Induction of an Enantiomeric Excess in a Calix[4]arene/Bipyridine-Based Chiral Copper(I) Complex

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Introduction of the non-complexing chiral (*S*)-2-methylbutoxy substituent close to the complexing site of a bis[(bipyridinyl)methoxy]calixarene podand resulted in the induction of an enantiomeric excess of *ca.* 30% in the corresponding chiral Cu^I complex. Structural investigations by high-resolution NMR studies led us to propose the left-handed prohelical $[Cu^I(bpy)_2]$ substructure for the major enantiomer.

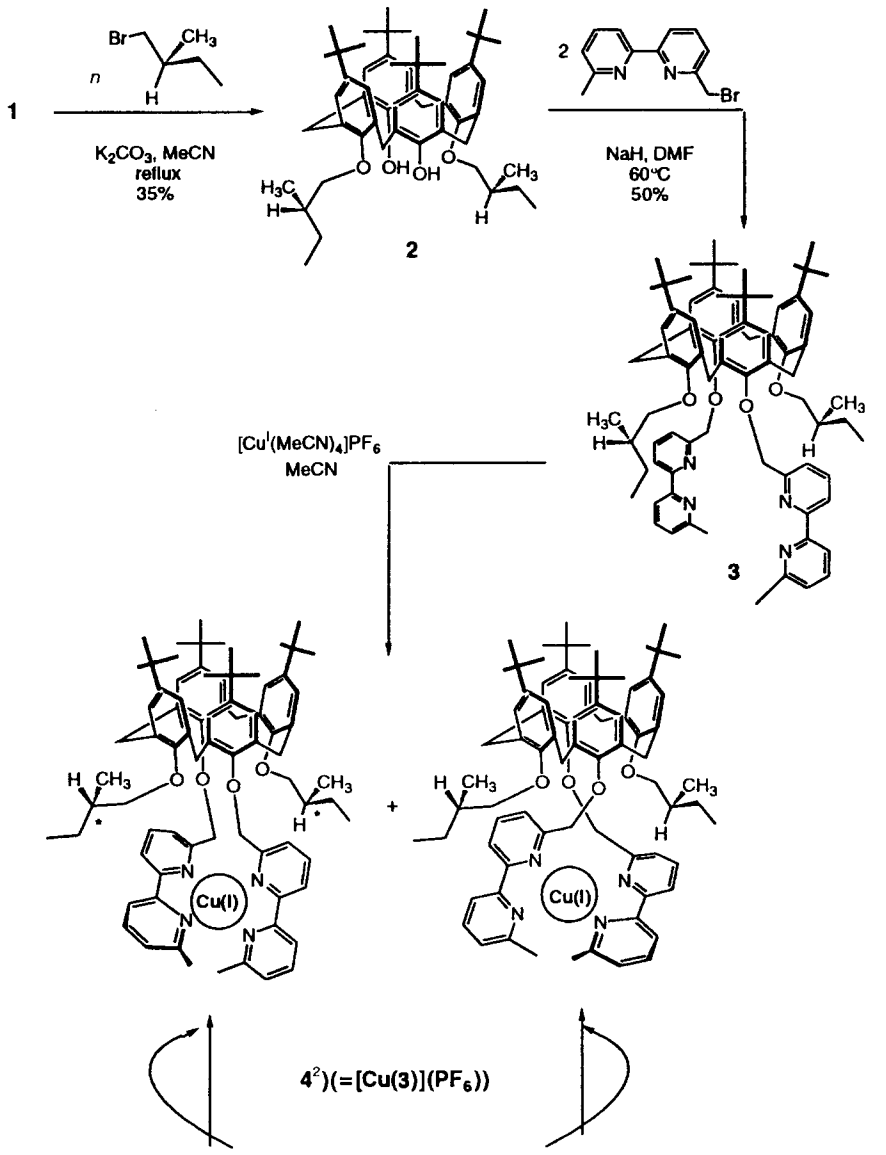
Introduction. – We have recently described the synthesis and the complexation properties towards copper(I) and copper(II) of a calix[4]arene podand incorporating in alternate positions two bipyridine complexing units and two pyridine moieties at the lower rim [1]. The hexafluorophosphate salt of its Cu^I complex crystallized fairly well in a toluene/CH_2Cl_2 medium, and X-ray crystal-structure analysis confirmed its racemic nature, deduced preliminarily from high-resolution NMR experiments. Thus, the calix[4]arene platform showed its ability to allow the organization of a prohelicity around a metallic centre, which should be of great interest in the design of new catalysts [2] or in the development of flexible enantioselectivity inducers in the growing family of bipyridine-based helicates [3].

