DOI: 10.1002/ejoc.200900642

# Towards Allosteric Receptors – Synthesis of Resorcinarene-Functionalized 2,2′-Bipyridines and Their Metal Complexes

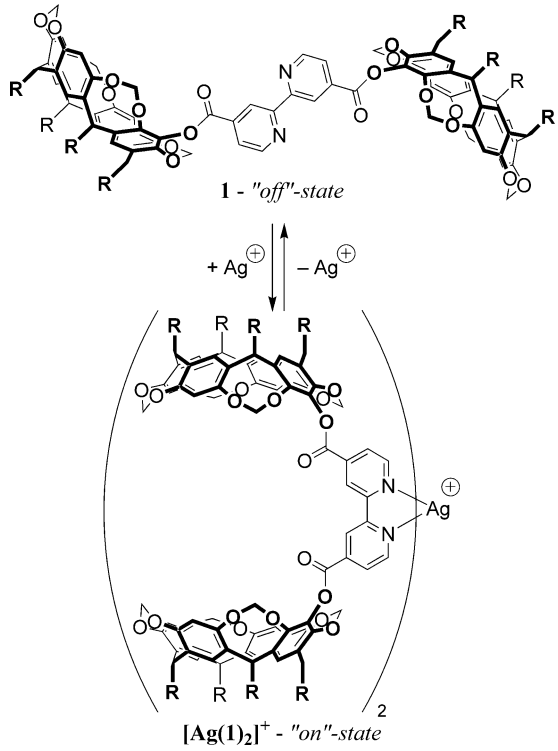
**Holger Staats,[a] Friederike Eggers,[b] Oliver Haß,[a] Frank Fahrenkrug,[b] Jens Matthey,[a] Ulrich Lüning,*[b] and Arne Lützen*[a]**

**Keywords:** Macrocycles / Calixarenes / Nitrogen heterocycles / Supramolecular chemistry / Allosteric receptors

Based on a first example of an allosteric hemicarcerand (**1**) we prepared four new 2,2′-bipyridines that carry resorcinarene moieties in a highly convergent manner. Upon coordination to suitable transition metal ions or their complexes these compounds undergo conformational changes in a way that they switch between "*open*" and "*closed*" forms (**2**, **3**, and **4**) or vice versa (**5**), thus, bringing together or separating the two functional moieties on the central bipyridine. Among the transition metal complexes that act as effectors for the conformational switching, $[Re(CO)_5Cl]$ and monomeric copper(I) complexes of sterically hindered 2,9-arylated 1,10-phenanthrolines proved to be very effective.


## Introduction

The transfer of principles of regulating mechanisms such as allosteric effects or self-assembly processes to artificial systems is both challenging and promising.[1] Our approach aims at the use of coordination to metal centers to achieve the formation of sophisticated supramolecular architectures or change their conformation in a defined manner in order to control a specific functional property.[2] The latter one can be achieved by employing cooperative effects in the selective association of more than one substrate to different binding sites of a single receptor.[1b] These trigger conformational rearrangements that switch on or off some function that is intrinsically embedded in different parts of the molecule, but which have to be specially arranged in space for an optimized cooperative action. Some time ago we were able to develop a heterotropic positive cooperative allosteric analogon (**1**)[3] of the well known resorcinarene-based container molecules, also called carcerands and hemicarcerands.[4] Its recognition behaviour towards non-polar substrates like the adamantyl ester of adamantyl carboxylic acid can be changed dramatically upon coordination of a transition metal ion as an effector or modulator to the central 2,2′-bipyridine unit which serves as an allosteric center (Scheme 1).[5]



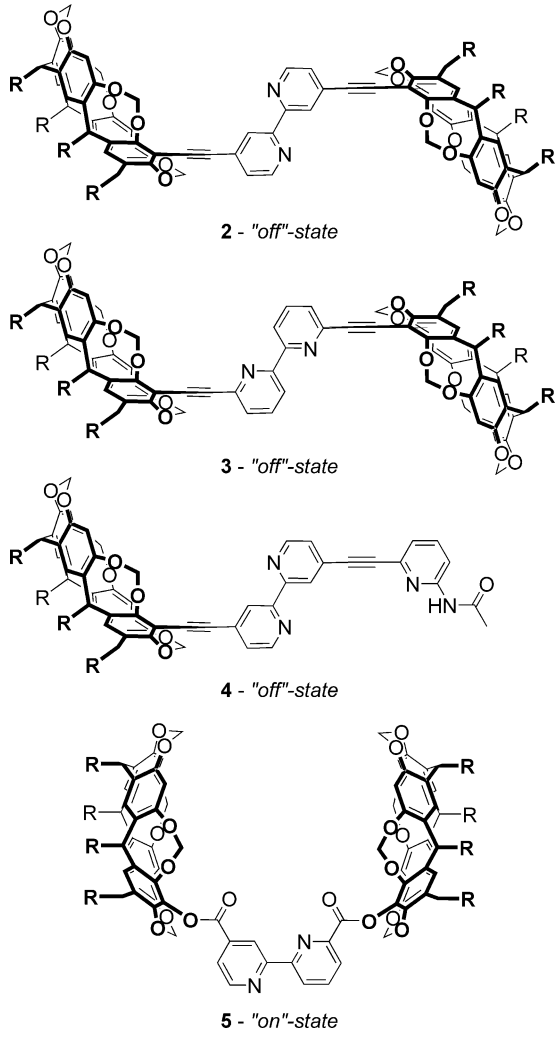

Scheme 1. "*On*"- ("*closed*") and "*off*"-*states* ("*open*") of allosteric receptor **1** (**1a** R = $C_5H_{11}$; **1b** R = $C_{11}H_{23}$).

After having performed a conceptional theoretical study on the influence of different substituents and substitution patterns on the energetics of the conformational switching of 2,2′-bipyridines between their *syn*- and *anti*-conformation,[6] we now took this approach a step further. In this

[a] Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn,
Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
Fax: +49-228-73-9608
E-mail: arne.luetzen@uni-bonn.de
[b] Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel,
Olshausenstr. 40, 24098 Kiel, Germany
Fax: +49-431-880-1558
E-mail: luening@oc.uni-kiel.de

account we report on the synthesis of a series of four new resorcinarene-functionalized 2,2′-bipyridines **2**–**5** (Scheme 2) and their metal complexes.




Scheme 2. Next generation of resorcinarene-functionalized 2,2′-bipyridines **2**–**5** (R = alkyl chains).

## Results and Discussion

Like **1**, the new receptors **2**, **3**, and **4** were all designed to act as heterotropic positive cooperative allosteric systems (Scheme 2). **1** and **2** differ in the linker group between the resorcinarenes and the bipyridine: whereas **1** has ester groups we employed ethynylene groups in **2**. **2** and **3** are constitutional isomers which leads to an important conceptional difference between them: in **1** and **2** the substrate and the effector binding sites are on different sides of the 2,2′-bipyridine due to its 4,4′-substitution pattern. However, a change of the substitution pattern from 4,4′ to 6,6′ in **3** leads to a situation where the binding sites of the substrate and the effector are now on the same side of the bipyridine thus bringing them in close contact.

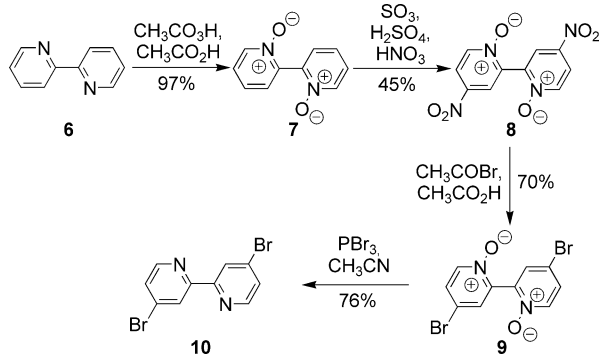
**4**, however, is a first example where we exchange one of the resorcinarene moieties against an acetylated aminopyridyl group to get a heterotopic system that offers two different binding sites for different functionalities of a substrate. Whereas the resorcinarene group has an affinity for non-polar alkyl or aryl groups the aminopyridine offers a hydrogen bonding pattern to bind polar groups like carboxylic acids.

Finally, **5** again has a different substitution pattern of the 2,2′-bipyridine. This leads to yet another concept because **5** is our first example designed to act as a heterotropic, negative cooperative allosteric system because coordination of the effector switches the conformation from a closed "*on*" to an open "*off*" form.

### Synthesis

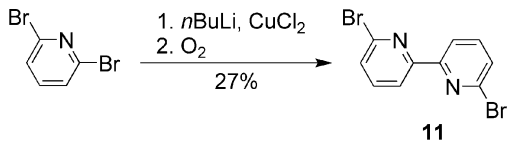
The synthesis of **2**–**5** requires 2,2′-bipyridine building blocks that are either symmetrically (4,4′- or 6,6′-) or non-symmetrically 4,6′-disubstituted. Furthermore, they all need a monofunctionalized resorcin[4]arene. In addition, **4** also needs the preparation of an acetylated aminopyridine building block that can be coupled to the 2,2′-bipyridine.

4,4′-Dibromo-2,2′-bipyridine (**10**) was obtained in a four step synthesis starting from 2,2′-bipyridine (**6**) (Scheme 3). Adapting a protocol of Sheldon et al. developed for the synthesis of 4,4′-dichloro-2,2′-bipyridine[7] 2,2′-bipyridine was converted into the corresponding bis(*N*-oxide) **7** upon reaction with peracetic acid. **7** was then subjected to a two-fold nitration followed by nucleophilic substitution and removal of the oxygen atoms to give **10** in an overall yield of 23%.




Scheme 3. Synthesis of 4,4′-dibromo-2,2′-bipyridine (**10**).

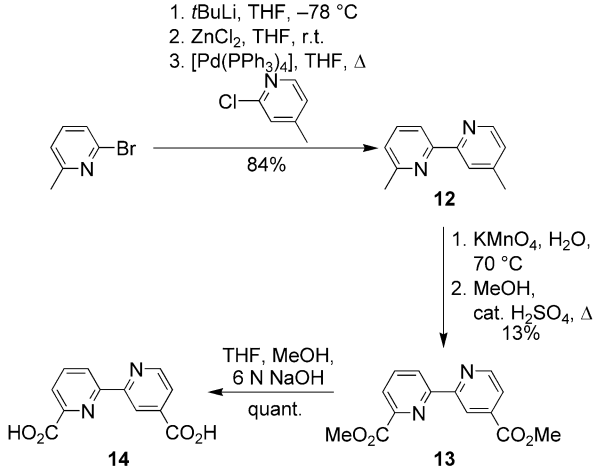
6,6′-Dibromo-2,2′-bipyridine (**11**) was prepared in moderate yield of 29% starting from commercially available 2,6-dibromopyridine in a copper-mediated Ullmann-like coupling reaction (Scheme 4) introduced by Holm et al. in 1973[8] and modified by Butler and Soucy-Breau.[9]




Scheme 4. Synthesis of 6,6′-dibromo-2,2′-bipyridine (**11**).

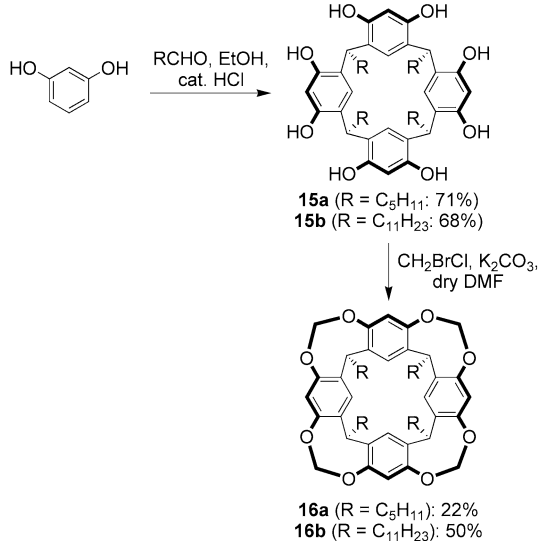
  

2,2′-Bipyridine-6,6′-dicarboxylic acid (**14**) was obtained in four steps starting from commercially available 2-chloro-4-methylpyridine and 2-bromo-6-methylpyridine (Scheme 5). Modified Negishi cross-coupling[10] of the two pyridines gave the corresponding dimethylated 2,2′-bipyridine **12** which was converted into the dicarboxylic acid **14** upon oxidation with potassium permanganate. Unfortunately, this compound is very insoluble in common organic solvents. Since the reaction did not work too well we had to transform crude **14** into the corresponding dimethyl ester **13** in order to isolate and purify it in this form which is the reason for the low yield. Subsequent saponification allowed isolation of the dicarboxylic acid **14**.



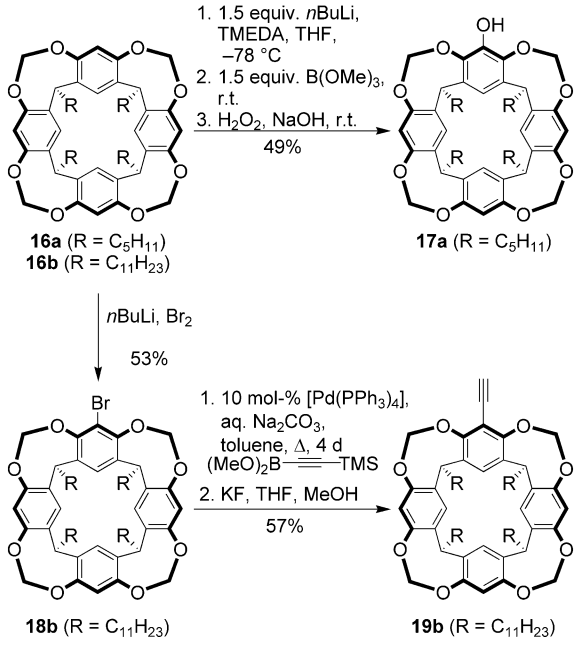

Scheme 5. Synthesis of 2,2′-bipyridine-6,6′-dicarboxylic acid (**14**).

Monohydroxylated and monoethynylated resorcinarenes **17** and **19** could both be prepared from non-functionalized cavitand **16** which could be synthesized in two steps from resorcinol (Scheme 6).[11,12]



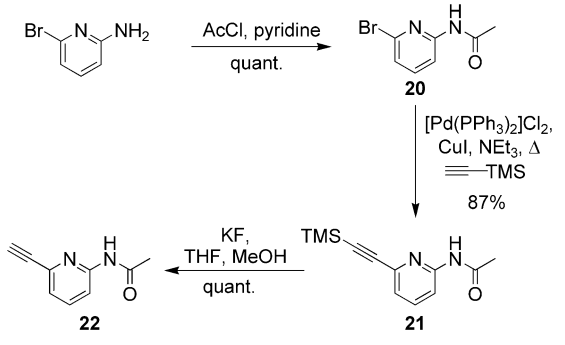

Scheme 6. Synthesis of cavitand **16**.

As shown in Scheme 7, monolithiation of **16** can then be used to introduce a number of functional groups as, for example, a hydroxy group (**17**, via borylation) or a bromine atom (**18**).[13] Interestingly, all Sonogashira as well as Negishi protocols that we tested to prepare the ethynylated cavitand **19** failed. However, its synthesis could finally be achieved by applying Suzuki cross-coupling conditions to the reaction of **18** with TMS-protected acetylene boronic acid dimethyl ester.[13]




Scheme 7. Synthesis of monofunctionalized cavitands **17**–**19**.

The aminopyridine building block **22** could be prepared in three steps starting from commercially available 2-amino-6-bromopyridine (Scheme 8). For this purpose, the amino group was first acetylated before we introduced the TMS-protected ethynyl group via Sonogashira cross-coupling. Final fluoride-mediated deprotection of the silyl group gave **22** in excellent overall yield.

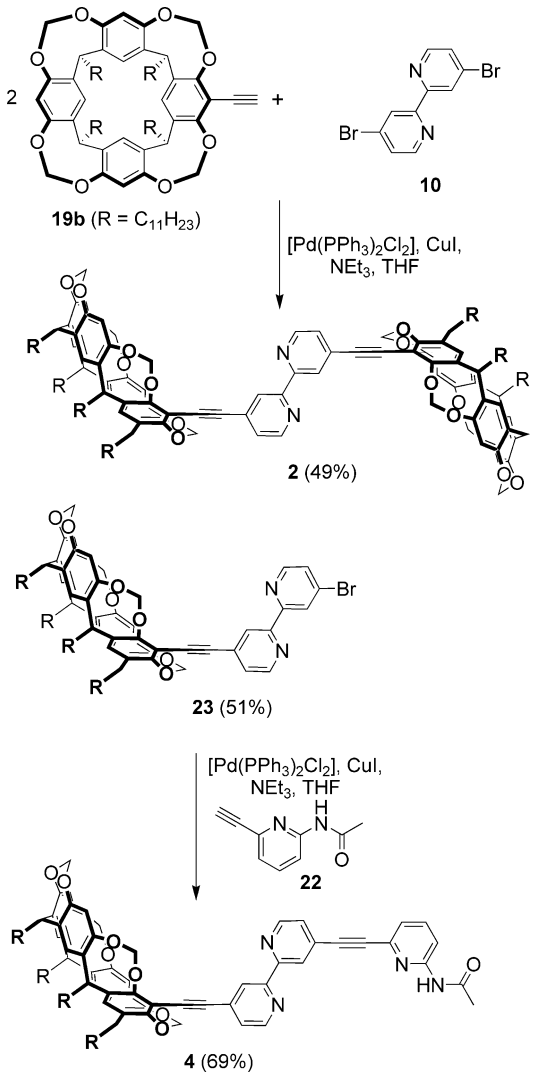



Scheme 8. Synthesis of 2-*N*-acetylamino-6-ethynylpyridine **22**.

