J = 8.3 Hz, 1H), 8.77 (d, J = 1.6 Hz, 1H), 8.68 (d, J = 8.1 Hz, 1H), 8.55 (d, J = 7.8 Hz, 1H), 8.53 – 8.47 (m, 3H), 8.38 (d, J = 2.3 Hz, 1H), 8.27 (dd, J = 8.3, 2.3 Hz, 1H), 8.01 (t, J = 7.8 Hz, 2H), 7.97 (dd, J = 8.0, 2.1 Hz, 1H), 7.93 (s, 2H), 7.74 (dd, J = 8.8, 1.4 Hz, 2H), 7.23 (m, 12H), 7.15-7.05 (m, 18H), 6.89 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 9.0 Hz, 2H), 5.27 (s, 2H), 4.79 (t, J = 4.8 Hz, 2H), 4.35 (t, J = 4.8 Hz, 2H), 1.30 (s, 27H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 155.7, 150.7, 148,5, 144.1, 141.0, 140.6, 138.3, 132.6, 132.5, 130.9, 130.8, 128.9, 124.2, 121.6, 115.9, 113.5, 113.2, 67.5, 66.4, 63.2, 50.1, 34.4, 31.5.

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