We thought that the enantioselectivity in this type of complex could simply be induced only by the presence of at least one non-complexing adjacent chiral substituent close to the metallic asymmetric centre: replacing the two pyridine moieties of the above-mentioned podand by a chiral substituent should give the ligand a chirospecificity leading to an enantiomeric excess of one of the two helices available with this structure, or, at best, to a single enantiomer. Introduction of chirality at the lower rim of the achiral calix[4]arene platform was performed *via* esterification reactions involving notably camphorsulfonyl derivatives [4], or alkylation reactions involving simple alkanes [5] or more sophisticated ones, such as glycidyl [6] and glycosyl groups [7].

Our choice was directed by the fact that the expected inductive effect should concentrate at the proximity of the $[Cu^I(bpy)_2]$ subunit without generating an important steric hindrance which could strongly modify the complexation process. Thus, on the basis of our preliminary modelization, glycidyl, camphorsulfonyl, and glycosyl groups were discarded. We found that the (*S*)-2-methylbutyl synthon, commercially available as bromide, and already used by *Shinkai* [5], corresponds to the above-mentioned conditions. Its chirality centre, close to the attachment region, should fit correctly in the groove of the prohelical complex substructure.

Ligands and Complex Syntheses (*Scheme*). – The first step involved the grafting at the lower rim of the tetra[*p*-(*tert*-butyl)]calix[4]arene[1]) (**1**), of two opposed (*S*)-2-methylbutyl units. This was performed by reacting **1** in MeCN with (+)-(*S*)-1-bromo-2-methylbutane in the presence of K_2CO_3. Thus, **2** was obtained pure after chromatography with a yield of 35%.

Scheme



[1]) Calix[4]arene = pentacyclo[19.3.1.1^{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-dodecaene; see *Formula* **2**, with four unsubstituted OH groups at the lower rim.

Reaction of **2** with 6-(bromomethyl)-6′-methyl-2,2′-bipyridine [8] in the presence of NaH in DMF afforded **3** with 50% yield after chromatography over alumina and silica gel. Reaction of **3** with $[Cu^{I}(MeCN)_4]PF_6$ in $CHCl_3$ gave the corresponding air-stable red copper(I) complex **4**[2]), which was obtained pure after chromatography over aluminium oxide with a yield of 90%.

NMR Study of Ligands. – ^{1}H-NMR Analysis of ligand **2** in $CDCl_3$ at 300 MHz showed notably two close *AB* systems at 3.33–4.36 and 3.34–4.32 ppm (J_{AB} 12.9 Hz), respectively, already indicating the influence of the two chirality centres on the bridging methylene protons. The methylbutyl-substituent pattern of **2** was similar to the ones obtained for analogue [5a] or simpler [5a][9] structures. In ligand **3**, the incorporation of the two bipyridine units resulted in the shielding of the whole methylbutyl pattern, probably due to heterocycle-current effects.

Thus, the methylbutyl groups of **2** give rise to a strong *ABX* system at 3.85 ppm for $MeCH_2CH(Me)CH_2O$, a *m* at 2.10 ppm for the H-atom at the chiral CH centre and 2 *m* at 1.85 and 1.54 ppm for $MeCH_2OH(Me)CH_2$; $MeCH_2CH(Me)CH_2$ appear as a *d* at 1.32 ppm, partially hidden by a *tert*-butyl resonance signal, and $MeCH_2CH(Me)CH_2$ as a *t* at 1.07 ppm. The $MeCH_2CH(Me)CH_2O$ resonance signal is shifted from 3.85 to 3.38 ppm in **3**, with spreading, indicating that the diastereotopic character of both protons is enhanced. The O–CH_2–bpy groups appear as an *AB* system at 5.39–5.44 ppm with very small outer peaks, indicating a slight discrimination between methylene protons due to the presence of the chiral methylbutyl neighbours.

NMR Study of Cu(I) Complex 4[2]). – The complex **4** was preliminarily studied in $CDCl_3$ at 300 MHz. It appears in fact as a mixture of two species slightly different in terms of chemical shifts but equivalent in terms of general pattern. As ES-MS analysis showed the presence of the species **4** alone, the two groups of signals were attributed to the two copper(I)-centered enantiomers available in this case. An approximate ratio of 65:35 was measured for the two species under these conditions, corresponding to an enantiomeric excess of 30%.

Attempts to isolate the major enantiomer by selective crystallization failed. In fact, the complex gave, in a $CHCl_3$/hexane mixture, crystals unsuitable for X-ray analysis. ^{1}H-NMR Study of a dilute or concentrated solution of these crystals in $CDCl_3$ showed that the ratio turned to 50:50, indicating that racemization occurred on crystallization, no complex being recovered in the filtrates. This ratio was found to be time-dependent and evolved to the previously mentioned one within 16 h. Controlled dilution experiments performed on a racemate solution showed that this ratio was not concentration-dependant, while heating the equilibrated solution at *ca.* 330 K did not result in racemization.