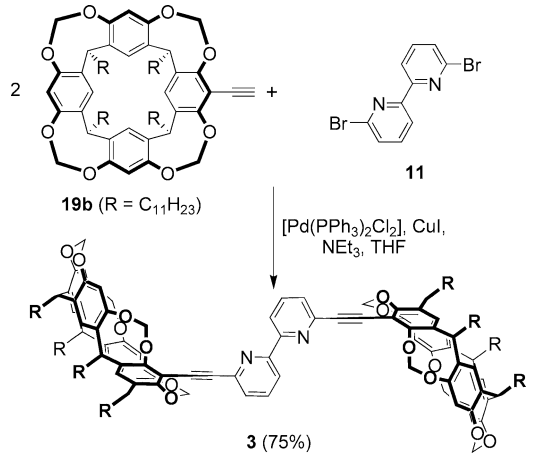
Sonogashira cross-coupling of 4,4′-dibromo-2,2′-bipyridine (**10**) with ethynylated cavitand **19** gave target compound **2** together with singly coupled bipyridine **23** which

could both be isolated in acceptable yields of 49% and 51%, respectively.[14] **23** could be used directly for a second Sonogashira reaction with **22** to yield **4** (Scheme 9).



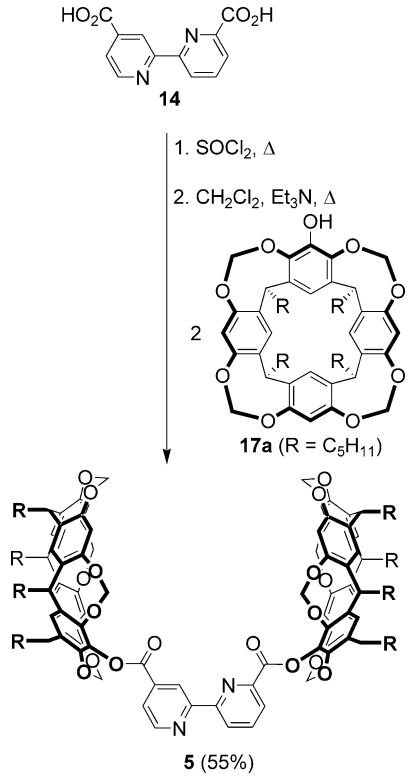

Scheme 9. Synthesis of resorcinarene-functionalized 2,2′-bipyridines **2** and **4**.




Scheme 10. Synthesis of resorcinarene-functionalized 2,2′-bipyridine **3**.

Target compound **3** was prepared in a similar way in a twofold Sonogashira reaction of resorcinarene **19** and bipyridine **11** in a very good yield of 75% (Scheme 10).

In order to activate dicarboxylic acid **14** for a twofold esterification it was transformed into the corresponding dicarboxylic acid dichloride by reaction with thionyl chloride and reacted without purification with hydroxylated cavitand **17** to give target compound **5** in 55% isolated yield (Scheme 11).




Scheme 11. Synthesis of resorcinarene-functionalized 2,2′-bipyridine **5**.

## Metal Coordination

Having achieved the synthesis of our resorcinarene-functionalized 2,2′-bipyridine ligands we studied their coordination behaviour towards a number of different transition metal ions or complexes thereof. In our initial study[3] silver(I) and copper(I) tetrafluoroborates were used to prepare metal complexes $[M\mathbf{1}_2]BF_4$. As expected these salts do also form stable complexes with our new ligands **2**–**5** as proven by NMR spectroscopy and ESI mass spectrometry. However, only **2** and **4** having the same substitution pattern of the central 2,2′-bipyridine as **1** do also form complexes of the same 1:2 metal-to-ligand stoichiometry as **1**. Changing the substitution pattern from 4,4′ to 6,6′ or 4,6′ like in **3** and **5** makes it impossible to form a 1:2 complex due to steric crowding. Thus, in these cases only 1:1 complexes could be observed which seem to carry coordinated solvent molecules to saturate the coordination sphere of the metal ions (Figure 1).

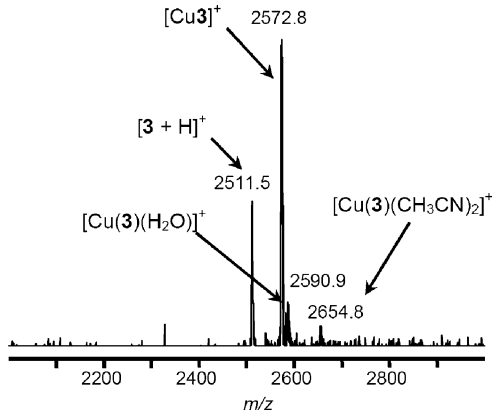



Figure 1. Positive ESI MS of a 1:1 mixture of **3** and $[Cu(CH_3CN)_4]BF_4$ in benzene/acetonitrile, 25:1.

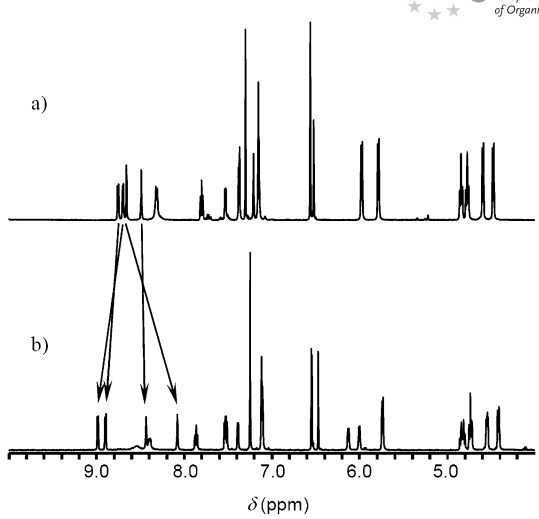
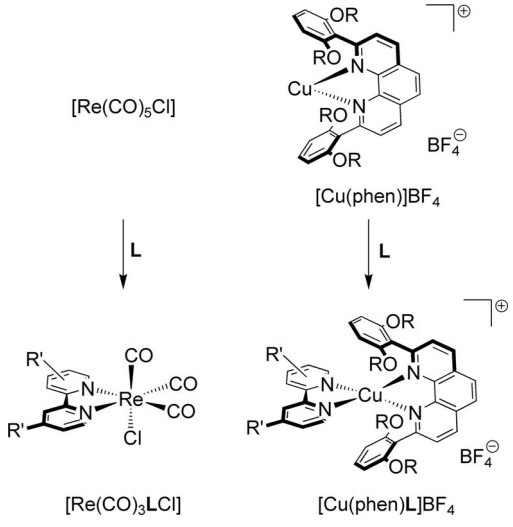



Figure 2. NMR spectra (500.1 MHz in $CDCl_3$ at 298 K) of a) ligand **4** and b) its rhenium complex $[Re(CO)_3(\mathbf{4})Cl]$ (the upfield region containing the alkyl signals is omitted).

The 1:2 metal-to-ligand stoichiometry found in the silver and copper complexes of **2** and **4**, however, is very inconvenient to study the host-guest chemistry of these compounds because this could lead to a very complicated equilibrium between 1:2:2, 1:2:1, 1:2:0 and some more metal-to-ligand-to-substrate assemblies which is very difficult to analyze. Thus, it would be much more convenient if one could selectively form 1:1 metal-to-ligand complexes. This can be achieved with metal complexes that offer only two coordination sites for the complexation of a single 2,2′-bipyridine moiety. Scheme 12 shows two possibilities that we tested in this context.




Scheme 12. Metal complexes that can only bind to a single 2,2′-bipyridine ligand (L = 2,2′-bipyridine ligand): pentacarbonylrhenium chloride (2,2′-bipyridine substitutes two carbonyl ligands) and sterically hindered 1,10-phenanthrolines (phen).

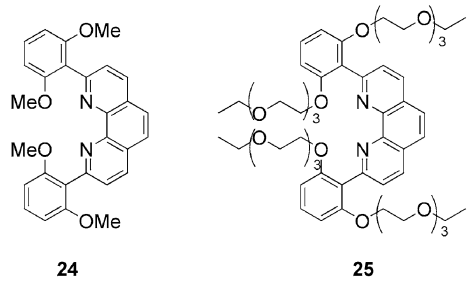
Pentacarbonylrhenium chloride was found to form stable orange 1:1 complexes with our ligands **2**, **4**, and **5** (Figure 2) that could (except for the complex of **5** that was found to undergo degradation when exposed to silica gel) even be purified by column chromatography on silica gel.

However, there are two important differences with the rhenium complex compared to the other effectors: first, due to the strongly coordinating chloride ion the resulting complexes are neutral species and thus should have different properties compared to the other complexes with the hardly coordinating anions that distribute more cationic charge into the ligand structure. Second, the binding of the rhenium to the 2,2′-bipyridine is usually thermodynamically and kinetically very stable so that it is virtually inert and survives even boiling in the presence of a 20-fold excess of even better chelate ligands like 1,10-phenanthroline. Although this is very nice to study the host-guest chemistry of our ligands bound to this effector, it is of course not, if it should act as an allosteric receptor that can be switched on and off several times. The only exception to this is again the rhenium complex of ligand **5**. In this case the rhenium can easily be removed from the ligand by adding EDTA solution.

Therefore, we turned our attention to heteroleptic complexes with two bidentate ligands.[15] If for instance copper(I) ions are mixed with two different bidentate ligands $L^1$ and $L^2$ in a 1:1:1 ratio, three possible complexes can form: two homoleptic complexes $L^1{}_2Cu^+$ and $L^2{}_2Cu^+$ and a heteroleptic complex $L^1L^2Cu^+$. The statistical distribution will be 1:2:1 but the use of sterically hindered ligands will change the composition. When the hindered ligands (e.g. $L^2$) are too large to form a $L^2{}_2Cu^+$ complex, the heteroleptic complex $L^1L^2Cu^+$ will form exclusively even when $L^1{}_2Cu^+$ was quite stable because only the formation of $L^1L^2Cu^+$ ensures that all ligands and all coordination sites of the copper(I) ion are occupied. Therefore, we have used here copper(I) complexes of sterically hindered 1,10-phenanthrolines that have originally been designed to be employed as concave reagents.[16] With these, no 2:1 complexes are formed, and the 1:1 complexes offer two remaining coordination sites for the binding of a single 2,2′-bipyridine. These complexes are very promising since they do also form

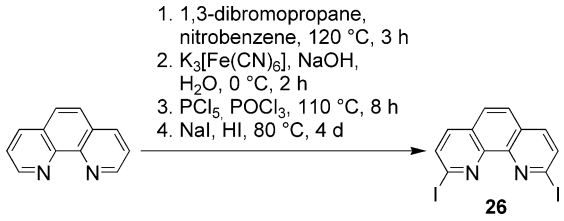
cationic species from which the 2,2′-bipyridine can be cleaved upon addition of an even stronger chelating ligand like another phenanthroline or ethylene diamine tetraacetic acid (EDTA). Furthermore, these compounds offer the possibility to fine-tune e.g. the solubility properties upon chemical modification of the phenanthrolines periphery. Thus, we chose previously prepared sterically hindered 2,9-arylated 1,10-phenanthroline **24**[16b,16l,16m,16n] as a first example. In order to make this compound more soluble in polar solvents like methanol which should be beneficial for the recognition of hardly polar substrates because of additional solvophobic effects, we decided to prepare also a new derivative carrying triethylene glycol chains (**25**) (Scheme 13).




Scheme 13. 2,9-Arylated 1,10-phenanthrolines **24** and **25**.

For the synthesis of **25**, two building blocks were prepared. One was 2,9-diiodo-1,10-phenanthroline (**26**) and the other one the boronic acid **27** which contained *ortho* triethylene glycol chains.

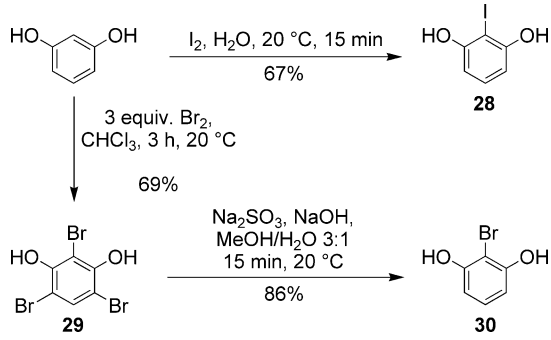
2,9-Diiodo-1,10-phenanthroline **26** was synthesized following the well known procedure described by Lewis et al.[17] and Yamada et al.[18] Starting from 1,10-phenanthroline, first chloro atoms were introduced in positions 2 and 9 (steps 1–3) and then a chloro-iodo exchange was accomplished[16k,19] (Scheme 14).



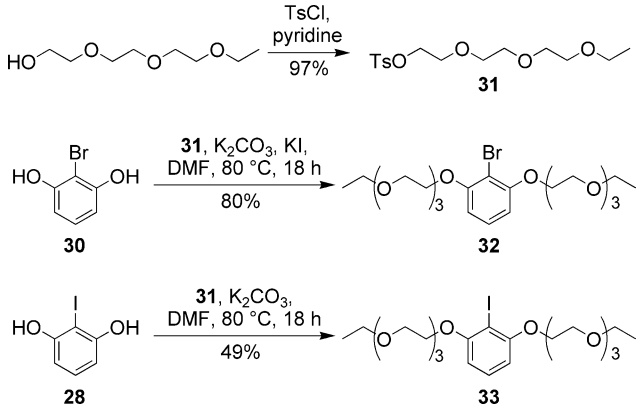

Scheme 14. Synthesis of 2,9-diiodo-1,10-phenanthroline (**26**).

Phenylboronic acid **27** was synthesized starting from resorcinol which was first halogenated with iodine or bromine following literature procedures to yield 2-iodo-[20] and 2-bromoresorcinol[21,22] (**28**) and (**30**) in one and in two steps, respectively, in about 70% (Scheme 15).

The phenol groups of the halogenated resorcinols **28** and **30** were then alkylated using the strategy of Williamson with 3,6,9-trioxaundecyl-(4-methylbenzene)sulfonate (**31**) (Scheme 16) to give triethylene glycolated **32** and **33**. Sulfonate **31** was synthesized from triethylene glycol monoethyl ether following a literature procedure.[23]

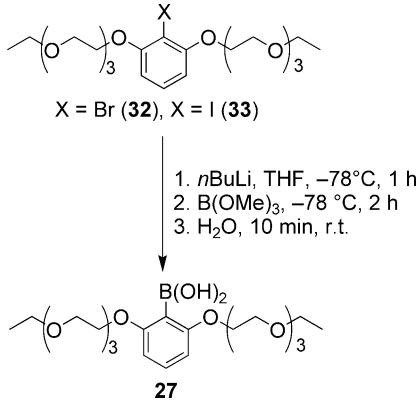



Scheme 15. Synthesis of 2-iodo- (**28**) and 2-bromoresorcinol (**30**).




Scheme 16. Synthesis of triethylene glycolated resorcinols **32** and **33**.

After alkylation, the boronic acid **27** was synthesized by halogen-lithium exchange and work-up with trimethylborate and hydrolysis (Scheme 17).

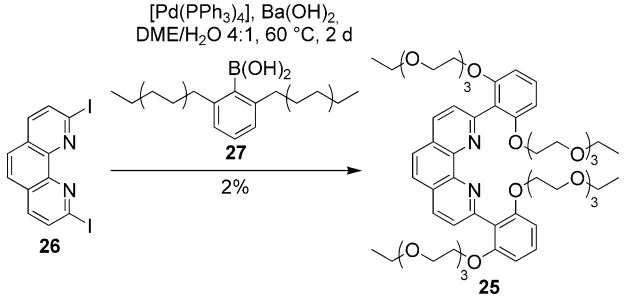



Scheme 17. Synthesis of boronic acid **27**.

Purification of the crude oily product by column chromatography was not successful but resulted in cleavage of the carbon–boron bond to give 1,3-bis(1,4,7,10-tetraoxa dodecyl)benzene (**34**). Therefore, crude **27** was used in the subsequent Suzuki reaction with 2,9-diiodo-1,10-phenanthroline **26** (Scheme 18).[24] The coupling was carried out in a solution of 1,2-dimethoxyethane (DME) and water (4:1) with tetrakis(triphenylphosphane)palladium(0) ([$Pd(PPh_3)_4$]) as catalyst and barium hydroxide as base.[25] Unfortunately,

this reaction turned out to be quite difficult also because monoarylated byproducts (**35** and **36**) were obtained which hampered the purification of **25** even more.




Scheme 18. Synthesis of 2,9-arylated 1,10-phenanthroline **25**.

**24** and **25** were then studied together with ligand **1b** with regard to their ability to form 1:1:1 complexes with copper(I) ions. As **24**, **25** could be proven to form only a 1:1 [Cu(**25**)]$BF_4$ complex with copper(I) ions but no dimeric species. Upon addition of **1b** to solutions of [Cu**24**]$BF_4$ and [Cu**25**]$BF_4$, we observed the almost instant and quantitative formation of [Cu(**24**)(**1b**)]$BF_4$ and [Cu(**25**)(**1b**)]$BF_4$ (Figure 3). As expected addition of an excess of **1b** does not lead to [Cu(**1b**)$_2$]$BF_4$ complexes but the heteroleptic[15] 1:1:1 complexes remained intact.

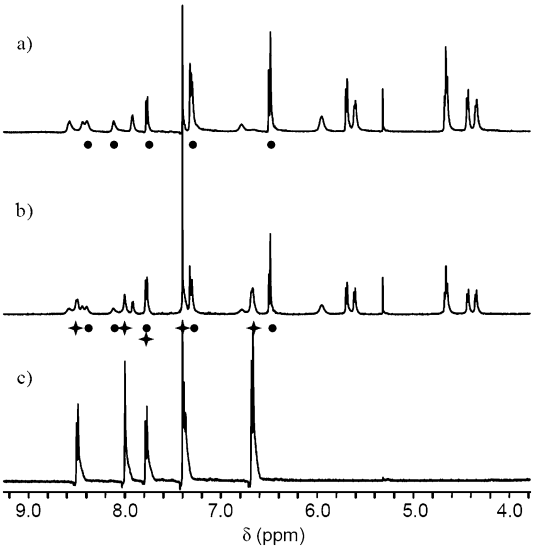



Figure 3. NMR spectra (500.1 MHz in [$D_6$]benzene/[$D_3$]acetonitrile (1:1) at 298 K) of a) a 1:1 mixture of [Cu(**24**)]$BF_4$ and **1b** showing only signals of the [Cu(**24**)(**1b**)]$BF_4$ complex, b) a 1:0.5 mixture [Cu(**24**)]$BF_4$ and **1b** showing signals of both the [Cu(**24**)(**1b**)]$BF_4$ complex and [Cu(**24**)]$BF_4$, and c) [Cu(**24**)]$BF_4$ (the upfield region containing the alkoxy and the alkyl signals is omitted, the star indicate phenanthroline proton signals of the [Cu(**24**)]$BF_4$ complex, the dot indicate phenanthroline proton signals of the [Cu(**24**)(**1b**)]$BF_4$ complex).