These results indicate that the chiral induction of the two methylbutyl groups is effective, and that a very slow exchange process occurs between both enantiomers. Discrimination between the two species was performed with the help of a TOCSY experiment at 500 MHz with a solution at equilibrium.

The bipyridine region is characterized by the expected *d*s and *t*s in the previously mentioned ratio which is not evidenced for the H–C(5) and H–C(4)[3]). H–C(3), which remains dedoubled, is stereosensitive. Three couples of *AB* systems are observed in the 6.50–2.50 ppm region. The first one, located at 6.367 and 5.300 ppm (major,

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[2]) The key number **4** refers to the PF_6 salt if not mentioned otherwise.

[3]) Arbitrary numbering. For systematic names, see *Exper. Part* and *Footnote 1*.

system **f**) and 6.308 and 5.242 ppm (minor, system **e**) is attributed to the OCH_2—bpy groups. No TOCSY correlation is found between these methylene protons and the corresponding heterocyclic protons. The two other couples, located at 4.421 and 3.240 ppm (major, system **d**) and 4.475 and 3.225 ppm (minor, system **c**), then 3.529 and 2.850 ppm (major, system **b**) and 3.463 and 2.832 ppm (minor, system **a**) are attributed to the Ar—CH_2—Ar groups.

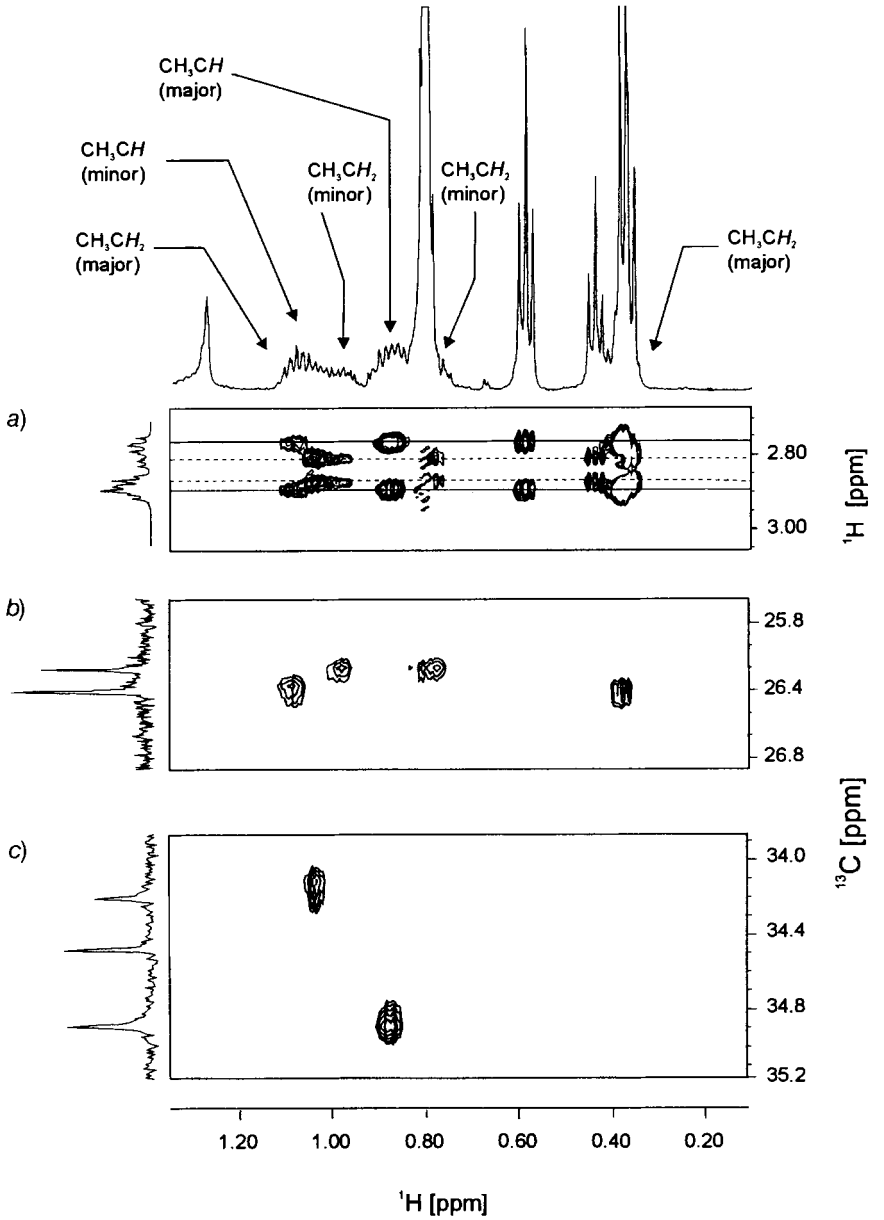

Fig. 1. *Attribution of methylbutyl protons in complex* **4**: a) *TOCSY*, b) *and* c) *HSQC*. At 500 MHz and 293 K in $CDCl_3$. Discrimination between the major (full lines) and minor (dotted lines) enantiomers.

The methylbutyl substituents are characterized by two groups of resonance signals in the observed ratio (*Fig. 1,a*). The $MeCH_2CH(Me)CH_2O$ protons appear as complex *m* patterns in the region 2.95–2.72 ppm resulting from the overlapping of two *ABX* systems, a spread one at 2.890 and 2.765 ppm and a strengthened one at 2.870 and 2.810 ppm. Both *m* are coupled to the corresponding series of methylbutyl resonance signals in the 1.10–0.30 ppm region. The complexity of the latter necessitated a $^1H,^{13}C$-HSQC analysis (*Fig. 1, b* and *c*) which shows notably that the $MeCH_2CH(Me)CH_2$ resonance signals of the major and the minor enantiomers are in fact *AB* (*m*) systems located at 1.068 and 0.369, and 0.968 and 0.762 ppm, respectively. The spreading of the former indicates a strong discrimination between the two corresponding protons which could be of importance in the structural analysis of this part of the complex. The $MeCH_2CH(Me)CH_2$ protons appear as *m* located at 0.874 and 1.036 ppm for the major and the minor enantiomers, respectively. The corresponding Me protons appear as *d*s at 0.377 and 0.361 ppm for the major and the minor species, respectively. Their strong shielding indicate that these groups experience a probable aromatic ring current effect.

Through-space ROESY correlations of structural importance (*Fig. 2*) are found between the bipyridine H–C(5')[3] and the upfield part of the OCH_2–bpy *AB* systems **e** and **f**, while no TOCSY correlation is encountered in this case. Smaller correlations are detected between H–C(5'), H–C(4'), and H–C(3') and the downfield part of the Ar–CH_2–Ar *AB* system **b**. The two groups of calixarenic aromatic resonance signals, $H_{ar}A$ and $H_{ar}B$, both correlate together and with the upfield parts of the Ar–CH_2–Ar *AB* systems **a**, **b** and **c**, **d**, indicating that the cone conformation is maintained in **4**. More precisely, the downfield part A_2 of $H_{ar}A$ is correlated with the systems **c**, **d**, and A_1 with the systems **a**, **b**. The fact that these interactions are weaker with $H_{ar}B$ than with $H_{ar}A$ indicates that the benzene rings A are strongly slanted and, in accordance with our previous work and with modelization, that they are carrying the bipyridine units. The upfield parts of the OCH_2-bpy *AB* systems **e** and **f** are correlated to the downfield parts of the Ar–CH_2–Ar *AB* systems **c**, **d**, confirming the helical nature of the complex subunit.

To determine whether the left- or right-handled prohelical mode corresponds to the major compound, we analyzed the ROESY interactions existing between the chiral alkyl groups and the remaining protons. In the major species, relevant interactions are found between the upfield part of the $MeCH_2CH(Me)CH_2O$ *ABX* system and the downfield parts of the *AB* systems **b** and **d**. The $MeCH_2CH(Me)CH_2$ *m* at 0.874 ppm correlates with H–C(3), H–C(3'), and the downfield parts of the *AB* systems **b** and **d**. The $MeCH_2CH(Me)CH_2$ *t* correlates strongly with

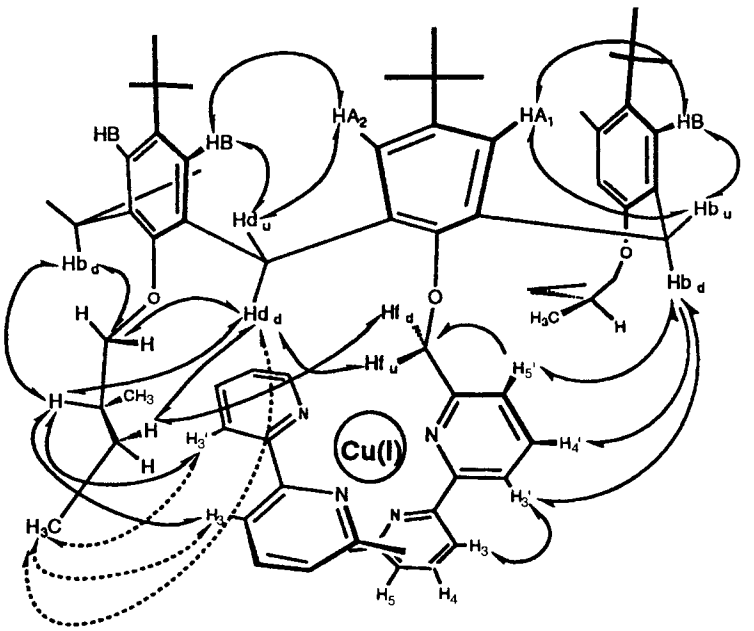

Fig. 2. *Schematic representation of significant ROESY interactions between protons in comple* **4**. u: upfield; d: downfield.