## Conclusions

We have synthesised four new resorcinarene-functionalized 2,2′-bipyridines in a highly convergent manner that were designed as potential allosteric receptors. All of these ligands could be demonstrated to bind to different transition metal salts or complexes which causes long-range conformational changes within the ligand structure thus switching between open and closed conformations (**2**, **3**, and **4**) or vice versa (**5**) upon addition of these effectors. Among these [$Re(CO)_5Cl$] and copper(I) complexes of sterically hindered 1,10-phenanthrolines proved to be very efficient to ensure 1:1 metal-to-ligand stoichiometries. We are currently evaluating the host-guest chemistry of these systems which will be reported in due course.

## Experimental Section

**General Remarks:** All solvents were distilled and thoroughly dried prior to use according to standard procedures. All syntheses with air- and moisture-sensitive compounds were performed under Schlenk conditions, with argon as the inert gas. For purification purposes column chromatography on silica gel or on basic alumina was applied. Solvents used as eluents for column chromatography were distilled prior to use. The preparative, centrifugally accelerated, thin-layer chromatograph (Chromatotron) was a model 7924T from Harrison Research. Detection was done under UV light (254 and 366 nm). Gas chromatography was performed with 6890 N (Agilent); split/splitless injector, split ratio 11:1, injector temp. 240 °C, FID detector temp. 250 °C. $^1H$ and $^{13}C$ NMR spectra were recorded at 298 K on a Bruker AC 200 (200 MHz), ARX 300 (300.1 MHz or 75.8 MHz), DMX 400 (400.1 MHz), DRX 500 (500.1 MHz or 125.8 MHz), or Avance 600 (600.1 MHz or 150 MHz) instruments, respectively. $^1H$ NMR chemical shifts are reported as $\delta$ values (ppm) relative to residual non-deuterated solvent as the internal standard. $^{13}C$ NMR chemical shifts are given in $\delta$ values (ppm) relative to the deuterated solvent as the internal standard. Unless otherwise noticed, signals were assigned on the basis of $^1H$, $^{13}C$, H,H-COSY, HSQC or HMQC, and HMBC-NMR experiments. IR spectra were measured on a Perkin–Elmer 1600 Series device. Mass spectra were taken on a Finnigan MAT 212 with data system MMS–ICIS (EI, CI, isobutane, ammonia), a Finnigan MAT 95 with data system DEC-Station 5000 (CI, isobutane or ammonia; HiRes-CI, isobutane or ammonia; FD), an A.E.I. MS-50 (EI; HiRes-EI), a Thermoquest Finnigan LCQ (ESI), a Q-ToF Ultima from Micromass (ESI, HiRes-ESI), a Finnigan MAT 8230 or MAT 8200 (EI, HiRes-EI), or on an Applied Biosystems Mariner ESI-TOF MS 5280 (ESI). Melting points were measured with a hot-stage microscope SM-Lux from Leitz or a SMP-20 from Büchi and are not corrected. Elemental analyses were carried out with a Fisons Instrument EA1108, an EuroVector instrument, or a Heraeus Vario EL. Please note that CHN-analyses could only be conducted with fluorine-free samples. Please also note that it is well known that the cavitand compounds with long alkyl chains generally do not give sufficient elemental analyses because they always contain some traces of solvent molecules. Thus, we did not perform these but give high-resolution MS data instead in most cases. Chemicals and reagents (except for the solvents) obtained from commercial sources were used as received. The following compounds were prepared according to published procedures: bis(resorcinarene)-functionalized 2,2′-bipyridine **1b**,[3] 2,2′-bipyridine *N*,*N*′-dioxide (**7**),[7] 4,4′-dinitro-2,2′-bipyridine *N*,*N*′-dioxide (**8**),[7] 6,6′-dibromo-2,2′-bipyridine (**11**),[9] 4,6′-dimethyl-2,2′-bipyridine (**12**),[10c] resorcin[4]arene **15a** [2,8,14,20-tetrapentylpentacyclo-(19. 3.1$^{3,7}$.1$^{9,13}$.1$^{15,19}$)-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecan-4,6,10,12,16,18,22,24-octol],[26] resorcin[4]-

arene **15b** [2,8,14,20-tetraundecylpentacyclo(19.3.1$^{3,7}$.1$^{9,13}$.1$^{15,19}$)-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecan-4,6,10,12,16,18,22,24-octol],[26] cavitand **16b** (1,21,23,25-tetraundecyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino-[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin),[13] brominated cavitand **18** (7-bromo-1,21,23,25-tetraundecyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]-benzo[1,2-*d*:5,4-*d*′]bis[1,3]-benzodioxocin),[13] ethynylated cavitand **19** (7-ethynyl-1,21,23,25-tetraundecyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin),[13] 2,9-bis[2,6-bis(methoxy)phenyl]-1,10-phenanthroline (**24**),[16a,16b] 2,9-dichloro-1,10-phenanthroline,[17,18] and 2,9-diiodo-1,10-phenanthroline (**26**).[17,18]

**Bis(resorcinarene)-Functionalized 2,2′-Bipyridine 2 and Resorcinarene-Functionalized 2,2′-Bipyridine 23:** A two-neck flask equipped with a septum and a reflux condenser was charged with 57 mg of **10** (0.18 mmol), 430 mg of **19** (0.36 mmol, 2 equiv.), 3.4 mg (18 μmol, 10 mol-%) of copper(I) iodide, and 13.6 mg [$Pd(PPh_3)_2Cl_2$] (10 mol-%) and repeatedly evacuated and flushed with argon. 15 mL of dry triethylamine and 10 mL of dry THF were added via syringe and the resulting mixture was heated to 40 °C for 24 h. After that time 20 mL of diethyl ether were added and the organic phase was washed four times with water and with brine and dried with potassium carbonate. Removing of the organic solvents in vacuo gave the crude product mixture which was subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 5:1 + 0.5% triethylamine) to yield 222 mg of **2** as an amorphous solid (89 μmol, 49%) as well as 130 mg of **23** also as an amorphous solid (92 μmol, 51%).

**2:** $R_f$ = 0.22 (*n*-hexane/ethyl acetate, 5:1 + 0.5% triethylamine). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.64 (d, $^3J$ = 4.9 Hz, 2 H, *bipy*-H), 8.39 (s, 2 H, *bipy*-H), 7.31 (d, $^3J$ = 4.9 Hz, 2 H, *bipy*-H), 7.16 (s, 2 H, *cav*-$H_{aryl}$), 7.11 (s, 4 H, *cav*-$H_{aryl}$), 7.10 (s, 2 H, *cav*-$H_{aryl}$), 6.51 (s, 4 H, *cav*-$H_{aryl}$), 6.48 (s, 2 H, *cav*-$H_{aryl}$), 5.92 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 5.74 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.80 (t, $^3J$ = 8.0 Hz, 4 H, *cav*-$H_{benzyl}$), 4.73 (t, $^3J$ = 8.0 Hz, 4 H, *cav*-$H_{benzyl}$), 4.54 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.43 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 2.30–2.15 (m, 16 H, *cav*-$H_{alkyl}$), 1.50–1.19 (m, 144 H, *cav*-$H_{alkyl}$), 0.88 (t, $^3J$ = 6.5 Hz, 24 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 27.8, 27.9, 29.4, 29.7, 29.8, 29.9, 31.9 (*cav*-$C_{alkyl}$), 36.3 (*cav*-$C_{benzyl}$), 36.4 (*cav*-$C_{benzyl}$), 86.4 ($C_{alkyne}$), 94.6 ($C_{alkyne}$), 99.1 (*cav*-$C_{acetal}$), 99.5 (*cav*-$C_{acetal}$), 111.9 (*cav*-$C_{aryl}$), 116.5 (2× *cav*-$C_{aryl}$), 120.7 (*cav*-$C_{aryl}$), 121.3 (*cav*-$C_{aryl}$), 122.9 (*cav*-$C_{aryl}$), 125.6 (*bipy*-$C_{aryl}$), 132.2 (*bipy*-$C_{aryl}$), 138.2, 138.3, 138.6, 138.7 (4× *cav*-$C_{aryl}$) 149.1 (*bipy*-$C_{aryl}$), 154.7, 154.8, 155.0, 155.6 (4× *cav*-$C_{aryl}$, *bipy*-$C_{aryl}$) ppm. MS (pos. ESI): *m*/*z* (%) = 2508.7 ([MH]$^+$, 100). HiRes-MS (pos. ESI) calcd. for $[C_{166}H_{229}N_2O_{16}]^+$ *m*/*z* = 2508.7234; found *m*/*z* = 2508.7310 (Δ = 3.0 ppm).

**23:** $R_f$ = 0.48 (THF/*n*-hexane, 2:3 + 0.5% triethylamine). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.66 ($^3J$ = 4.4 Hz, 1 H, *bipy*-H), 8.62 (s, 1 H, *bipy*-H), 8.48 (br. s, 2 H, 2× *bipy*-H), 7.50 (d, 1 H, *bipy*-H), 7.31 (d, $^3J$ = 4.4 Hz, 1 H, *bipy*-H), 7.16 (s, 1 H, *cav*-$H_{aryl}$), 7.11 (s, 2 H, *cav*-$H_{aryl}$), 7.10 (s, 1 H, *cav*-$H_{aryl}$), 6.52 (s, 2 H, *cav*-$H_{aryl}$), 6.47 (s, 1 H, *cav*-$H_{aryl}$), 5.92 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 5.74 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 4.79 (t, $^3J$ = 7.7 Hz, 2 H, *cav*-$H_{benzyl}$), 4.73 (t, $^3J$ = 7.7 Hz, 2 H, *cav*-$H_{benzyl}$), 4.54 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 4.43 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 2.29–2.13 (m, 8 H, *cav*-$H_{alkyl}$), 1.49–1.17 (m, 72 H, *cav*-$H_{alkyl}$), 0.88 (t, $^3J$ = 7.2 Hz, 12 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 27.8, 27.9, 29.4, 29.7, 29.8, 29.9, 31.9 (*cav*-$C_{alkyl}$), 36.3 (*cav*-$C_{benzyl}$), 36.4 (*cav*-$C_{benzyl}$), 86.6 ($C_{alkyne}$), 94.5 ($C_{alkyne}$), 99.1 (*cav*-$C_{acetal}$), 99.5 (*cav*-$C_{acetal}$), 111.9 (*cav*-$C_{aryl}$), 116.4, 116.5 (*cav*-$C_{aryl}$), 120.7 (*cav*-$C_{aryl}$), 121.4 (*cav*-$C_{aryl}$), 123.1 (*bipy*-$C_{aryl}$), 124.8 (*bipy*-$C_{aryl}$), 125.9 (*bipy*-$C_{aryl}$), 127.3 (*bipy*-$C_{aryl}$), 132.4 (*bipy*-$C_{aryl}$), 134.1 (*bipy*-$C_{aryl}$), 138.2, 138.3, 138.4, 138.6, 138.7 (5× *cav*-$C_{aryl}$) 149.2 (*bipy*-$C_{aryl}$), 149.8 (*bipy*-$C_{aryl}$), 154.7, 154.8, 155.0, 155.7 (4× *cav*-$C_{aryl}$), 156.5 (2× *bipy*-$C_{aryl}$) ppm. MS (CI, isobutane, pos. mode): *m*/*z* (%) = 1411.8 (100) [MH]$^+$. HiRes-MS (pos. ESI) calcd. for $[C_{88}H_{118}{}^{81}BrN_2O_8]^+$ *m*/*z* = 1411.8081; found *m*/*z* = 1411.8170 (Δ = –6.0 ppm).

**Bis(resorcinarene)-Functionalized 2,2′-Bipyridine 3:** A two-neck flask equipped with a septum and a reflux condenser was charged with 25 mg of **19** (0.08 mmol), 190 mg of **11** (0.16 mmol, 2 equiv.), 1.5 mg (8 μmol, 10 mol-%) of copper(I) iodide, and 6 mg of [$Pd(PPh_3)_2Cl_2$] (10 mol-%) and repeatedly evacuated and flushed with argon. 15 mL of dry triethylamine and 10 mL of dry THF were added via syringe and the resulting mixture was heated to 40 °C for 24 h. After that time 20 mL of diethyl ether were added and the organic phase was washed four times with water and with brine and dried with sodium sulfate. Removing of the organic solvents in vacuo gave the crude product mixture which was subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 5:1 + 0.5% triethylamine) to yield 150 mg of **3** as an amorphous solid (60 μmol, 75%). $R_f$ = 0.10 (*n*-hexane/ethyl acetate, 5:1 + 0.5% triethylamine). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.64 (d, $^3J$ = 4.9 Hz, 2 H, *bipy*-H), 8.39 (s, 2 H, *bipy*-H), 7.31 (d, $^3J$ = 4.9 Hz, 2 H, *bipy*-H), 7.16 (s, 2 H, *cav*-$H_{aryl}$), 7.11 (s, 4 H, *cav*-$H_{aryl}$), 7.10 (s, 2 H, *cav*-$H_{aryl}$), 6.51 (s, 4 H, *cav*-$H_{aryl}$), 6.48 (s, 2 H, *cav*-$H_{aryl}$), 5.92 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 5.74 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.80 (t, $^3J$ = 8.0 Hz, 4 H, *cav*-$H_{benzyl}$), 4.73 (t, $^3J$ = 8.0 Hz, 4 H, *cav*-$H_{benzyl}$), 4.54 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.43 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 2.30–2.15 (m, 16 H, *cav*-$H_{alkyl}$), 1.50–1.19 (m, 144 H, *cav*-$H_{alkyl}$), 0.88 (t, $^3J$ = 6.5 Hz, 24 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 27.8, 27.9, 29.4, 29.7, 29.8, 29.9, 31.9 (*cav*-$C_{alkyl}$), 36.3 (*cav*-$C_{benzyl}$), 36.4 (*cav*-$C_{benzyl}$), 91.6, 94.4 (2× $C_{alkyne}$), 99.1 (*cav*-$C_{acetal}$), 99.5 (*cav*-$C_{acetal}$), 112.0 (*cav*-$C_{aryl}$), 116.6 (2× *cav*-$C_{aryl}$), 120.5 (*bipy*-$C_{aryl}$), 120.7 (2× *cav*-$C_{aryl}$), 121.0 (*cav*-$C_{aryl}$), 127.5 (*bipy*-$C_{aryl}$), 137.2 (*bipy*-$C_{aryl}$), 138.2, 138.3, 138.4, 138.6 (4× *cav*-$C_{aryl}$), 142.3 (*bipy*-$C_{aryl}$), 154.7, 154.8, 155.0 (4× *cav*-$C_{aryl}$), 155.7 (*bipy*-$C_{aryl}$) ppm. MS (pos. ESI): *m*/*z* (%) = 2508.7 ([MH]$^+$, 100). HiRes-MS (pos. ESI) calcd. for $[C_{166}H_{229}N_2O_{16}]^+$ *m*/*z* = 2508.7234; found *m*/*z* = 2508.7327 (Δ = 3.7 ppm).