H–C(3), H–C(3'), and **d** downfield, and weakly with H–C(4) and H–C(5). The downfield part of the MeC*H*$_2$CH(Me)CH$_2$ *AB*(*m*) system correlates strongly with **d** downfield and **f** downfield, weakly with **f** upfield but not with heterocyclic protons. Under the conditions of an association of the (*S*)-2-methylbutyl units and a Cu^{I}-centered left handled prohelical system in the major species, the upfield part of the MeC*H*$_2$CH(Me)CH$_2$ *ABm* system should correlate with **f** upfield, **d** downfield, and the heterocyclic protons H–C(3'), H–C(3), H–C(4), and H–C(5), and the MeCH$_2$CH(*Me*)CH$_2$ *d* with **b** downfield, **f** downfield, and at least with H–C(5') and H–C(4'). Some of these correlations (*Fig. 3*) are observed in the corresponding regions. Unfortunately, the strong overlapping of these alkyl resonance signals do not allow us to analyze precisely these interactions.

According to the ball-and-stick model, the specific ROESY interactions between the chiral alkyl groups and the remaining protons of the major species could occur only with an association of the (*S*)-2-methylbutyl units and a Cu^{I}-centered left-handed prohelical system.

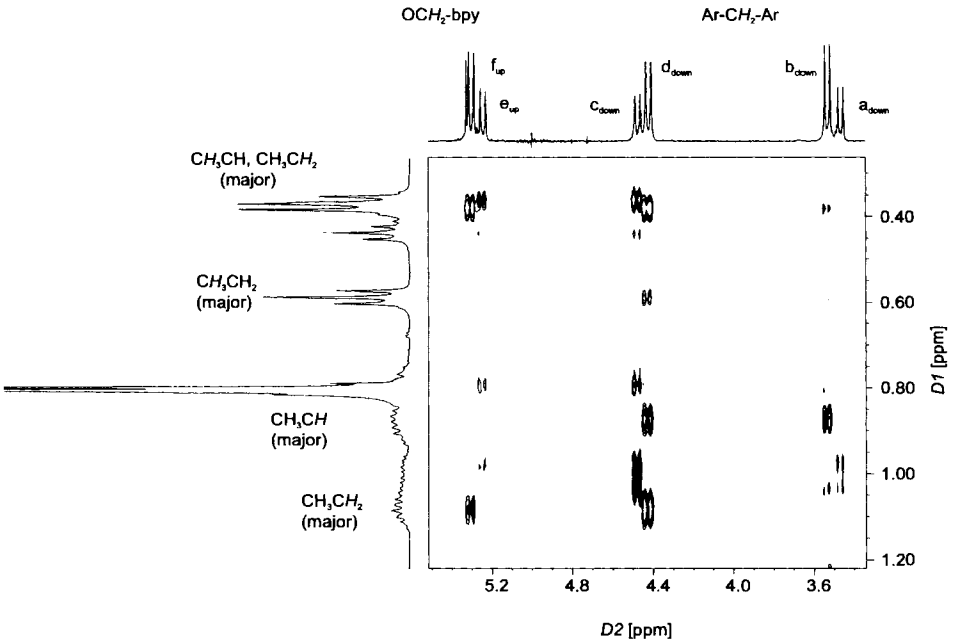

Fig. 3. *ROESY Correlations between methylbutyl and some methylene protons in complex* **4**. At 500 MHz and 293 K in $CDCl_3$. up: upfield; down: downfield.

^{1}H,^{15}N-HMBC NMR Study. – A natural-abundance ^{1}H,^{15}N-HMBC experiment, initiated with bithiazole complexes in a previous paper [10f], was applied to ligand **3** and complex **4**, taking 6,6'-dimethyl-2,2'-bipyridine (dmbpy) and its Cu^{I} complex as references. The experiments were conducted in $CDCl_3$ at 293 K, with $MeNO_2$ as internal standard (capillary tube; + 381.65 ppm *vs.* NH_3, ref. of *Bruker*). The ^{15}N-NMR chemical shifts (see *Table*) show that only very slight differences exist between the free dmbpy and ligand **3**. Surprisingly, *a contrario* to the results in the bithiazole series, the N(1) and N(2) atoms[3]) of **3** are not well-differentiated, indicating a small influence of the CH_2O group on the $^{15}N_2$ resonance.

Table. *^{15}N-NMR Chemical Shifts* [ppm] *of Some Bipyridine-Containing Species*[a])

	dmbpy	$[Cu(dmbp)_2](PF_6)$		**3**	**4**[2])
				major	minor
N(1)[b]) (correlated to Me)	−76.65	−121.15	−77.15	−117.90	−118.13
N(2)[b]) (correlated to CH_2O)	−76.65	−121.15	−76.85	−122.67	−122.25

[a]) Solvent $CDCl_3$, $MeNO_2$ as internal standard; 293 K; ^{1}H,^{15}N-HMBC experiment. [b]) Arbitrary numbering.