**Resorcinarene-Functionalized 2,2′-Bipyridine 4:** A two-neck flask equipped with a septum and a reflux condenser was charged with 70 mg of **23** (0.05 mmol), 16 mg of **22** (0.1 mmol, 2 equiv.), 1.0 mg (5 μmol, 10 mol-%) of copper(I) iodide, and 3.5 mg (10 mol-%) of [$Pd(PPh_3)_2Cl_2$] and repeatedly evacuated and flushed with argon. 10 mL of dry triethylamine were added via syringe and the resulting mixture was refluxed for 18 h. After that time 20 mL of ethyl acetate were added and the organic phase was washed four times with water and with brine and dried with sodium sulfate. Removing of the organic solvents in vacuo gave the crude product mixture which was subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 2:1 + 0.5% triethylamine) to yield 138 mg of **4** as an amorphous solid (93 μmol, 69%). $R_f$ = 0.21 (*n*-hexane/ethyl acetate, 2:1 + 0.5% triethylamine). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.70 (d, $^3J$ = 5.2 Hz, 1 H, *bipy*-H), 8.65 (d, $^3J$ = 4.9 Hz, 1 H, *bipy*-H), 8.61 (s, 1 H, *bipy*-H), 8.44 (s, 1 H, *bipy*-H), 8.25 (br. s, 1 H, NH), 8.26 (d, $^3J$ = 7.9 Hz, 1 H, *py*-H), 7.75 (dd, $^3J$ = 7.9, $^3J$ = 7.6 Hz, 1 H, *py*-H), 7.48 (d, $^3J$ = 5.2 Hz, 1 H, *bipy*-H), 7.32 (m, 2 H, *py*-H, *bipy*-H), 7.16 (1 H, *cav*-$H_{aryl}$), 7.11 (s, 2 H,

*cav*-$H_{aryl}$), 7.10 (s, 1 H, *cav*-$H_{aryl}$), 6.51 (s, 2 H, *cav*-$H_{aryl}$), 6.47 (s, 1 H, *cav*-$H_{aryl}$), 5.93 (d, $^2J$ = 7.3 Hz, 2 H, *cav*-$H_{acetal}$), 5.75 (d, $^2J$ = 7.3 Hz, 2 H, *cav*-$H_{acetal}$),4.79 (t, $^3J$ = 8.0 Hz, 2 H, *cav*-$H_{benzyl}$), 4.72 (t, $^3J$ = 8.0 Hz, 2 H, *cav*-$H_{benzyl}$), 4.55 (d, $^2J$ = 7.3 Hz, 2 H, *cav*-$H_{acetal}$), 4.43 (d, $^2J$ = 7.3 Hz, 2 H, *cav*-$H_{acetal}$), 2.26–2.18 (m, 8 H, *cav*-$H_{alkyl}$), 2.21 [s, 3 H, –C(O)C$H_3$], 1.46–1.20 (m, 72 H, *cav*-$H_{alkyl}$), 0.88 (t, $^3J$ = 6.7 Hz, 12 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.9 (*cav*-$C_{alkyl}$), 24.7 [–C(O)*C*H$_3$], 27.8, 27.9, 29.4, 29.7, 29.8, 29.9, 31.9 (*cav*-$C_{alkyl}$), 36.3 (*cav*-$C_{benzyl}$), 36.4 (*cav*-$C_{benzyl}$), 86.6, 86.7, 94.5 (4× $C_{alkyne}$), 99.1 (*cav*-$C_{acetal}$), 99.5 (*cav*-$C_{acetal}$), 111.9 (*cav*-$C_{aryl}$), 114.4 (*py*-$C_{aryl}$), 116.6 (2× *cav*-$C_{aryl}$), 120.7 (2× *cav*-$C_{aryl}$), 121.4 (*cav*-$C_{aryl}$), 123.0 (*py*-$C_{aryl}$), 123.8 (*bipy*-$C_{aryl}$), 125.8, 125.9 (2× *bipy*-$C_{aryl}$), 131.5 (*bipy*-$C_{aryl}$), 132.5 (*bipy*-$C_{aryl}$), 138.2, 138.3, 138.6, 138.7 (4× *cav*-$C_{aryl}$, *bipy*-$C_{aryl}$), 139.1 (*py*-$C_{aryl}$), 139.7 (*py*-$C_{aryl}$), 149.0 (*bipy*-$C_{aryl}$), 149.2 (*bipy*-$C_{aryl}$), 151.4 (*py*-$C_{aryl}$), 154.7, 154.8, 155.0, 155.7 (4× *cav*-$C_{aryl}$, 2× *bipy*-$C_{aryl}$), 168.8 [–*C*(O)CH$_3$] ppm. MS (CI, isobutane, pos. mode): *m*/*z* (%) = 1489.7 (100) $[MH]^+$. HiRes-MS (pos. ESI) calcd. for $[C_{97}H_{125}N_4O_9]^+$ *m*/*z* = 1490.9480; found *m*/*z* = 1490.9402 (Δ = –5.2 ppm).

**Bis(resorcinarene)-Functionalized 2,2′-Bipyridine 5:** A two-neck flask equipped with a septum and a reflux condenser was charged with 56.6 mg (0.232 mmol) of **14** and repeatedly evacuated and flushed with argon. 10 mL of thionyl chloride were added via syringe and the resulting mixture was heated to reflux for 16 h. The excess of thionylchloride was removed in vacuo and the residue flushed with argon. A second two-neck flask equipped with a septum was charged with 400 mg (0.480 mmol, 2.2 equiv.) of **17** and repeatedly evacuated and flushed with argon. 15 mL of dry dichloromethane were added via syringe and the resulting solution was transferred via syringe to the diacid chloride. After adding 5 mL of dry triethylamine the mixture was refluxed for 2 d. The mixture was diluted with dichloromethane, washed with water (3 × 20 mL) and brine, and dried with sodium sulfate. After removal of the solvents the residue was subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 2:1) to give 239 mg of the desired diester (128 μmol, 55%). $R_f$ = 0.30 (*n*-hexane/ethyl acetate, 2:1). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 9.07 (d, $^4J$ = 1.4 Hz, 1 H, *bipy*-H), 8.91 (d, $^3J$ = 4.8 Hz, 1 H, *bipy*-H), 8.71 (d, $^3J$ = 7.2 Hz, 1 H, *bipy*-H), 8.26 (d, $^3J$ = 7.2 Hz, 1 H, *bipy*-H), 8.06 (dd, $^3J$ = 7.2, $^3J$ = 7.2 Hz, 1 H, *bipy*-H), 7.96 (dd, $^3J$ = 4.8, $^4J$ = 1.4 Hz, 1 H, *bipy*-H), 7.13 (s, 2 H, *cav*-$H_{aryl}$), 7.12 (s, 2 H, *cav*-$H_{aryl}$), 7.09 (s, 1 H, *cav*-$H_{aryl}$), 7.08 (s, 1 H, *cav*-$H_{aryl}$), 6.56 (s, 1 H, *cav*-$H_{aryl}$), 6.55 (s, 1 H, *cav*-$H_{aryl}$), 6.43 (s, 2 H, *cav*-$H_{aryl}$), 6.41 (s, 2 H, *cav*-$H_{aryl}$), 5.74–5.70 (m, 4 H, *cav*-$H_{acetal}$), 5.60 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 5.56 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 4.76–4.70 (m, 8 H, *cav*-$H_{benzyl}$), 4.65–4.63 (m, 4 H, *cav*-$H_{acetal}$), 4.40 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 4.35 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 2.24–2.20 (m, 16 H, *cav*-$H_{alkyl}$), 1.43–1.33 (m, 48 H, *cav*-$H_{alkyl}$), 0.94 (m, 24 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 27.6 (*cav*-$C_{alkyl}$), 29.9 (*cav*-$C_{alkyl}$), 32.1 (*cav*-$C_{alkyl}$), 36.4 (*cav*-$C_{benzyl}$), 36.7 (*cav*-$C_{benzyl}$), 99.3 (*cav*-$C_{acetal}$), 99.8 (*cav*-$C_{acetal}$), 116.9 (*cav*-$C_{aryl}$), 117.4 (2× *cav*-$C_{aryl}$), 117.8 (*cav*-$C_{aryl}$), 120.5 (*cav*-$C_{aryl}$), 121.7 (*bipy*-$C_{aryl}$), 123.7 (*bipy*-$C_{aryl}$), 125.4 (*bipy*-$C_{aryl}$), 126.5 (*bipy*-$C_{aryl}$), 136.9 (*bipy*-$C_{aryl}$), 137.6, 138.7, 138.8, 139.1, 139.3 (8× *cav*-$C_{aryl}$), 138.3 (*bipy*-$C_{aryl}$), 146.3 (*bipy*-$C_{aryl}$), 150.3 (*bipy*-$C_{aryl}$), 154.7, 155.0 (8× *cav*-$C_{aryl}$), 155.8 (*bipy*-$C_{aryl}$), 156.6 (*bipy*-$C_{aryl}$), 164.0 (*bipy*-$C_{aryl}$), 164.6 (*bipy*-$C_{aryl}$) ppm. MS (pos. ESI): *m*/*z* (%) = 1875.0 ($[MH]^+$, 100). HiRes-MS (pos. ESI) calcd. for $[C_{116}H_{132}N_2O_{20} + H]^+$ *m*/*z* = 1874.9485; found *m*/*z* = 1875.0000 (Δ = 27.5 ppm).

**4,4′-Dibromo-2,2′-bipyridine *N*,*N*′-Dioxide (9):**[27b] 40 mL of acetyl bromide were added to a suspension of 3.8 g (13.6 mmol) of 4,4′-dinitro-2,2′-bipyridine *N*,*N*′-dioxide in 60 mL of glacial acetic acid and heated to 100 °C for 2 h. The resulting yellow-brownish solution was cooled to 0 °C and poured into 125 g of ice. Neutralisation with concd. sodium hydroxide solution resulted in precipitation of the product which was collected by filtration, washed with water and dried in vacuo to yield 3.30 g of the desired product as a white solid (9.5 mmol, 70%). The analytical data were in accordance with the ones found in the literature.[27b]

**4,4′-Dibromo-2,2′-bipyridine (10):**[27] A suspension of 767 mg (2.22 mmol) of **9** in 5 mL of phosphorus tribromide und 100 mL of anhydr. acetonitrile was heated to reflux for 4 h. After cooling down to room temp., the solution was poured onto ice. The pH of the resulting mixture was adjusted to pH 11 with 6 N aq. sodium hydroxide. Then the mixture was extracted repeatedly with chloroform. The combined organic extract was dried with sodium carbonate. Evaporation of the solvents gave the crude product which was recrystallised from a 1:1 mixture of ethanol and water to give 530 mg of **10** as a colourless crystalline solid (1.69 mmol, 76%); m.p. 140 °C ref.[27a] 141–142 °C. $^1$H and $^{13}$C NMR spectroscopic data are in accordance with the literature data[27b] MS (CI, isobutane): *m*/*z* (%) = 315.0 (100) $[MH]^+$.

**Methyl 6-[4-(Methoxycarbonyl)pyridin-2-yl]pyridine-2-carboxylate (13):** 1.00 g (5.43 mmol) of **10** and 6.00 g (38.0 mmol) of potassium permanganate were suspended in 100 mL of water. The mixture was stirred for 24 h at 70 °C. After filtration the precipitate was washed with 10 mL of 1 N aq. sodium hydroxide. The filtrate was extracted with dichloromethane (2 × 20 mL) and then neutralized with 2 N aq. hydrochloric acid. The solvents were evaporated in vacuo and the residue was dissolved in 200 mL of methanol. 3 mL of concd. sulfuric acid were added. The solution was stirred under reflux for 12 h. After filtration the solvents were removed in vacuo, the residue was dissolved in ethyl acetate, washed with water (3 × 20 mL) and with brine (1 × 20 mL), and dried with sodium sulfate. After evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 2:1 + 5% triethylamine) to give 193 mg of the desired product as a colourless solid (0.71 mmol, 13%). $R_f$ = 0.81 (*n*-hexane/ethyl acetate, 2:1 + 5% triethylamine); m.p. 205 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.04, 3.99 (s, 6 H, –COOC$H_3$), 7.89 (d, $^3J$ = 4.9 Hz, 1 H, 5-H), 7.98 (dd, $^3J$ = 7.7, $^3J$ = 7.7 Hz, 1 H, 4′-H), 8.16 (d, $^3J$ = 7.7 Hz, 1 H, 5′-H), 8.60 (d, $^3J$ = 7.7 Hz, 1 H, 3′-H), 8.82 (d, $^3J$ = 4.9 Hz, 1 H, 6-H), 9.00 (s, 1 H, 3-H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 52.7, 52.9 (–O*C*H$_3$), 121.1 (C-3), 123.3 (C-5), 124.6 (C-3′), 125.4 (C-5′), 138.1 (C-4′), 138.9 (C-4), 147.8 (C-6′), 149.8 (C-6), 155.5 (C-2′), 156.3 (C-2), 165.5 (C-4-*C*OO), 165.7 (C-6′-*C*OO) ppm. MS (EI, 70 eV, pos. mode): *m*/*z* (%) = 214.1 (100) $[M - C_2H_2O_2]^+$, 272.1 (10) $[M]^{\cdot+}$. HiRes-MS (EI, 70 eV, pos. mode): calcd. for $[C_{14}H_{12}N_2O_4]^{\cdot+}$ 272.0797; found 272.0797 (Δ = 0.0 ppm).

**2,2′-Bipyridine-4,6′-dicarboxylic Acid (14):** Diester **13** could be saponified in quantitative manner upon treatment with 6 N aq. sodium hydroxide in boiling THF/methanol for 1 h. Acidifying of the mixture with aq. hydrochloric acid led to precipitation of the desired product. Due to the very low solubility of this compound it was not characterised further but used directly for the synthesis of **5**.

**Cavitand 16a (1,21,23,25-Tetrapentyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis-[1,3]benzodioxocin):**[28] 7.69 g (10.0 mmol) of resorcinarene **15a** were dissolved in 150 mL of anhydr. DMF. 22.1 g (160 mmol, 16 equiv.) of anhydr. potassium carbonate and 6.5 mL (100 mmol, 10 equiv.) of bromochloromethane were added and the resulting

mixture was heated to 70 °C for 4 d. Every 24 h another 6.5 mL (100 mmol, 10 equiv.) of bromochloromethane were added. The reaction mixture was quenched with brine and filtered. The filtrate was washed repeatedly with water, washed with brine, and dried with magnesium sulfate. 15 mL of methanol was added and the mixture was reduced until the product precipitated as a slightly brownish solid which was collected and dried in vacuo; yield 1.80 g (2.1 mmol, 22%). The analytical data are in accordance with the ones found in the literature.[28]

**Hydroxy-Functionalized Cavitand 17a (7-Hydroxy-1,21,23,25-tetrapentyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino-[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin):** In order to eliminate traces of dichloromethane which tends to associate with these kind of cavitands 3.00 g (3.67 mmol) of cavitand **16a** were dissolved in 20 mL of dry THF. The solvent was evaporated and the residue was heated to 80 °C at $10^{-3}$ mbar for 1 h. This procedure was repeated twice. The remaining cavitand was dissolved in 60 mL of dry THF. 0.60 mL (4.0 mmol, 1.1 equiv.) of *N*,*N*′-tetramethylethylenediamine (TMEDA) was added and the mixture was cooled down to –78 °C. At this temperature, 2.61 mL (4.04 mmol of a 1.55 M solution in *n*-hexane, 1.1 equiv.) of *n*-butyllithium was added slowly via syringe. The resulting mixture was stirred for 30 min at –78 °C. 0.46 mL (4.0 mmol, 1.1 equiv.) of trimethylborate was added and the cooling bath was removed. After one hour of stirring at room temp., 3 mL of 3 N aq. sodium hydroxide and 3 mL of 30% aq. hydrogen peroxide were added and the resulting mixture was stirred for 18 h before it was poured into 10% aq. sodium disulfite. The organic layer was separated and the aqueous phase was extracted twice with ethyl acetate (2 × 25 mL). The combined organic phases were washed with sat. aq. sodium hydrogen carbonate, water, and brine, dried with magnesium sulfate, and concentrated in vacuo. The resulting residue was subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 3:1) to give 1.50 g of the desired product (1.8 mmol, 49%). $R_f$ = 0.36 (*n*-hexane/ethyl acetate, 3:1). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 9.4 (br. s, 1 H, –OH), 7.10 (s, 3 H, *cav*-$H_{aryl}$), 6.64 (s, 1 H, *cav*-$H_{aryl}$), 6.49 (s, 2 H, *cav*-$H_{aryl}$), 6.47 (s, 1 H, *cav*-$H_{aryl}$), 5.83 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 5.73 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 4.72 (t, $^3J$ = 8.2 Hz, 2 H, *cav*-$H_{benzyl}$), 4.70 (t, $^3J$ = 8.2 Hz, 2 H, *cav*-$H_{benzyl}$), 4.43 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 4.42 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 2.23–2.19 (m, 8 H, *cav*-$H_{alkyl}$), 1.45–1.30 (m, 24 H, *cav*-$H_{alkyl}$), 0.91 (t, $^3J$ = 7.1 Hz, 12 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 27.5 (*cav*-$C_{alkyl}$), 29.7 (*cav*-$C_{alkyl}$), 29.8 (*cav*-$C_{alkyl}$), 32.0 (*cav*-$C_{alkyl}$), 36.3 (*cav*-$C_{benzyl}$), 36.6 (*cav*-$C_{benzyl}$), 99.5, 99.7 (2 × *cav*-$C_{acetal}$), 109.5 (*cav*-$C_{aryl}$), 116.3, 116.5 (2 × *cav*-$C_{aryl}$), 120.6, 120.9 (2 × *cav*-$C_{aryl}$), 138.4, 138.5, 138.6, 140.9, 142.0, 154.8, 154.9 (9 × *cav*-$C_{aryl}$) ppm. MS (neg. ESI): *m*/*z* (%) = 813.5 ([M – H]$^-$, 100).

***N*-(6-Bromopyridin-2-yl)acetamide (20):**[29] A two-neck flask equipped with a septum and a reflux condenser was charged with 1.04 g (6.00 mmol) of 2-amino-6-bromopyridine and repeatedly evacuated and flushed with argon. After dissolving the compound in 20 mL of anhydr. pyridine and 0.47 mL (6.6 mmol, 1.1 equiv.) of freshly distilled acetyl chloride were added via syringe. After 30 min, TLC control revealed complete consumption of the starting material and the mixture was quenched with 20 mL of water. The pH was adjusted to 7 and the resulting mixture was cooled to –30 °C. The precipitate was collected, washed twice with water, and dried in vacuo to give 910 mg of the product as a crystalline solid (4.2 mmol, 71%). The analytical data were in accordance with the ones found in the literature.[29]

***N*-(6-{2-[Trimethylsilyl]ethynyl}pyridin-2-yl)acetamide (21):** A two-neck flask equipped with a septum and a reflux condenser was charged with 430 mg (2.00 mmol) of **20**, 70 mg of $[Pd(PPh_3)_2Cl_2]$ (10 mol-%), and 38 mg (200 μmol, 10 mol-%) of copper(I) iodide and repeatedly evacuated and flushed with argon. 20 mL of dry triethylamine and 0.74 mL (2.2 mmol, 1.1 equiv.) of trimethylsilylacetylene were added via syringe and the resulting solution was heated to 50 °C for 18 h. After that time, 20 mL of water and 20 mL of ethyl acetate were added. The layers were separated and the organic layer was washed twice with water, washed with brine, and dried with sodium sulfate. After removal of the solvents in vacuo the residue was subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 3:1 + 0.5% triethylamine) to give 405 mg of the desired product (1.74 mmol, 87%). $R_f$ (*n*-hexane/ethyl acetate, 3:1 + 0.5% triethylamine): 0.48; m.p. 191 °C. $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.31 (br. s, 1 H, –NH), 8.15 (d, $^3J$ = 8.2 Hz, 1 H, 3-H), 7.64 (dd, $^3J$ = 8.2, $^3J$ = 7.7 Hz, 1 H, 4-H), 7.19 (d, $^3J$ = 7.7 Hz, 1 H, 5-H), 2.16 [s, 3 H, –C(O)C$H_3$], 0.25 [s, 9 H, –Si(C$H_3$)$_3$] ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 168.7 [*C*(O)CH$_3$], 151.2 (C-2), 140.7 (C-6), 138.6 (C-4), 123.4 (C-5), 113.8 (C-3), 102.9 ($C_{alkyne}$), 95.1 ($C_{alkyne}$), 24.6 [C(O)*C*H$_3$], –0.3 [–Si(*C*H$_3$)$_3$] ppm. MS (EI, 70 eV, pos. mode): *m*/*z* (%) = 232.0 (74) $[M]^{+\cdot}$, 189.9 (94) $[M - CH_3]^+$, 174.9 (100) $[M - NHC(O)CH_3]^+$. HiRes-MS (CI, isobutane) calcd. for $[C_{12}H_{17}N_2OSi]^+$ *m*/*z* = 233.1110; found *m*/*z* = 233.1107 (Δ = –1.3 ppm).

***N*-(6-Ethynylpyridin-2-yl)acetamide (22):** 70 mg (0.30 mmol) of **21** and 50 mg (ca. 3 equiv.) of KF were dissolved in 10 mL of a 1:1 mixture of THF and methanol and stirred at room temp. until TLC monitoring revealed complete consumption of the starting material. The solvents were evaporated in vacuo and the residue was dissolved in 20 mL of diethyl ether. The solution was washed twice with water, washed with brine (20 mL each), and dried with sodium sulfate. The solvent was removed in vacuo and the residue subjected to column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 1:1 + 0.5% triethylamine) to give the crude product as a brownish solid. This was further purified by flash chromatography (eluent: *n*-hexane/ethyl acetate, 5:1 + 0.5% triethylamine) to give 48 mg (0.3 mmol, quant.) of **22** as colourless crystals. $R_f$ = 0.52 (*n*-hexane/ethyl acetate, 1:1 + 0.5% triethylamine); m.p. 119 °C. $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.20 (d, $^3J$ = 8.2 Hz, 1 H, 3-H), 8.14 (br. s, 1 H, –NH), 7.68 (dd, $^3J$ = 6.6, $^3J$ = 8.2 Hz, 1 H, 4-H), 7.22 (d, $^3J$ = 6.6 Hz, 1 H, 5-H), 3.13 (s, 1 H, –C≡C*H*), 2.18 (s, 3 H, –C$H_3$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 168.8 [–*C*(O)CH$_3$], 151.4 (C-2), 139.9 (C-6), 138.7 (C-4), 123.4 (C-5), 114.2 (C-3), 82.1 (–C≡*C*H), 77.3 (–*C*≡CH), 24.7 [–C(O)*C*H$_3$] ppm. MS (EI, 70 eV, pos. mode): *m*/*z* (%) = 160.2 (23) $[M]^{+\cdot}$, 118.2 (100) $[M - Ac]^+$. HiRes-MS (EI, 70 eV, pos. mode) calcd. for $[C_9H_8N_2O]^{+\cdot}$ *m*/*z* = 160.0637; found *m*/*z* = 160.0637 (Δ = 0.0 ppm).

**2,9-Bis[2,6-bis(1,4,7,10-tetraoxadodecyl)phenyl]-1,10-phenanthroline (25). Method A:** Crude 2,6-bis(1,4,7,10-tetraoxadodecyl)phenylboronic acid (**27**, 382 mg, max. 805 μmol) and 2,9-dichloro-1,10-phenanthroline (65.6 mg, 267 μmol) were dissolved in 1,2-dimethoxyethane (8 mL) and water (2 mL). After addition of tetrakis(triphenylphosphane)palladium(0) (32.7 mg, 28.4 μmol) and barium hydroxide octahydrate (389 mg, 1.21 mmol), the mixture was stirred under nitrogen at 60 °C for 16 h. Cooling to room temp. was followed by addition of dichloromethane and water (5 mL each) and separation of the layers. The water layer was extracted with dichloromethane (5 mL). The combined organic layer was washed with brine (10 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography [silica gel, ethyl acetate, $R_f$(**16**) ≈ 0.10]. It was only possible to isolate the monoaryl-substituted phenanthroline. MS (ESI, pos. mode, $CHCl_3$/MeOH, crude product):

*m/z* (%) = 1059 (42) $[M + Na]^+$, 1037 (12) $[M + H]^+$, 665 (100) [**16** + Na]$^+$.

**Method B:** 2,9-Diiodo-1,10-phenanthroline (**26**, 212 mg, 869 μmol) was dissolved in 1,2-dimethoxyethane (23 mL) and crude 2,6-bis(1,4,7,10-tetraoxadodecyl)phenylboronic acid (**27**, 1.25 g, max. 2.63 mmol), $[Pd(PPh_3)_4]$ (106 mg, 86.9 μmol), barium hydroxide octahydrate (1.27 g, 3.94 mmol) and water (5.8 mL) were added, and the suspension was stirred under nitrogen at 60 °C for 18 h. After cooling to room temp., additional $[Pd(PPh_3)_4]$ (20 mg, 16 μmol) and crude 2,6-bis(1,4,7,10-tetraoxadodecyl)phenylboronic acid (**26**, 300 mg, max. 631 mmol) was added, and the mixture was stirred under nitrogen at 60 °C for another 42 h. Dichloromethane and water (25 mL each) were added at room temp. and the layers were separated. The water layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (20 mL) and dried with magnesium sulfate. The solvent was evaporated in vacuo and the crude material was purified by column chromatography on silica gel [eluent: ethyl acetate → dichloromethane/5% methanol, $R_f$ (ethyl acetate) = 0.05] to yield 84 mg of a product mixture, which was again purified by chromatography (chromatotron 1 mm, silica gel, dichloromethane/3% methanol) to yield 20 mg of brown oil (19.3 μmol, 2%). $R_f$ = 0.05 (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 2926 (aliph. C–H), 1593, 1459 (arom. C=C), 1250, 1111 (C–O–C) cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.05 (t, $^3J$ = 7.0 Hz, 12 H, –$CH_3$), 3.32–3.47 (m, 40 H, –$OCH_2$–), 3.63 (t, $^3J$ = 4.6 Hz, 8 H, $ArOCH_2CH_2$–), 4.05–4.20 (m, 8 H, $ArOCH_2$–), 6.83 (d, $^3J$ = 8.4 Hz, 4 H, 3,5-$C_{Ar}$H), 7.43 (t, $^3J$ = 8.2 Hz, 2 H, 4-$C_{Ar}$H), 7.89 (d, $^3J$ = 8.2 Hz, 2 H, 3,8-$C_{Phen}$H), 7.94 (s, 2 H, 5,6-$C_{Phen}$H), 8.39 (d, $^3J$ = 8.3 Hz, 2 H, 4,7-$C_{Phen}$H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 14.9 (q, $CH_3$), 66.5 (t, $OCH_2CH_3$), 67.5, 68.4, 69.0, 69.4, 70.0, 70.3 (t, –$OCH_2$–), 106.9 (d, 3,5-$C_{Ar}$), 118.9 (s, 2,6-$C_{Ar}$), 126.6 (d, 5,6-$C_{Phen}$), 127.6 (d, 3,8-$C_{Phen}$), 127.8 (s, 2,9-$C_{Phen}$), 131.2 (d, 4-$C_{Ar}$), 136.3 (d, 4,7-$C_{Phen}$), 144.8 (s, 4a,6a-$C_{Phen}$), 154.5 (s, 10a,10b-$C_{Phen}$), 157.0 (s, 1-$C_{Ar}$) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 1037 (54) $[M]^{\cdot+}$, 992 (14) $[M - C_2H_5O]^+$, 963 (9) $[M - C_4H_9O]^+$, 947 (11) $[M - C_4H_9O_2]^+$, 919 (5) $[M - C_6H_{13}O]^+$, 903 (68) $[M - C_6H_{13}O]^+$, 890 (66) $[M - C_7H_{14}O_3]^+$, 877 (47) $[M - C_8H_{16}O_3]^+$, 832 (13) $[C_{46}H_{49}N_2O_{12}]^+$, 847 (10) $[C_{46}H_{59}N_2O_{13}]^+$, 787 (14) $[C_{44}H_{55}N_2O_{11}]^+$, 730 (12) $[C_{40}H_{45}N_2O_{11}]^+$, 729 (10) $[C_{41}H_{49}N_2O_{10}]^+$. MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* (%) = 1059.5 (99) $[M + Na]^+$, 1037.5 (100) $[M + H]^+$. HiRes-MS (ESI, pos. mode, $CHCl_3$/MeOH): calcd. for $[C_{56}H_{80}N_2O_{16} + H]^+$ *m/z* = 1037.5581; found *m/z* = 1037.5518 (Δ = –6.1 ppm), calcd. for $[C_{55}{}^{13}CH_{80}N_2O_{16} + H]^+$ *m/z* = 1038.5614; found *m/z* = 1038.5609 (Δ = 0.6 ppm).

**2,6-Bis(1,4,7,10-tetraoxadodecyl)phenylboronic Acid (27). Method A:** 2-Bromo-1,3-bis(1,4,7,11-tetraoxadodecyl)benzene (**32**, 410 mg, 805 μmol) was dissolved in dry THF (11 mL) and cooled to –78 °C. After addition of *n*-butyllithium (0.35 mL, 0.89 mmol, 2.6 M in hexanes), the solution was stirred at –78 °C for 1 h, before adding trimethylborate (0.28 mL, 2.7 mmol) and stirring for another 1.5 h. During this time, the solution was warmed to room temp. The mixture was hydrolyzed with water (20 mL) and the layers were separated. The water layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layer was washed with brine (20 mL) and dried with magnesium sulfate. The solvent was evaporated in vacuo to yield 360 mg of the colourless crude liquid (yield approx. 90%).

**Method B:** 2-Iodo-1,3-bis(1,4,7,10-tetraoxadodecyl)benzene (**33**, 2.75 g, 4.96 mmol) was dissolved in dry THF (37 mL) under nitrogen and cooled to –78 °C. *n*-Butyllithium (2.15 mL, 5.44 mmol, 2.6 M in hexanes) was added and the solution was stirred at –78 °C for 1 h. After addition of trimethylborate (1.62 mL, 16.4 mmol), the solution was stirred for 2 h while it was warmed to room temp. The mixture was hydrolyzed with water (20 mL) and the layers were separated. The water layer was extracted with diethyl ether (3 × 10 mL) and the combined organic layer was washed with brine (10 mL) and dried with magnesium sulfate. The solvent was evaporated in vacuo to yield 1.90 g of the light yellow crude liquid (yield approx. 80%). IR (film): $\tilde{\nu}$ = 3507 (OH), 2869 (aliph. C–H), 1596, 1453 (arom. C=C), 1256, 1101 (C–O–C) cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.20 (t, $^3J$ = 7.0 Hz, 6 H, –$CH_3$), 3.52 (q, $^3J$ = 7.0 Hz, 4 H, –$OCH_2CH_3$), 3.56–3.75 (m, 16 H, –$CH_2O$–), 3.93 ($m_c$, 4 H, 2,6-$C_{Ar}OCH_2CH_2O$), 4.10 ($m_c$, 4 H, 2,6-$C_{Ar}OCH_2$), 6.59 (d, $^3J$ = 8.3 Hz, 2 H, 4,6-$C_{Ar}$H), 7.21 (t, $^3J$ = 8.3 Hz, 1 H, 5-$C_{Ar}$H), 7.33 [s, 2 H, -$B(OH)_2$] ppm. MS (CI, isobutane, pos. mode): *m/z* (%) = 474 (1) $[M]^{\cdot+}$, 431 (100) $[C_{22}H_{38}O_8 + H]^+$, 117 (24) $[C_6H_{13}O_2]^+$.

**2-Iodoresorcinol (28):** Was synthesized following a literature procedure[20] starting from resorcinol (6.00 g, 54.4 mmol, recrystallized from toluene), and iodine (14.8 g, 58.3 mmol) in 50 mL of water to yield 8.52 g (36.1 mmol, 67%) of colourless crystals, ref.[20] 72%; m.p. 91 °C, ref.[20] 93 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 5.34 (s, 2 H, OH), 6.53 (d, $^3J$ = 8.1 Hz, 2 H, 4,6-$C_{Ar}$H), 7.10 (t, $^3J$ = 8.2 Hz, 1 H, 5-$C_{Ar}$H) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 236 (100) $[M]^{\cdot+}$.

**2,4,6-Tribromoresorcinol (29):** Was synthesized from resorcinol (10.0 g, 90.8 mmol) in chloroform (91 mL), bromine (14.5 mL, 45.5 g, 285 mmol) in chloroform (22 mL) following a literature procedure[22] to yield colourless crystals (21.7 g, 62.7 mmol, 69%), ref.[3] 97%; m.p. 110 °C, ref.[22] 111 °C. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.95 (s, 2 H, OH), 7.60 (s, 1 H, 5-$C_{Ar}$H) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 350, 348, 346, 344 (31, 95, 100, 32) $[M]^{\cdot+}$, 332, 330, 328, 326 (2, 6, 7, 2) $[M - H_2O]^{\cdot+}$.

**2-Bromoresorcinol (30):** Was synthesized from 1,3,5-tribromo-2,4-dihydroxybenzene (19.3 g, 55.5 mmol) using sodium sulfite (13.8 g, 111 mmol) and sodium hydroxide (4.33 g, 111 mmol) in water (139 mL) and methanol (28 mL) following a literature procedure[21] to yield 9.00 g (47.6 mmol, 86%) of colourless needles, ref.[16a] 65%; m.p. 98 °C, ref.[21] 102.5 °C. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.41 (s, 2 H, OH), 6.60 (d, $^3J$ = 8.4 Hz, 2 H, 4,6-$C_{Ar}$H), 7.12 (t, $^3J$ = 8.4 Hz, 1 H, 5-$C_{Ar}$H) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 190, 188 (98, 100) $[M]^{\cdot+}$.

**3,6,9-Trioxaundecyl-(4-methylbenzene)sulfonate (31):** Was synthesized following a literature procedure[23] from triethylenglycol monoethyl ether (3.84 mL, 22.0 mmol) in pyridine (4 mL) with *p*-toluenesulfonic chloride (4.20 g, 22.0 mmol) in pyridine (12 mL). After work-up, the crude material was dried at 100 mbar for 2.5 h to yield 6.06 g of a colourless liquid (18.2 mmol, 83%), ref.[23] 97%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.20 (t, $^3J$ = 7.0 Hz, 2 H, –$OCH_2CH_2$–), 2.45 (s, 3 H, 4-$C_{Ar}CH_3$), 3.51 (q, $^3J$ = 7.0 Hz, 2 H, –$OCH_2CH_3$), 3.56–3.64 [m, 8 H, –$(OCH_2CH_2)_2O$–], 3.69 (t, $^3J$ = 4.9 Hz, 2 H, –$SO_2OCH_2CH_2$), 4.16 (t, $^3J$ = 4.9 Hz, 2 H, –$SO_2OCH_2$), 7.34 (d, $^3J$ = 8.3 Hz, 2 H, 3,5-$C_{Ar}$H), 7.80 (d, $^3J$ = 8.3 Hz, 2 H, 2,6-$C_{Ar}$) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 332 (1) $[M]^{\cdot+}$, 243 (7) $[M - OCH_2CH_2OCH_2CH_3]^+$, 199 (100) $[C_9H_{11}O_3S]^+$, 155 (58) $[C_7H_7O_2S]^+$, 91 (84) $[C_7H_7]^+$. MS (CI, isobutane, pos. mode): *m/z* (%) = 333 (100) $[M + H]^+$.

**2-Bromo-1,3-bis(1,4,7,10-tetraoxadodecyl)benzene (32):** 2-Bromoresorcinol (**30**) (2.00 g, 10.6 mmol) was dissolved in dry *N*,*N*-dimethylformamide (45 mL). After addition of 8.72 g (62.9 mmol) of potassium carbonate and 8.73 g (26.3 mmol) of 3,6,9-trioxaundecyl-(4-methylbenzene)sulfonate (**31**), the mixture was stirred at 60 °C under nitrogen for 16 h. The solvent was then evaporated in vacuo and the residue was dissolved in 2 N sodium hydroxide solu-

tion and ethyl ether (20 mL each). After separation of the layers, the water layer was extracted with ethyl ether (3 × 20 mL). The combined organic layer was washed with 2 N sodium hydroxide solution (2 × 20 mL) and with brine (20 mL). After drying with magnesium sulfate, the solvent was evaporated in vacuo. The crude material was purified by column chromatography on silica gel (eluent: cyclohexane/ethyl acetate, 1:2) to yield 4.30 g of a colourless liquid (8.48 mmol, 80%). $R_f$ = 0.26 (cyclohexane/ethyl acetate, 1:2). IR (film): $\tilde{\nu}$ = 2972, 2869 (aliph. C–H), 1597, 1452 (arom. C=C), 1177, 1109 (C–O–C), 775 ($C_{Ar}$–H) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 1.21 (t, $^3J$ = 7.0 Hz, 6 H, –$CH_3$), 3.52 (q, $^3J$ = 7.0 Hz, 4 H, –OC$H_2$$CH_3$), 3.57–3.61 (m, 4 H, –C$H_2$$OCH_2CH_3$), 3.64–3.71 (m, 8 H, –$OCH_2$–), 3.79–3.83 (m, 4 H, –$OCH_2$–), 3.92 ($m_c$, 4 H, –$OCH_2$–), 4.18 ($m_c$, 4 H, –$CH_2$OAr), 6.57 (d, $^3J$ = 8.3 Hz, 2 H, 4,6-$C_{Ar}$H), 7.17 (t, $^3J$ = 8.3 Hz, 1 H, 5-$C_{Ar}$H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 16.4 (q, –$CH_3$), 67.9 (t, –C$H_2$$CH_3$), 70.5, 70.8, 71.1, 71.9, 72.0, 72.5 (t, –$CH_2$–), 103.7 (s, 2-$C_{Ar}$), 107.7 (d, 4,6-$C_{Ar}$), 129.4 (d, 5-$C_{Ar}$), 158.0 (s, 1,3-$C_{Ar}$) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 511, 509 (2) $[M + H]^+$, 510, 508 (6,5) $[M]^{\cdot+}$, 429 (3) $[M – Br]^+$, 179 (7) $[C_8H_{18}O_4 + H]^+$, 161 (30) $[C_8H_{17}O_3]^+$, 117 (44) $[C_6H_{13}O_2]^+$, 73 (100) $[C_4H_9O]^+$. MS (CI, isobutane, pos. mode): *m/z* (%) = 511, 509 (38, 36) $[M + H]^+$, 161 (48) $[C_8H_{17}O_3]^+$, 117 (73) $[C_6H_{13}O_2]^+$, 73 (100) $[C_4H_9O]^+$. HiRes-MS (EI, 70 eV, pos. mode): calcd. for $[C_{22}H_{37}{}^{79}BrO_3]^{\cdot+}$ *m/z* = 508.1671; found *m/z* = 508.1672 (Δ = 0.1 ppm), calcd. for $[C_{22}H_{37}{}^{81}BrO_3]^{\cdot+}$ *m/z* = 510.1655; found *m/z* = 510.1651 (Δ = –0.4 ppm). $C_{22}H_{37}BrO_3$ (508.17), calcd. C 51.87, H 7.32; found C 51.75, H 7.29.