Upon complexation of Cu^I, the N-atoms of dmbpy experience, as expected, a strong upfield shift of 44.50 ppm, similar to those obtained for N(1) (40.75 ppm, major; 40.98 ppm, minor) and N(2) (45.82 ppm, major; 45.40 ppm, minor) between **3** and **4**. It is interesting to notice that the discrimination between both enantiomers of **4** is available with this technique, the analysis being in this case greatly simplified by the fact that the two compounds have slightly different ^{1}H-NMR spectra.

Conclusion. – The tetra[*p*-(*tert*-butyl)]calix[4]arene has shown its ability to act as a spatial organizing platform in the building of podands incorporating various kinds of biheterocycles, which display an interesting chelating behaviour towards Cu^I species [10]. High-resolution NMR studies completed by an X-ray crystal-structure analysis of one of these complexes showed that it was a metal-centered racemate [1]. Introduction of the non-complexing chiral (*S*)-2-methylbutyl substituent close to the coordination site resulted in the induction of an enantiomeric excess of *ca.* 30% in the corresponding Cu^I complex. This excess was measured by ^{1}H-NMR, the two enantiomers displaying slightly different resonance signals which were attributed by TOCSY, HSQC, and ROESY experiments. The latter suggest that the major enantiomer is the Cu^I-centered left-handled prohelical system. Attempts to separate these complexes by selective crystallization resulted in fact in an exhaustive racemization; enantiomeric excess was restored in solution within *ca.* 16 h. Introduction of stronger inductive effects in such structures is now in progress.

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Experimental Part

General. All commercially available products were used without further purification unless specified otherwise. UV Spectra: CH_2Cl_2, 298 K; *Shimadzu-UV-2401-PC* apparatus; λ_{max} in nm, ε in l mol^{-1} cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM 300* (300.13 and 75.3 MHz, resp.) or *Bruker DRX 500* (500.13 and 125.75 MHz, resp.); $SiMe_4$ as internal standard, chemical shifts δ in ppm, J in Hz. ^{15}N-NMR: *Bruker DRX 500* (50.68 MHz); $MeNO_2$ as internal standard. The acquisition parameters were for TOCSY: SW = 4496 Hz; time domain = 4096 points; $(\gamma/2\pi)B_1$ = 10 kHz, spin lock time = 100 ms; NS = 8. For compensated ROESY: SW = 4496 Hz; time domain = 4096 points for the $F2$ dimension, 512 points for the $F1$ dimension, relaxation delay $D1$ = 2.5 s, mixing time τ_m = 200 ms with a $(\gamma/2\pi)B_1$ = 2.5 kHz, NS = 4. For ^{1}H,^{13}C gradient phase sensitive HSQC: $SW(^1H)$ = 5000 Hz, $SW(^{13}C)$ = 20120 Hz, time domain = 4096 points for the $F2$ dimension, 1024 points for the $F1$ dimension, NS = 8. For ^{1}H,^{15}N absolute mode gradient HMBC: $SW(^1H)$ = 4006 Hz, $SW(^{15}N)$ = 506 Hz, time domain = 8192 points for the $F2$ dimension, 64 points extended to 128 points by linear prediction for the $F1$ dimension, NS = 220; long-range mixing time = 50 ms. T = 293 K. Data were processed with the 2DWinNMR package in the phase-sensitive mode with a square sinbell window function in the two dimensions. Mass spectra

(electrospray, ES) were recorded on a *Platform Micromass* apparatus at the Service Central d'Analyse du CNRS, Solaize. Elemental analyses were performed at the Service Central de Microanalyse, Ecole Supérieure de Chimie, Montpellier.