**2-Iodo-1,3-bis(1,4,7,10-tetraoxadodecyl)benzene (33):** 2-Iodoresorcinol (**28**) (434 mg, 1.84 mmol) was dissolved in dry *N*,*N*-dimethylformamide (8 mL), and potassium carbonate (1.52 g, 11.0 mmol) and 3,6,9-trioxaundecyl-(4-methylbenzene)sulfonate (**31**) (1.52 g, 4.57 mmol) were added. The mixture was stirred at 60 °C under nitrogen for 16 h and the solvent was evaporated in vacuo. The residue was dissolved in 2 N sodium hydroxide solution and diethyl ether (20 mL each). After separation of the layers, the water layer was extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with 2 N sodium hydroxide solution (2 × 15 mL) and with brine (15 mL), dried with magnesium sulfate and the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: cyclohexane/ethyl acetate, 1:2) to yield 500 mg of a colourless liquid (899 μmol, 49%). $R_f$ = 0.34 (cyclohexane/ethyl acetate, 1:2). IR (film): $\tilde{\nu}$ = 2970, 2867 (aliph. C–H), 1587, 1450 (arom. C=C), 1253, 1103 (C–O–C) $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.20 (t, $^3J$ = 7.0 Hz, 6 H, –$CH_3$), 3.52 (q, $^3J$ = 7.0 Hz, 4 H, –OC$H_2$$CH_3$), 3.57–3.60 (m, 4 H, –C$H_2$$OCH_2CH_3$), 3.65–3.70 (m, 8 H, –$OCH_2$–), 3.80–3.83 (m, 4 H, –C$H_2$$OCH_2CH_2OAr$), 3.92 ($m_c$, 4 H, –OC$H_2$$CH_2OAr$), 4.17 ($m_c$, 4 H, –$CH_2$OAr), 6.49 (d, $^3J$ = 8.3 Hz, 2 H, 4,6-$C_{Ar}$H), 7.20 (t, $^3J$ = 8.3 Hz, 1 H, 5-$C_{Ar}$H) ppm. $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 15.1 (q, –$CH_3$), 66.5, 69.2, 69.4, 69.8, 70.6, 70.7, 71.2 (t, –$CH_2$–), 79.2 (s, 2-$C_{Ar}$), 105.6 (d, 4,6-$C_{Ar}$), 129.6 (d, 5-$C_{Ar}$), 159.0 (s, 1,3-$C_{Ar}$) ppm. MS (EI, 70 eV, pos. mode): *m/z* (%) = 556.6 (16) $[M]^{\cdot+}$, 429.5 (4) $[M – I]^+$, 161 (27) $[C_8H_{17}O_3 + H]^+$, 117 (49) $[C_6H_{13}O_2]^+$, 73 (100) $[C_4H_9O]^+$. MS (CI, isobutane, pos. mode): *m/z* (%) = 557.6 (71) $[M + H]^+$, 117 (100) $[C_6H_{13}O_2]^+$. HiRes-MS (ESI, pos. mode, MeOH): $C_{22}H_{37}IO_8$ (556.15); calcd. for $[C_{22}H_{37}IO_8+Na]^+$ *m/z* = 579.1425; found *m/z* = 579.1419 (Δ = –1 ppm), calcd. for $[C_{21}{}^{13}CH_{37}IO_8+Na]^+$ *m/z* = 580.1460; found *m/z* = 580.1449 (Δ = –1.9 ppm). $C_{22}H_{37}IO_8$ (556.15), calcd. C 47.49, H 6.70. $C_{22}H_{37}IO_8 \cdot 0.2\ CH_2Cl_2$, calcd. C 46.50, H 6.57; found C 46.46, H 6.64.

**1,3-Bis(1,4,7,10-tetraoxadodecyl)benzene (34):** It was not possible to purify the crude boronic acid **18** by column chromatography over silica gel. All attempts only resulted in decomposition. Also, variations of solvents, of composition of the solvent mixture or of the amount of silica gel did not allow a successful purification. The only isolated product was colourless liquid 1,3-bis(1,4,7,10-tetraoxadodecyl)benzene (silica gel, ethyl acetate, $R_f$ = 0.50). IR (film): $\tilde{\nu}$ = 2869 (aliph. C–H), 1592, 1452 (arom. C=C), 1123 (C–O–C) $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.21 (t, $^3J$ = 7.0 Hz, 6 H, –$CH_3$), 3.52 (q, $^3J$ = 7.0 Hz, 4 H, –OC$H_2$$CH_3$), 3.57–3.60 (m, 4 H, –C$H_2$$OCH_2CH_3$), 3.64–3.70 (m, 8 H, –$OCH_2$–), 3.72–3.75 (m, 4 H, –C$H_2$$OCH_2CH_2OAr$), 3.85 ($m_c$, 4 H, –OC$H_2$$CH_2OAr$), 4.10 ($m_c$, 4 H, –$CH_2$OAr), 6.49–6.52 (m, 3 H, 2,4,6-$C_{Ar}$H), 7.14 ($m_c$, 1 H, 5-$C_{Ar}$H) ppm. $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 15.1 (q, –$CH_3$), 66.6, 67.3, 69.6, 69.8, 70.6, 70.7, 70.8 (t, –$CH_2$–), 101.7 (d, 2-$C_{Ar}$), 107.0 (d, 4,6-$C_{Ar}$), 129.7 (d, 5-$C_{Ar}$), 159.9 (s, 1,3-$C_{Ar}$) ppm. MS (EI, 70 eV): *m/z* (%) = 430 (100) $[M]^{\cdot+}$, 371 (4) $[M – C_3H_7O]^+$, 358 (7) $[M – C_4H_8O]^+$, 270 (6) $[C_{14}H_{22}O_5]^+$, 117 (73) $[C_6H_{13}O_2]^+$, 111 (28) $[C_6H_6O_2]^+$. HiRes-MS (ESI, pos. mode, $CHCl_3$/MeOH): $C_{22}H_{38}O_8$ (430.26); calcd. for $[C_{22}H_{38}O_8+Na]^+$ *m/z* = 453.2459; found *m/z* = 453.2455 (Δ = –0.9 ppm), calcd. for $[C_{21}{}^{13}CH_{38}O_8 + Na]^+$ *m/z* = 454.2493; found *m/z* = 454.2459 (Δ = –7.5 ppm). $C_{22}H_{38}O_3$ (430.26), calcd. C 61.37, H 8.90. $C_{22}H_{38}O_3 \cdot 0.05\ CH_2Cl_2$, calcd. C 60.91, H 8.83; found C 60.72, H 8.96.

**2-[2,6-Bis(1,4,7,10-tetraoxadodecyl)phenyl]-9-chloro-1,10-phenanthroline (35):** Monoaryl-substituted phenanthroline **35** was isolated from the reaction following method A (see above) after column chromatography on silica gel (eluent: ethyl acetate); yield: 20 mg (31 μmol, 12%) as a yellow oil. $R_f$ = 0.10 (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 2867 (aliph. C–H), 1589, 1453 (arom. C=C), 1260, 1118 (C–O–C) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 1.16 (t, $^3J$ = 7.0 Hz, 6 H, –$CH_3$), 3.32–3.36 (m, 4 H, –OC$H_2$$CH_3$), 3.38–3.49 (m, 16 H, –$OCH_2$–), 3.67 (t, $^3J \approx$ 4.9 Hz, 4 H, ArOC$H_2$C$H_2$–), 4.20 (t, $^3J \approx$ 4.9 Hz, 4 H, Ar$OCH_2$–), 6.73 (d, $^3J$ = 8.4 Hz, 2 H, 3,5-$C_{Ar}$H), 7.32 (t, $^3J$ = 8.3 Hz, 1 H, 4-$C_{Ar}$H), 7.58 (d, $^3J$ = 8.3 Hz, 1 H, 3-$C_{Phen}$H), 7.77 (d, $^3J$ = 8.7 Hz, 1 H, 8-$C_{Phen}$H), 7.81 (d, $^3J$ = 8.3 Hz, 1 H, 5-$C_{Phen}$H*), 7.85 (d, $^3J$ = 8.8 Hz, 1 H, 7-$C_{Phen}$H), 8.19 (d, $^3J$ = 8.4 Hz, 1 H, 6-$C_{Phen}$H*), 8.23 (d, $^3J$ = 8.3 Hz, 1 H, 4-$C_{Phen}$H) ppm (* assignments might be interchanged). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 15.1 (q, –$CH_2$–), 66.5 (t, –C$H_2$$CH_3$), 69.4, 69.5, 69.6, 70.35, 70.37, 70.5 (t, –$OCH_2$–), 107.2 (d, 3,5-$C_{Ar}$), 121.2 (s, 1-$C_{Ar}$), 123.8 (d, 3-$C_{Phen}$), 125.1 (d, 8-$C_{Phen}$), 127.0 (s, 6a-$C_{Phen}$), 127.2 (s, 4a-$C_{Phen}$), 127.3 (d, 5-$C_{Phen}$), 127.6 (d, 6-$C_{Phen}$), 130.1 (d, 4-$C_{Ar}$), 134.8 (d, 4-$C_{Phen}$), 138.6 (d, 7-$C_{Phen}$), 144.5 (s, 10b-$C_{Phen}$), 146.1 (s, 9-$C_{Phen}$), 150.9 (s, 10a-$C_{Phen}$), 155.5 (s, 2,6-$C_{Ar}$), 157.8 (s, 2-$C_{Phen}$) ppm (please note that the assignment of the protons of the phenanthroline unit and of the aromatic carbon signals has been carried out parallel to known signals for related phenanthrolines, but is not proved by HSQC or HMBC spectra). MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* (%) = 667, 665 (39, 100) $[M + Na]^+$. MS (EI, 70 eV, pos. mode): *m/z* (%) = 644, 642 (9, 15) $[M]^{\cdot+}$, 599, 597 (3, 9) $[M – C_2H_5O]^+$, 555, 553 (14, 20 $[M – C_4H_9O_2]^+$, 511, 509 (24, 47) $[C_{28}H_{30}ClN_2O_5]^+$, 497, 495 (46, 100) $[C_{27}H_{28}ClN_2O_5]^+$. $C_{34}H_{43}ClN_2O_8$ (642.27), calcd. C 63.49, H 6.74, N 4.36. $C_{34}H_{43}ClN_2O_8 \cdot 1H_2O$, calcd. C 61.76, H 6.86, N 4.24; found C 61.78, H 6.76, N 3.97.

**2-[2,6-Bis(1,4,7,10-tetraoxadodecyl)phenyl]-9-iodo-1,10-phenanthroline (36):** Monoaryl-substituted phenanthroline **36** was isolated from the reaction following method B (see above) after column chromatography on silica gel (eluent: ethyl acetate); yield: 56 mg (76 μmol, 19%) of a yellow oil. $R_f$ = 0.10 (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 2868 (aliph. C–H), 1573, 1472 (arom. C=C), 1252, 1110 (C–O–C) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 1.17 (t, $^3J$ = 7.0 Hz, 6 H, –$CH_3$), 3.35–3.40 (m, 4 H, –OC$H_2$$CH_3$), 3.42–3.50 (m, 16 H,-–$OCH_2$–), 3.71 (t, $^3J \approx$ 4.9 Hz, 4 H, ArOC$H_2$C$H_2$–), 4.25 (t, $^3J \approx$

4.9 Hz, 4 H, $ArOCH_2$–), 6.76 (d, $^3J$ = 8.4 Hz, 2 H, 3,5-$C_{Ar}H$), 7.33 (t, $^3J$ = 8.3 Hz, 1 H, 4-$C_{Ar}H$), 7.73 (d, $^3J$ = 8.8 Hz, 1 H, 6-$C_{Phen}H$*), 7.835 (d, $^3J$ = 8.3 Hz, 1 H, 8-$C_{Phen}H$), 7.84 (d, $^3J$ = 8.3 Hz, 1 H, 3-$C_{Phen}H$), 7.86 (d, $^3J$ = 8.8 Hz, 1 H, 5-$C_{Phen}H$*), 7.96 (d, $^3J$ = 8.3 Hz, 1 H, 7-$C_{Phen}H$), 8.22 (d, $^3J$ = 8.4 Hz, 1 H, 4-$C_{Phen}H$) ppm (* assignments might be interchanged). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 15.2 (t, –$CH_2$–), 66.6 (t, –$CH_2CH_3$), 69.6, 69.7, 69.9, 70.4, 70.5, 70.6 (t, –$OCH_2$–), 107.8 (d, 3,5-$C_{Ar}$), 118.6 (s, 9-$C_{Phen}$), 121.5 (s, 1-$C_{Ar}$), 125.4 (d, 3-$C_{Phen}$), 127.35 (s, 6a-$C_{Phen}$), 127.37 (d, 5-$C_{Phen}$), 127.5 (d, 6-$C_{Phen}$), 127.5 (s, 4a-$C_{Phen}$), 130.2 (d, 4-$C_{Ar}$), 133.3 (d, 8-$C_{Phen}$), 134.8 (d, 4-$C_{Phen}$), 137.0 (d, 7-$C_{Phen}$), 144.4 (s, 10b-$C_{Phen}$), 147.5 (s, 10a-$C_{Phen}$), 155.5 (s, 2-$C_{Phen}$), 158.0 (s, 2,6-$C_{Ar}$) ppm (please not that the assignment of the protons of the phenanthroline unit and of the aromatic carbon signals has been carried out parallel to known signals for related phenanthrolines, but is not proved by HSQC or HMBC spectra.). MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* (%) = 757 (100) $[M + Na]^+$, 734 (62) $[M + H]^+$. $C_{34}H_{43}IN_2O_8$ (734.21), calcd. C 55.59, H 5.90, N 3.81. $C_{34}H_{43}IN_2O_8 \cdot 0.5H_2O$, calcd. C 54.91, H 5.96, N 3.77; found C 54.77, H 5.94, N 3.74.

**[Cu(24)(1b)]$BF_4$:** 12.7 mg (5.0 μmol) of **1b** were dissolved in 0.5 mL of a 1:1 mixture of [$D_6$]benzene/[$D_3$]acetonitrile. 3.0 mg (5.0 μmol, 1 equiv.) of [Cu(**24**)]$BF_4$ were dissolved in 0.5 mL of a 1:1 mixture of [$D_6$]benzene/[$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by $^1H$ NMR spectroscopy and ESI MS. $^1H$ NMR (500.1 MHz, $C_6D_6/CD_3CN$, 1:1, 298 K): $\delta$ = 8.59 (m, 2 H, *phen*-$H_{phen}$), 8.46 (m, 2 H, *bipy*-H), 8.41 (s, 2 H, *bipy*-H), 8.13 (s, 2 H, *phen*-$H_{phen}$), 7.95 (d, $^3J$ = 4.4 Hz, 2 H, *bipy*-H), 7.79 (d, $^3J$ = 8.2 Hz, 2 H, *phen*-$H_{phen}$), 7.34 (s, 4 H, *cav*-$H_{aryl}$), 7.33 (s, 2 H, *cav*-$H_{aryl}$), 7.13 (s, 2 H, *cav*-$H_{aryl}$), 6.81 (m, 2 H, *phen*-$H_{aryl}$), 6.52 (m, 2 H, *cav*-$H_{aryl}$), 6.50 (m, 2 H, *cav*-$H_{aryl}$), 5.97 (s, 4 H, *phen*-$H_{aryl}$), 5.71 (d, $^2J$ = 7.4 Hz, 4 H, *cav*-$H_{acetal}$), 5.63 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.68 (t, $^3J$ = 8.0 Hz, 8 H, *cav*-$H_{benzyl}$), 4.45 (d, $^2J$ = 7.4 Hz, 4 H, *cav*-$H_{acetal}$), 4.36 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 3.29 (br. s, 12 H, –$OCH_3$), 2.32 (m, 16 H, *cav*-$H_{alkyl}$), 1.42–1.24 (m, 144 H, *cav*-$H_{alkyl}$), 0.84 (m, 24 H, *cav*-$H_{alkyl}$) ppm (please note that the assignment was done solely on the basis of the $^1H$ NMR spectroscopic data and the comparison with known complexes). MS (ESI, pos. mode): *m/z* (%) = 3062.8 ([Cu(**24**)(**1b**)]$^+$, 100, matching isotope pattern). HiRes-MS (pos. ESI) calcd. for $[C_{192}H_{252}N_4O_{24}Cu]^+$ *m/z* = 3062.7971; found *m/z* = 3062.8315 (Δ = 11.2 ppm).