*5,11,17,23-Tetra(*tert*-butyl)-26,28-bis[(*S*)-2-methylbutoxy]calix[4]arene-25,27-diol* (**2**). A suspension of calixarene **1** (0.4 g, 0.615 mmol) and finely powdered K_2CO_3 (0.2 g, 1.45 mmol) in HPLC-grade MeCN (20 ml) was refluxed under N_2 for 10 min. (+)-(*S*)-1-Bromo-2-methylbutane (0.16 ml, 1.3 mmol) was then added, followed by *ca.* 10 mg of anh. LiI. Reflux was continued for 24 h with addition of 1 equiv. of (+)-(*S*)-1-bromo-2-methylbutane after 4 h. The mixture was then evaporated and the residue chromatographed (SiO_2, CH_2Cl_2/hexane 1:2): pure **2** (0.16 g, 35%). UV: 284.5 (7300), 292.5 (7300). ^{1}H-NMR ($CDCl_3$, 300 MHz)[3]: 1.01 (*s*, 2 Me_3C); 1.07 (*t*, *J* = 7.0, 2 *Me*CH_2); 1.32 (*d*, *J* = 7.0, 2 *Me*CH); 1.33 (*s*, 2 Me_3C); 1.54 (*m*, 2 H of MeCH_2); 1.85 (*m*, 2 H of MeCH_2); 2.10 (*m*, 2 CH); 3.849 (*oct.*, 2 CH_2O); 3.33–4.36 ('*q*', *AB*, J_{AB} = 12.9, 2 Ar–CH_2–Ar); 3.34–4.32 ('*q*', *AB*, J_{AB} = 12.9, 2 Ar–CH_2–Ar); 6.85 (*s*, 4 H, Ar); 7.09 ('*q*', *AB*, J_{AB} = 2.6, 4 H, Ar); 7.73 (*s*, 2 OH). ^{13}C-NMR ($CDCl_3$, 75 MHz)[3]): 11.75 (*Me*CH_2); 16.85 (*Me*CH); 26.25 (Me*C*H_2); 31.10 (*Me*$_3$C); 31.61 (Ar–*C*H_2–Ar); 31.81 (*Me*$_3$C); 33.86 (Me$_3$*C*); 33.99 (Me$_3$*C*); 36.11 (CH); 81.57 (CH_2O); 125.02, 125.05, 125.48, 125.43 (CH of Ar); 127.58, 127.76, 132.68, 132.79, 141.19, 146.72, 149.84, 151.11 (C_o, C_{ipso}, C_p of Ar). ES-MS (pos. mode): 811.6 ([**2** + Na]$^+$). Anal. calc. for $C_{54}H_{76}O_4$ (789.20): C 82.18, H 9.70, O 8.11; found: C 82.34, H 9.92, O 8.19.

*6,6''-{{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis[(*S*)-2-methylbutoxy]calix[4]arene-25,27-diyl}bis(oxymethylene)}bis[6'-methyl-2,2'-bipyridine]* (**3**). A mixture of **2** (0.15 g, 0.19 mmol) and NaH (0.045 g, 1.9 mmol) in dry DMF (5 ml) was heated at 60° under N_2 for 1 h. After cooling to r.t., 6-(bromomethyl)-6'-methyl-2,2'-bipyridine (0.1 g, 0.38 mmol) was added. The reaction was monitored by TLC (Al_2O_3, hexane/CH_2Cl_2 4:1). The monobipyridine species was formed, and the temp. was raised to 60°. After 6 h, the mixture was cooled and MeOH (0.5 ml) added. After evaporation, the residue was dissolved in CH_2Cl_2 (30 ml) and washed with H_2O (30 ml). After drying, the org. phase was evaporated, then cleaned over a short column of alumina, and chromatographed (silica gel, CH_2Cl_2): 0.11 g (50%) of **3**. UV: 291.0 (33900), 304.3 (sh, 19330). ^{1}H-NMR ($CDCl_3$, 300 MHz)[3]): 0.68 (*t*, *J* = 7.4, 2 *Me*CH_2); 0.77 (*d*, *J* = 6.6, 2 *Me*CH); 0.89 (*s*, 2 Me_3C); 0.95 (*m*, 2 H of MeCH_2); 1.30 (*s*, 2 Me_3C); 1.37 (*m*, 2 H of MeCH_2); 1.65 (*m*, 2 CH); 2.64 (*s*, 2 *Me*–bpy); 3.06, 4.37 ('*q*', *AB*, J_{AB} = 12.5, 2 Ar–CH_2–Ar); 3.08, 4.43 ('*q*', *AB*, J_{AB} = 12.5, 2 Ar–CH_2–Ar); 3.38 (*AB oct.*, 2 CH_2O); 5.39–5.44 ('*q*', *AB*, J_{AB} = 12.87, 2 OCH_2–bpy); 6.55 (*s*, 4 H, Ar); 7.05 ('*q*', *AB*, J_{AB} = 2.5, 4 H, Ar); 7.13 (*d*, *J* = 7.4, 2 H of bpy); 7.61 (*t*, *J* = 7.7, 2 H of bpy); 8.07 (*d*, *J* = 7.7, 2 H of bpy); 7.80–7.95 (*d* + *t*, 4 H of bpy); 8.35 (*dd*, *J* = 6.6, 2.6, 2 H of bpy). ^{13}C-NMR ($CDCl_3$, 75 MHz)[3]): 11.08 (*Me*CH_2); 16.78 (*Me*CH); 24.67 (*Me*–bpy); 26.31 (Me*C*H_2); 31.07, 31.13 (Ar–*C*H_2–Ar); 31.24, 31.72 (*Me*$_3$C); 33.62, 34.00 (Me$_3$*C*); 35.19 (CH); 77.31 (O*C*H_2–bpy); 81.41 (CH_2O); 118.37, 119.49, 122.97, 123.69, 136.90, 137.04 (CH of bpy); 124.67, 124.73, 125.51, 125.61 (CH of Ar); (C(2), C(2'), C(6), C(6') of bpy; C_o, C_p, C_{ipso} of Ar). ES-MS (pos. mode): 1153.7 ([**3** + H]$^+$). Anal. calc. for $C_{78}H_{96}N_4O_4$ (1153.65): C 81.21, H 8.39, N 4.85; found: C 81.08, H 8.23, N 4.88.