**[Cu(25)]$BF_4$:** 5.2 mg (5.0 μmol) of **25** were dissolved in 800 μL of a 2:1 mixture of [$D_1$]chloroform/[$D_4$]MeOH. 1.6 mg (5.0 μmol, 1 equiv.) of [Cu($CH_3CN$)$_4$]$BF_4$ were dissolved in 200 μL of a 2:1 mixture of [$D_1$]chloroform/[$D_4$]MeOH. The solutions were combined and heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by $^1H$ NMR spectroscopy and ESI MS. $^1H$ NMR (400.1 MHz, $CDCl_3$/[$D_4$]MeOH 2:1, 298 K): $\delta$ = 8.29 (d, $^3J$ = 8.2 Hz, 2 H, $H_{phen}$), 7.79 (s, 2 H, $H_{phen}$), 7.74 (m, $^3J$ = 8.2 Hz, 2 H, $H_{phen}$), 7.13 (m, $^3J$ = 8.3 Hz, 2 H, $H_{aryl}$), 6.46 (d, $^3J$ = 8.3 Hz, 4 H, $H_{aryl}$), 3.93–3.88 (m, 16 H, –$OCH_2$–), 3.42–3.22 (m, 40 H, –$OCH_2$–), 0.93 (m, 12 H, –$OCH_2CH_3$) ppm (referenced on residual $CHCl_3$, please note that the assignment was done solely on the basis of the $^1H$ NMR spectroscopic data and the comparison with known complexes). MS (ESI, pos. mode): *m/z* (%) = 1099.4 ([Cu(**25**)]$^+$, 45, matching isotope pattern), 1037.6 [**25** + H]$^+$, (100).

**[Cu(25)(1b)]$BF_4$:** 5.1 mg (2.0 μmol) of **1b** were dissolved in 0.5 mL of a 2:1 mixture of [$D_1$]chloroform/[$D_4$]MeOH. 400 μL of the 5 mM solution of [Cu(**25**)]$BF_4$ (2.0 μmol, 1 equiv.) was added and heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by $^1H$ NMR spectroscopy and ESI MS. $^1H$ NMR (400.1 MHz, $CDCl_3$/[$D_4$]MeOH 2:1, 298 K): $\delta$ = 8.43 (d, $^3J$ = 8.3 Hz, 2 H, *phen*-$H_{phen}$), 8.31 (d, $^3J$ = 5.2 Hz, 2 H, *bipy*-H), 8.23 (s, 2 H, *bipy*-H), 7.95 (s, 2 H, *phen*-$H_{phen}$), 7.82 (d, $^3J$ = 5.2 Hz, 2 H, *bipy*-H), 7.70 (d, $^3J$ = 8.3 Hz, 2 H, *phen*-$H_{phen}$), 6.95 (s, 4 H, *cav*-$H_{aryl}$), 6.93 (s, 2 H, *cav*-$H_{aryl}$), 6.87 (s, 2 H, *cav*-$H_{aryl}$), 6.59 (t, $^3J$ = 8.4 Hz, 2 H, *phen*-$H_{aryl}$), 6.32 (s, 2 H, *cav*-$H_{aryl}$), 6.28 (s, 4 H, *cav*-$H_{aryl}$), 5.79 (d, $^3J$ = 8.4 Hz, 4 H, *phen*-$H_{aryl}$), 5.50 (d, $^2J$ = 7.2 Hz, 4 H, *cav*-$H_{acetal}$), 5.41 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.52 (t, $^3J$ = 7.9 Hz, 4 H, *cav*-$H_{benzyl}$), 4.51 (t, $^3J$ = 7.6 Hz, 4 H, *cav*-$H_{benzyl}$), ≈ 4.3–4.2 (m, 8 H, *cav*-$H_{acetal}$, buried under the water signal), 3.57–3.53 (m, 4 H, –$OCH_2$–), 3.40–3.20 (m, 52 H, –$OCH_2$–), 2.05–1.97 (m, 16 H, *cav*-$H_{alkyl}$), 1.25–1.00 (m, 144 H, *cav*-$H_{alkyl}$), 0.82 (m, 12 H, –$OCH_2CH_3$), 0.63 (m, 24 H, *cav*-$H_{alkyl}$) ppm (referenced on residual $CHCl_3$, please note that the assignment was done solely on the basis of the $^1H$ NMR spectroscopic data and the comparison with known complexes). MS (ESI, pos. mode): *m/z* (%) = 3648.3 (100, matching isotope pattern) [Cu(**25**)(**1b**)]$^+$.

**[Re(CO)$_3$(2)Cl]:** 250.8 mg of **2** (100 μmol) and 36.2 mg (100 μmol, 1 equiv.) of pentacarbonylrhenium chloride were dissolved in 5 mL of chloroform and heated to 50 °C for 1 h. 280 mg (quant.) of the desired complex could be isolated after column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate, 1:1 + 0.5% triethylamine). $R_f$ = 0.95 (*n*-hexane/ethyl acetate, 1:1 + 0.5% triethylamine). $^1H$ NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.95 (d, $^3J$ = 6.1 Hz, 2 H, *bipy*-H), 8.08 (s, 2 H, *bipy*-H), 7.42 (d, $^3J$ = 6.1 Hz, 2 H, *bipy*-H), 7.24 (s, 2 H, *cav*-$H_{aryl}$), 7.11 (s, 4 H, *cav*-$H_{aryl}$), 7.10 (s, 2 H, *cav*-$H_{aryl}$), 6.54 (s, 2 H, *cav*-$H_{aryl}$), 6.53 (s, 2 H, *cav*-$H_{aryl}$), 6.47 (s, 2 H, *cav*-$H_{aryl}$), 5.92 (d, $^2J$ = 7.2 Hz, 4 H, *cav*-$H_{acetal}$), 5.72 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 5.71 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 4.80 (t, $^3J$ = 8.2 Hz, 4 H, *cav*-$H_{benzyl}$), 4.73 (t, $^3J$ = 8.2 Hz, 4 H, *cav*-$H_{benzyl}$), 4.54 (d, $^2J$ = 7.2 Hz, 4 H, *cav*-$H_{acetal}$), 4.41 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 4.40 (d, $^2J$ = 7.2 Hz, 2 H, *cav*-$H_{acetal}$), 2.30–2.17 (m, 16 H, *cav*-$H_{alkyl}$), 1.49–1.19 (m, 144 H, *cav*-$H_{alkyl}$), 0.87 (m, 24 H, *cav*-$H_{alkyl}$) ppm. $^{13}C$ NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 27.9, 29.4, 29.7, 29.8, 29.9, 31.9 (*cav*-$C_{alkyl}$), 36.3, 36.4 (*cav*-$C_{benzyl}$), 92.4 (2× $C_{alkyne}$), 99.1 (*cav*-$C_{acetal}$), 99.5 (*cav*-$C_{acetal}$), 110.9 (*cav*-$C_{aryl}$), 116.6 (*cav*-$C_{aryl}$), 120.5, 120.6 (*cav*-$C_{aryl}$), 122.8 (*cav*-$C_{aryl}$), 124.9 (*bipy*-$C_{aryl}$), 128.8 (*bipy*-$C_{aryl}$), 134.6 (*bipy*-$C_{aryl}$), 137.9, 138.3, 138.9, 139.0 (*cav*-$C_{aryl}$) 152.9 (*bipy*-$C_{aryl}$), 154.6, 154.9, 155.2, 155.3, 155.9 (4× *cav*-$C_{aryl}$, *bipy*-$C_{aryl}$), 189.0, 196.8 (CO) ppm. MS (ESI, neg. mode): *m/z* (%) = 2541.5 (100, matching isotope pattern) [($Re(CO)_3Cl$(**2**) + $CH_3O)_2$]$^{2-}$.

**[Ag(2)$_2$]$BF_4$:** 25.1 mg (10.0 μmol) of **2** were dissolved in 1 mL of [$D_6$]benzene. 1.4 mg (5.0 μmol, 0.5 equiv.) of [Ag($NCCH_3$)$_2$]$BF_4$ were dissolved in 40 μL of [$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the slightly yellow solution of the desired silver(I) complex which was characterised by NMR spectroscopy. Please note that the mass of the 2:1 complex (M([$C_{332}H_{456}AgN_4O_{32}$]$^+$) = 5123.05 g/mol) was beyond the mass which we could measure accurately with our equipment. However, no signal for a [Ag(**2**)]$BF_4$ complex carrying only one ligand could be detected. $^1H$ NMR (500.1 MHz, $C_6D_6/CD_3CN$, 25:1, 298 K): $\delta$ = 8.49 (m, 2 H, *bipy*-H), 8.42 (m, 2 H, *bipy*-H), 7.61 (s, 2 H, *cav*-$H_{aryl}$), 7.54 (s, 6 H, *cav*-$H_{aryl}$), 7.24 (m, 2 H, *bipy*-H), 6.73 (s, 4 H, *cav*-$H_{aryl}$), 6.59 (s, 2 H, *cav*-$H_{aryl}$), 6.08 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 5.72 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 5.21 (t, $^3J$ = 7.7 Hz, 4 H, *cav*-$H_{benzyl}$), 5.14 (t, $^3J$ = 7.7 Hz, 4 H, *cav*-$H_{benzyl}$), 4.78 (d, $^2J$ = 7.1 Hz, 4 H, *cav*-$H_{acetal}$), 4.49 (d, $^2J$ = 7.1 Hz, 4 H,

*cav*-$H_{acetal}$), 2.45–2.28 (m, 16 H, *cav*-$H_{alkyl}$), 1.50–1.13 (m, 144 H, *cav*-$H_{alkyl}$), 0.92 (t, $^3J$ = 6.6 Hz, 24 H, *cav*-$H_{alkyl}$) ppm.

**[Cu(2)$_2$]BF$_4$:** 25.1 mg (10.0 μmol) of **2** were dissolved in 1 mL of [$D_6$]benzene. 1.6 mg (5.0 μmol, 0.5 equiv.) of [Cu(NCCH$_3$)$_4$]BF$_4$ were dissolved in 40 μL of [$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by NMR spectroscopy. Please note that the mass of the 2:1 complex (M([$C_{332}H_{456}CuN_4O_{32}$]$^+$) = 5078.73 g/mol) was beyond the mass which we could measure accurately with our equipment. However, no signal for a [Cu(**2**)]BF$_4$ complex carrying only one ligand could be detected. $^1$H NMR (500.1 MHz, $C_6D_6$/$CD_3CN$, 25:1, 298 K): $\delta$ = 9.04 (m, 2 H, *bipy*-H), 8.55 (m, 2 H, *bipy*-H), 7.98 (m, 2 H, *bipy*-H), 7.70–7.50 (m, 8 H, *cav*-$H_{aryl}$), 6.69 (br. s, 4 H, *cav*-$H_{aryl}$), 6.44 (br. s, 2 H, *cav*-$H_{aryl}$), 5.97 (m, 4 H, *cav*-$H_{acetal}$), 5.76 (m, 4 H, *cav*-$H_{acetal}$), 5.31–5.10 (m, 8 H, *cav*-$H_{benzyl}$), 4.70 (m, 4 H, *cav*-$H_{acetal}$), 4.53 (m, 4 H, *cav*-$H_{acetal}$), 2.54–2.33 (m, 16 H, *cav*-$H_{alkyl}$), 1.58–1.27 (m, 144 H, *cav*-$H_{alkyl}$), 1.02 (m, 24 H, *cav*-$H_{alkyl}$) ppm.

**[Ag(3)]BF$_4$:** 25.1 mg (10.0 μmol) of **3** were dissolved in 1 mL of [$D_6$]-benzene. 1.4 mg (5.0 μmol, 0.5 equiv.) of [Ag(NCCH$_3$)$_2$]BF$_4$ were dissolved in 40 μL of [$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the slightly yellow solution of the desired silver(I) complex which was characterised by NMR spectroscopy and ESI MS. $^1$H NMR (500.1 MHz, $C_6D_6$/$CD_3CN$, 25:1, 298 K): $\delta$ = 8.04 (d, $^3J$ = 5.5 Hz, 2 H, *bipy*-H), 7.67 (br. s, 2 H, *bipy*-H), 7.55–7.42 (m, 10 H, *cav*-$H_{aryl}$, *bipy*-H), 6.79 (br. s, 6 H, *cav*-$H_{aryl}$), 6.30 (d, $^2J$ = 5.4 Hz, 4 H, *cav*-$H_{acetal}$), 5.92 (d, $^2J$ = 5.4 Hz, 4 H, *cav*-$H_{acetal}$), 5.29 (m, 4 H, *cav*-$H_{benzyl}$), 5.21–5.08 (m, 8 H, *cav*-$H_{acetal}$, *cav*-$H_{benzyl}$ 4), 4.75 (d, $^2J$ = 5.4 Hz, 4 H, *cav*-$H_{acetal}$), 2.55–2.25 (m, 16 H, *cav*-$H_{alkyl}$), 1.68–1.10 (m, 144 H, *cav*-$H_{alkyl}$), 0.92 (t, $^3J$ = 6.6 Hz, 24 H, *cav*-$H_{alkyl}$) ppm. MS (ESI, pos. mode): *m*/*z* (%) = 2617.5 ([Ag(**3**)]$^+$, 100, matching isotope pattern, just a trace signal for a [Ag(**3**)$_2$]$^+$ ion could be detected in an ESI-QToF experiment which resulted most likely from non-specific aggregation).

**[Cu(3)]BF$_4$:** 25.1 mg (10.0 μmol) of **3** were dissolved in 1 mL of [$D_6$]-benzene. 1.6 mg (5.0 μmol, 0.5 equiv.) of [Cu(NCCH$_3$)$_4$]BF$_4$ were dissolved in 40 μL of [$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by NMR spectroscopy and ESI MS. $^1$H NMR (500.1 MHz, $C_6D_6$/$CD_3CN$, 25:1, 298 K): $\delta$ = 8.02 (m, 2 H, *bipy*-H), 7.72–7.42 (m, 12 H, 3× *cav*-$H_{aryl}$, 2× *bipy*-H), 6.60 (br. s, 2 H, *cav*-$H_{aryl}$), 6.53 (br. s, 4 H, *cav*-$H_{aryl}$), 5.71 (m, 4 H, *cav*-$H_{acetal}$), 5.56 (m, 4 H, *cav*-$H_{acetal}$), 5.08 (m, 4 H, *cav*-$H_{benzyl}$), 4.87 (m, 4 H, *cav*-$H_{benzyl}$), 4.43 (m, 4 H, *cav*-$H_{acetal}$), 4.36 (m, 4 H, *cav*-$H_{acetal}$), 2.63–2.26 (m, 16 H, *cav*-$H_{alkyl}$), 1.67–1.11 (m, 144 H, *cav*-$H_{alkyl}$), 0.92 (t, $^3J$ = 7.2 Hz, 24 H, *cav*-$H_{alkyl}$) ppm. MS (ESI, pos. mode): *m*/*z* (%) = 2572.8 ([Cu(**3**)]$^+$, 100, matching isotope pattern, just a trace signal for a [Cu(**3**)$_2$]$^+$ ion could be detected in an ESI-QToF experiment which resulted most likely from non-specific aggregation).

**[Re(CO)$_3$(4)Cl]:** 149.0 mg (100 μmol) of **4** and 36.2 mg (100 μmol, 1 equiv.) of pentacarbonylrhenium chloride were dissolved in 5 mL of chloroform and heated to 50 °C for 1 h. Evaporation of the solvent and purification of the orange residue by column chromatography of silica gel (eluent: *n*-hexane/ethyl acetate, 1:1 + 0.5% triethylamine) gave 62 mg of the pure complex as an orange solid (35 μmol, 35%). $R_f$ = 0.50 (*n*-hexane/ethyl acetate, 1:1 + 0.5% triethylamine). $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 8.99 (d, $^3J$ = 5.5 Hz, 1 H, *bipy*-H), 8.90 (d, $^3J$ = 5.5 Hz, 1 H, *bipy*-H), 8.54 (br. s, 1 H, –NH), 8.44 (s, 1 H, *bipy*-H), 8.39 (d, $^3J$ = 7.7 Hz, 1 H, *py*-H), 8.08 (s, 1 H, *bipy*-H), 7.86 (dd, $^3J$ = 8.0, $^3J$ = 7.7 Hz, 1 H, *py*-H), 7.53 (d, $^3J$ = 5.5 Hz, 1 H, *bipy*-H), 7.52 (d, $^3J$ = 8.0 Hz, 1 H, *py*-H), 7.39 (d, $^3J$ = 5.5 Hz, 1 H, *bipy*-H), 7.25 (s, 1 H, *cav*-$H_{aryl}$), 7.12 (s, 2 H, *cav*-$H_{aryl}$), 7.11 (s, 1 H, *cav*-$H_{aryl}$), 6.55 (s, 1 H, *cav*-$H_{aryl}$), 6.54 (s, 1 H, *cav*-$H_{aryl}$), 6.47 (s, 1 H, *cav*-$H_{aryl}$), 6.12 (d, $^2J$ = 7.1 Hz, 1 H, *cav*-$H_{acetal}$), 6.00 (d, $^2J$ = 7.1 Hz, 1 H, *cav*-$H_{acetal}$), 5.74 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 4.84 (t, $^3J$ = 8.2 Hz, 1 H, *cav*-$H_{benzyl}$), 4.81 (t, $^3J$ = 8.2 Hz, 1 H, *cav*-$H_{benzyl}$), 4.73 (t, $^3J$ = 8.2 Hz, 2 H, *cav*-$H_{benzyl}$), 4.57–4.51 (m, 2 H, *cav*-$H_{acetal}$), 4.41 (d, $^2J$ = 7.1 Hz, 2 H, *cav*-$H_{acetal}$), 2.29–2.18 (m, 8 H, *cav*-$H_{alkyl}$), 2.25 [s, 3 H, –C(O)C$H_3$], 1.49–1.20 (m, 72 H, *cav*-$H_{alkyl}$), 0.88 (t, $^3J$ = 7.2 Hz, 12 H, *cav*-$H_{alkyl}$) ppm. $^{13}$C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta$ = 14.1 (*cav*-$C_{alkyl}$), 22.7 (*cav*-$C_{alkyl}$), 24.7 [–C(O)*C*H$_3$], 27.9, 29.4, 29.7, 29.8, 29.9, 31.9 (*cav*-$C_{alkyl}$), 36.3, 36.4 (*cav*-$C_{benzyl}$), 86.5 ($C_{alkyne}$), 92.5 (2× $C_{alkyne}$), 95.0 ($C_{alkyne}$), 99.3 (*cav*-$C_{acetal}$), 99.5 (*cav*-$C_{acetal}$), 110.9 (*cav*-$C_{aryl}$), 116.6 (*py*-$C_{aryl}$), 120.5, 120.6 (*cav*-$C_{aryl}$), 122.9 (*cav*-$C_{aryl}$), 124.5 (*py*-$C_{aryl}$), 124.8 (*bipy*-$C_{aryl}$), 126.0 (*bipy*-$C_{aryl}$), 128.8 (*bipy*-$C_{aryl}$), 129.1 (*bipy*-$C_{aryl}$), 133.2 (*bipy*-$C_{aryl}$), 134.5 (*bipy*-$C_{aryl}$), 137.9, 138.3, 138.4, 138.8 (*cav*-$C_{aryl}$) 139.0 (*py*-$C_{aryl}$), 151.6 (*py*-$C_{aryl}$), 152.8 (*bipy*-$C_{aryl}$), 153.0 (*bipy*-$C_{aryl}$), 154.7, 154.8, 155.1, 155.2, 155.3, 156.0, 156.1 (3× *cav*-$C_{aryl}$, 2× *bipy*-$C_{aryl}$, *py*-$C_{aryl}$), 168.9 [–*C*(O)CH$_3$], 188.9, 196.8 (CO) ppm. MS (ESI, pos. mode): *m*/*z* (%) = 1818.8 ([Re(CO)$_3$Cl(**4**) + Na]$^+$, 100, matching isotope pattern).

**[Ag(4)$_2$]BF$_4$:** 14.9 mg (10.0 μmol) of **4** were dissolved in 1 mL of [$D_6$]benzene. 1.4 mg (5.0 μmol, 0.5 equiv.) of [Ag(NCCH$_3$)$_2$]BF$_4$ were dissolved in 40 μL of [$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the slightly yellow solution of the desired silver(I) complex which was characterised by NMR spectroscopy and ESI MS. $^1$H NMR (500.1 MHz, $C_6D_6$/$CD_3CN$, 25:1, 298 K): $\delta$ = 9.03–8.84, 8.71–8.51, 8.397, 8.272, 7.60, 7.52, 7.36 (m, 10 H, –NH, 6× *bipy*-H, 3× *py*-H), 7.03 (br. s, 3 H, *cav*-$H_{aryl}$), 6.78 (br. s, 2 H, *cav*-$H_{aryl}$), 6.61 (br. s, 1 H, *cav*-$H_{aryl}$), 6.21 (m, 2 H, *cav*-$H_{acetal}$), 5.76 (m, 2 H, *cav*-$H_{acetal}$), 5.20 (m, 2 H, *cav*-$H_{benzyl}$), 5.14 (m, 2 H, *cav*-$H_{benzyl}$), 4.89 (m, 2 H, *cav*-$H_{acetal}$), 4.52 (m, 2 H, *cav*-$H_{acetal}$), 2.46–2.28 [br. s, 3 H, –C(O)C$H_3$], 2.01–1.86 (m, 8 H, *cav*-$H_{alkyl}$), 1.50–1.00 (m, 72 H, *cav*-$H_{alkyl}$), 0.95–0.88 (m, 12 H, *cav*-$H_{alkyl}$) ppm. MS (ESI, pos. mode): *m*/*z* (%) = 3087.8 (100) [Ag(**4**)$_2$]$^+$. HiRes-MS (pos. ESI) calcd. for [$C_{194}H_{247}AgN_8O_{18}$]$^+$ *m*/*z* = 3087.7852; found *m*/*z* = 3087.7810 ($\Delta$ = –1.4 ppm).

**[Cu(4)$_2$]BF$_4$:** 14.9 mg (10.0 μmol) of **4** were dissolved in 1 mL of [$D_6$]benzene. 1.6 mg (5.0 μmol, 0.5 equiv.) of [Cu(NCCH$_3$)$_4$]BF$_4$ were dissolved in 40 μL of [$D_3$]acetonitrile. The solutions were combined and heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by NMR spectroscopy and ESI MS. Unfortunately, the NMR spectra showed only very broad signals (even at low temperatures) which did not allow any assignment of individual signals. MS (ESI, pos. mode): *m*/*z* (%) = 3041.8 (100) [Cu(**4**)$_2$]$^+$. HiRes-MS (pos. ESI) calcd. for [$C_{194}H_{247}CuN_8O_{18}$]$^+$ *m*/*z* = 3041.8008; found *m*/*z* = 3041.7556 ($\Delta$ = –14.9 ppm).

**[Re(CO)$_3$(5)Cl]:** 50.0 mg (26.7 μmol) of **5** and 9.7 mg (26.7 μmol, 1 equiv.) of [Re(CO)$_5$Cl] were dissolved in 5 mL of chloroform and heated to 60 °C for 24 h. The solution was diluted with 25 mL of dichloromethane, extracted twice with water (2 mL). Evaporation of the solvent gave 58 mg (quant.) of the pure complex as an orange solid. $^1$H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta$ = 9.35 (d, $^3J$ = 4.8 Hz, 1 H, *bipy*-H), 8.89 (d, $^4J$ = 1.4 Hz, 1 H, *bipy*-H), 8.59 (d, $^3J$ = 7.2 Hz, 1 H, *bipy*-H), 8.48 (d, $^3J$ = 7.2 Hz, 1 H, *bipy*-H), 8.33 (dd, $^3J$ = 7.2, $^3J$ = 7.2 Hz, 1 H, *bipy*-H), 8.13 (dd, $^3J$ = 4.8, $^4J$ = 1.4 Hz, 1 H, *bipy*-H), 7.14–7.10 (m, 6 H, *cav*-$H_{aryl}$), 6.58 (s, 1 H,

*cav*-$H_{aryl}$), 6.57 (s, 1 H, *cav*-$H_{aryl}$), 6.51 (s, 2 H, *cav*-$H_{aryl}$), 6.42 (s, 2 H, *cav*-$H_{aryl}$), 5.77 (m, 2 H, *cav*-$H_{acetal}$), 5.69 (m, 2 H, *cav*-$H_{acetal}$), 5.59 (m, 2 H, *cav*-$H_{acetal}$), 5.58 (m, 2 H, *cav*-$H_{acetal}$), 4.82–4.63 (m, 8 H, *cav*-$H_{benzyl}$), 4.47 (m, 4 H, *cav*-$H_{acetal}$), 4.38 (m, 2 H, *cav*-$H_{acetal}$), 4.32 (m, 2 H, *cav*-$H_{acetal}$), 2.24–2.20 (m, 16 H, *cav*-$H_{alkyl}$), 1.43–1.33 (m, 48 H, *cav*-$H_{alkyl}$), 0.91 (m, 24 H, *cav*-$H_{alkyl}$) ppm. MS (ESI, neg. mode): *m/z* (%) = 2259.0 ($[Re(CO)_3Cl(\mathbf{5}) + Br]^-$, 30, matching isotope pattern).

**[Ag(5)]$BF_4$:** 20.0 mg (10.7 μmol) of **5** were dissolved in 2 mL of [$D_6$]-benzene. From this solution 400 μL was transferred into an NMR tube. 5.9 mg (21.4 μmol) of $[Ag(NCCH_3)_2]BF_4$ were dissolved in 1 mL of [$D_3$]acetonitrile. 100 μL of the silver(I) salt's solution was also transferred to the NMR tube. The resulting mixture was heated to 40 °C for 30 min to give an almost colourless solution of the desired silver(I) complex which was characterised by NMR spectroscopy and ESI MS. Unfortunately, the NMR spectra showed only very broad signals (even at low temperatures) which did not allow any assignment of individual signals. MS (ESI, pos. mode): *m/z* (%) = 1981.0 (100) $[Ag(\mathbf{5})]^+$. HiRes-MS (pos. ESI) calcd. for $[C_{116}H_{132}AgN_2O_{20}]^+$ *m/z* = 1981.8449; found *m/z* = 1981.7807 (Δ = –32.3 ppm).

**[Cu(5)]$BF_4$:** 20.0 mg (10.7 μmol) of **5** were dissolved in 2 mL of [$D_6$]-benzene. From this solution 400 μL was transferred into an NMR tube. 6.7 mg (21.4 μmol) of $[Cu(NCCH_3)_4]BF_4$ were dissolved in 1 mL of [$D_3$]acetonitrile. 100 μL of the copper(I) salt's solution was also transferred to the NMR tube. The resulting mixture was heated to 40 °C for 30 min to give the deep red solution of the desired copper(I) complex which was characterised by NMR spectroscopy and ESI MS. Unfortunately, the NMR spectra showed only very broad signals (even at low temperatures) which did not allow any assignment of individual signals. MS (ESI, pos. mode): *m/z* (%) = 1977.9 (100) $[Cu(\mathbf{5})(CH_3CN)]^+$. HiRes-MS (pos. ESI) calcd. for $[C_{118}H_{135}CuN_3O_{20}]^+$ *m/z* = 1978.8967; found *m/z* = 1978.9160 (Δ = 9.8 ppm).

## Acknowledgments

We would like to thank the Deutsche Forschungsgemeinschaft (DFG) (SFB 624) for financial support.

[1] a) F. Hof, S. L. Craig, C. Nuckolls, J. Rebek Jr., *Angew. Chem.* **2002**, *114*, 1556–1578; *Angew. Chem. Int. Ed.* **2002**, *41*, 1488–11508; b) L. Kovbasyuk, R. Krämer, *Chem. Rev.* **2004**, *104*, 3161–3187; c) D. M. Vriezema, M. C. Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445–1489.

[2] C. A. Schalley, A. Lützen, M. Albrecht, *Chem. Eur. J.* **2004**, *10*, 1072–1080.

[3] A. Lützen, O. Haß, T. Bruhn, *Tetrahedron Lett.* **2002**, *43*, 1807–1811.

[4] a) D. J. Cram, M. J. Cram, *Container Molecules and Their Guests*, Royal Society of Chemistry, Cambridge, **1994**; b) J. C. Sherman, *Tetrahedron* **1995**, *51*, 3395–3422.

[5] For a comprehensive list of references using 2,2′-bipyridines as allosteric centres, see references 7–16 in ref.[6].

[6] S. Zahn, W. Reckien, B. Kirchner, H. Staats, J. Matthey, A. Lützen, *Chem. Eur. J.* **2009**, *15*, 2572–2580.

[7] G.-J. ten Brink, I. W. C. E. Arends, M. Hoogenrad, G. Verspui, R. A. Sheldon, *Adv. Synth. Catal.* **2003**, *345*, 497–505.

[8] J. E. Parks, B. E. Wagner, R. H. Holm, *J. Organomet. Chem.* **1973**, *56*, 53–66.

[9] I. R. Butler, C. Soucy-Breau, *Can. J. Chem.* **1991**, *69*, 1117–1123.

[10] a) A. Lützen, M. Hapke, *Eur. J. Org. Chem.* **2002**, 2292–2297; b) A. Lützen, M. Hapke, H. Staats, J. Bunzen, *Eur. J. Org. Chem.* **2003**, 3948–3957; c) U. Kiehne, J. Bunzen, H. Staats, A. Lützen, *Synthesis* **2007**, 1061–1069; d) M. Hapke, H. Staats, I. Wallmann, A. Lützen, *Synthesis* **2007**, 2711–2719; e) M. Hapke, L. Brandt, A. Lützen, *Chem. Soc. Rev.* **2008**, *37*, 2782–2797.

[11] K. Paek, K. Joo, M. Kim, Y. Kim, *Bull. Korean Chem. Soc.* **1995**, *16*, 477–478.

[12] Please note that monofunctionalized cavitands can also be prepared in a functionalization-defunctionalization approach: a) J. L. Irwin, M. S. Sherburn, *J. Org. Chem.* **2000**, *65*, 602–605; b) J. L. Sherburn, M. S. Sherburn, *J. Org. Chem.* **2000**, *65*, 5846–5848; c) J. L. Irwin, M. S. Sherburn, *Org. Lett.* **2001**, *3*, 225–227.

[13] O. Hass, A. Schierholt, M. Jordan, A. Lützen, *Synthesis* **2006**, 519–526.

[14] Compound **23** could also be prepared selectively by using a slight excess of bipyridine **10** compared to cavitand **19**. However, the yield obtained in this approach was almost identical. Since the separation of **2** and **23** did not cause any severe trouble we sticked to the method depicted in Scheme 9.

[15] a) M. Schmittel, U. Lüning, M. Meder, A. Ganz, C. Michel, M. Hederich, *Heterocycl. Commun.* **1997**, *3*, 493–498; b) M. Schmittel, A. Ganz, *Synlett* **1997**, 710–712; c) M. Schmittel, A. Ganz, *Chem. Commun.* **1997**, 999–1000. The formation of heteroleptic complexes can also be seen through the eyes of dynamic combinatorial chemistry. There, numerous investigations have been carried out to study the influence of the relative stabilities of individual components on the final composition of the dynamic combinatorial libraries. The final mixture will be that with the lowest total free enthalpy and thus the most stable member need not exist in highest concentration. Some examples: d) P. T. Corbett, J. K. M. Sanders, S. Otto, *J. Am. Chem. Soc.* **2005**, *127*, 9390–9392; e) P. T. Corbett, J. K. M. Sanders, S. Otto, *Chem. Eur. J.* **2008**, *14*, 2153–2166; f) K. Severin, *Chem. Eur. J.* **2004**, *10*, 2565–2580; g) V. Saggiomo, U. Lüning, *Chem. Commun.* **2009**, 3711–3713.

[16] a) U. Lüning, *Liebigs Ann. Chem.* **1987**, 949–955; b) U. Lüning, M. Müller, *Chem. Ber.* **1990**, *123*, 643–645; c) U. Lüning, M. Müller, M. Gelbert, K. Peters, H. G. von Schnering, M. Keller, *Chem. Ber.* **1994**, *127*, 2297–2306; d) M. Hagen, U. Lüning, *Chem. Ber./Recueil* **1997**, *130*, 231–234; e) F. Löffler, M. Hagen, U. Lüning, *Synlett* **1999**, 1826–1828; f) B. Meynhardt, U. Lüning, C. Wolff, C. Näther, *Eur. J. Org. Chem.* **1999**, 2327–2335; g) M. Gelbert, U. Lüning, *Supramol. Chem.* **2001**, *12*, 435–444; h) M. Bühl, F. Terstegen, F. Löffler, B. Meynhardt, S. Kierse, M. Müller, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2001**, 2151–2160; i) U. Lüning, F. Fahrenkrug, *Eur. J. Org. Chem.* **2006**, 916–923; j) S. Konrad, M. Bolte, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2006**, 4717–4730; k) F. Eggers, U. Lüning, *Eur. J. Org. Chem.* **2009**, 2328–2341; l) U. Lüning, M. Abbass, F. Fahrenkrug, *Eur. J. Org. Chem.* **2002**, 3294–3303; m) R. Cacciapaglia, S. Di Stefano, F. Fahrenkrug, U. Lüning, L. Mandolini, *J. Phys. Org. Chem.* **2004**, *17*, 350–355; n) U. Lüning, F. Fahrenkrug, *Eur. J. Org. Chem.* **2004**, 3119–3127.

[17] J. Lewis, T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.* **1980**, 736–742.

[18] M. Yamada, Y. Nakamura, S. Kuroda, I. Shimao, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2710–2712.

[19] F. Fahrenkrug, Ph. D. Thesis, Christian-Albrechts-Universität zu Kiel, **2003**.

[20] T. Hamura, T. Hosoya, H. Yamaguchi, Y. Kuriyama, M. Tanabe, M. Miyamoto, Y. Yasui, T. Matsumoto, K. Suzuki, *Helv. Chim. Acta* **2002**, *85*, 3589–3604.

[21] E. Kiehlmann, R. W. Lauener, *Can. J. Chem.* **1989**, *67*, 335–344.

[22] T. L. Davis, J. W. Hill, *J. Am. Chem. Soc.* **1929**, *51*, 493–504.

[23] F. Bellouard, F. Chuburu, J.-J. Yaouanc, H. Handel, Y. LeMest, *Eur. J. Org. Chem.* **1999**, 3257–3261.

[24] Please note that experiments with 2,9-dichloro-1,10-phenanthroline and related boronic acids were not successful even

with broad variation of the reaction conditions, so the iodo compound **26** has to be used instead.
[25] Please note that because of the unknown amount of boronic acid **27** in the crude product and incomplete conversion, additional crude boronic acid **27** and tetrakis(triphenylphosphane)palladium(0) were added after 18 h and the mixture was stirred for another 20 h to yield the desired product **25**.
[26] a) L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, D. J. Cram, *J. Org. Chem.* **1989**, *54*, 1305–1312; b) D. J. Cram, S. Karbach, H.-E. Kim, C. B. Knobler, E. F. Maverick, J. L. Ericson, R. C. Helgeson, *J. Am. Chem. Soc.* **1988**, *110*, 2229–2237.
[27] This compound has been described before. However, it was synthesised in a different way: a) G. Maerker, F. H. Case, *J. Am. Chem. Soc.* **1958**, *80*, 2745–2748; b) D. Wenkert, R. B. Woodward, *J. Org. Chem.* **1983**, *48*, 283–289.
[28] This compound has been described before. However, it was synthesised in a different way: a) Y. Aoyama, Y. Tanaka, S. Sugahara, *J. Am. Chem. Soc.* **1989**, *111*, 5397–5404; b) D. J. Cram, L. M. Tunstad, C. B. Knobler, *J. Org. Chem.* **1992**, *57*, 528–535.
[29] This compound has been described before. However, it was synthesised in a different way: P. L. Ferrarini, G. Biagi, O. Livi, G. Primofiore, M. Carpene, *J. Heterocycl. Chem.* **1981**, *18*, 1007–1010.

Received: June 12, 2009
Published Online: August 27, 2009