*{6,6''-{{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis[(*S*)-2-methylbutoxy}calix[4]arene-25,27-diyl}bis(oxymethylene)}bis[6'-methyl-2,2'-bipyridine]}copper(I) Hexafluorophosphate* (**4**). A soln. of podand **3** (0.1 g, 0.087 mmol) in MeCN (5 ml) was mixed with $[Cu^I(MeCN)_4](PF_6)$ (0.033 g, 0.087 mmol). The resulting orange soln. was stirred for 10 min and the solvent evaporated. The residue was dissolved in CH_2Cl_2 and chromatographed (Al_2O_3, CH_2Cl_2) to give pure **4** (0.105 g, 90%). UV: 266.5 (28300), 273.4 (25600), 303.0 (34000), 315.1 (sh, 24490), 448.0 (MLCT, 5100). ^{1}H-NMR ($CDCl_3$, 500 MHz)[3]): major enantiomer: 0.377 (*d*, *J* = 7.3, 2 *Me*CH); 0.369, 1.068 (*ABm*, 2 MeCH_2); 0.586 (*t*, *J* = 7.3, 2 *Me*CH_2); 0.804 (*s*, 2 Me_3C); 0.874 (*m*, 2 MeC*H*); 1.415 (*s*, 2 Me_3C); 1.757 (*s*, 2 *Me*–bpy); 2.765, 2.890 ('*oct.*', *ABm*, 2 MeCH_2CH(Me)CH_2O); 2.880, 3.529 ('*q*', *AB*, J_{AB} = 12.8, 2 Ar–CH_2–Ar, **b**); 3.240, 4.420 ('*q*', *AB*, J_{AB} = 12.8, 2 Ar–CH_2–Ar, **d**); 5.300–6.367 ('*q*', *AB*, J_{AB} = 12.8, 2 OCH_2–bpy, **f**); 6.316 (*s*, 4 H, Ar, B); 7.185 (*ABm*, 4 H, Ar, A); 7.350 (*d*, *J* = 7.3, 2 H–C(5) of bpy); 7.390 (*d*, *J* = 7.3, 2 H–C(5') of bpy); 8.015 (*t*, *J* = 7.3, 2 H–C(4) of bpy); 8.169 (*t*, *J* = 7.3, 2 H–C(4') of bpy); 8.300 (*d*, *J* = 7.3, 2 H–C(3) of bpy); 8.500 (*d*, *J* = 7.3, 2 H–C(3') of bpy); minor enantiomer: 0.361 (*d*, *J* = 7.3, 2 *Me*CH); 0.434 (*t*, *J* = 7.3, 2 *Me*CH_2); 0.762, 0.968 (*ABm*, 2 MeCH_2); 0.797 (*s*, 2 Me_3C); 1.036 (*m*, 2 MeC*H*); 1.410 (*s*, 2 Me_3C); 1.757 (*s*, 2 *Me*–bpy); 2.810, 2.870 ('*oct.*', *ABm*, 2 MeCH_2CH(Me)CH_2O); 2.865, 3.463 ('*q*', *AB*, J_{AB} = 12.8, 2 Ar–CH_2–Ar, **a**); 3.225, 4.475 ('*q*', *AB*, J_{AB} = 12.3, 2 Ar–CH_2–Ar, **c**); 5.242–6.308 ('*q*', *AB*, J_{AB} = 12.3, 2 OCH_2–bpy, **e**); 6.316 (*s*, 4 H, Ar, B); 7.185 (*ABm*, 4 H, Ar, A); 7.35 (*d*, *J* = 7.3, 2 H–C(5) of bpy); 7.382 (*d*, *J* = 7.3, 2 H–C(5') of bpy); 8.015 (*t*, *J* = 7.3, 2 H–C(4) of bpy); 8.175 (*t*, *J* = 7.3, 2 H–C(4') of bpy); 8.314 (*d*, *J* = 7.3, 2 H–C(3) of bpy); 8.511 (*d*, *J* = 7.3, 2 H–C(3') of bpy). ES-MS (pos. mode): 1216.8 ([**3** + Cu]$^+$). Anal. calc. for $C_{78}H_{96}CuF_6N_4O_4P$ (1362.23): C 68.77, H 7.10, N 4.11; found: C 68.52, H 7.22, N 3.79.

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