We have shown here that supramolecular films composed of dipolar rodcoil molecules self-organize into polar macroscopic materials showing piezoelectric activity. Most importantly, the state with net polarization appears to have thermodynamic stability and to involve interactions between polar domains in the film and the substrate. Furthermore, our experiments strongly suggest that molecular aggregates present in these materials are important for the observed properties. This observation supports the concept that great potential exists in the supramolecular design of materials.

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Unusual Smectic Ordering of Unlocked Copper Bis-(terpyridine) Complexes[**]

Raymond Ziessel,[*] Laurent Douce, Abdelkrim El-ghayoury, Anthony Harriman, and Antoine Skoulios

Supramolecular liquid crystals have now been engineered by way of hydrogen bonding, donor-acceptor interactions, or by cation complexation; the latter leading to the formation of metallomesogens.[1] Individual molecules within these organized networks act cooperatively to fulfill a useful function, such as thermochromism, ferroelectricity, nonlinear optical effects, or gelation. The anticipation that such structures might be used to construct molecular devices has been augmented by many examples of complex supramolecular architectures, such as discrete and infinite helices, hydrogen-bonded or π-π interacting networks, three-dimensional assemblies with defined channels, cucurbituril and similar molecules, highly symmetric coordination clusters, and organometallic polymers.[2] Increasing the extent of molecular ordering, however, to form organized macroscopic structures has proven difficult. Two important examples include silver complexes, constructed from polycatenar scaffolds, forming columnar liquid-crystalline mesophases,[3] and the description of the macroscopic ordering of a metallo-helicate (**B**).[4] It has also been shown that various pyridino-functionalized Schiff-base ligands coordinated to a tetrahedral copper(I) center assemble into columnar liquid-crystalline materials (**A**).[5] These latter structures, being rather rigid, appear to lack useful physical or catalytic properties.

We have sought to improve this situation by introducing more flexibility into the supermolecular structure but without detracting from its ability to assemble into organized networks. This delicate operation can be achieved by using a central core constructed from a terpyridine (terpy) ligand bearing two imino appendages equipped with phasmidic tails (long chains bound to the ends of a rodlike core). Complexation to copper(I) cations gives the first thermotropic terpy-based metallomesogens. Metallomesogens formed from tridentate ligands are rare, but lyotropic mesophases have been generated from ruthenium(II)-terpy complexes,[6] while the related terdentate (C,N,N) ligands cyclometalated to palladium(II) centers[7] are known to display a monotropic nematic phase.

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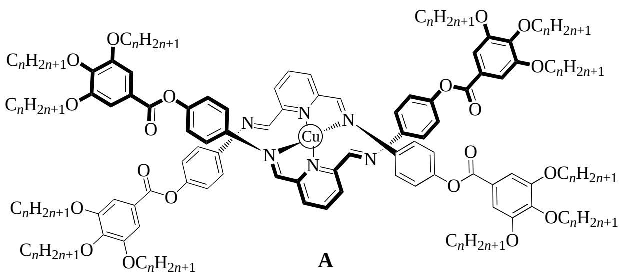
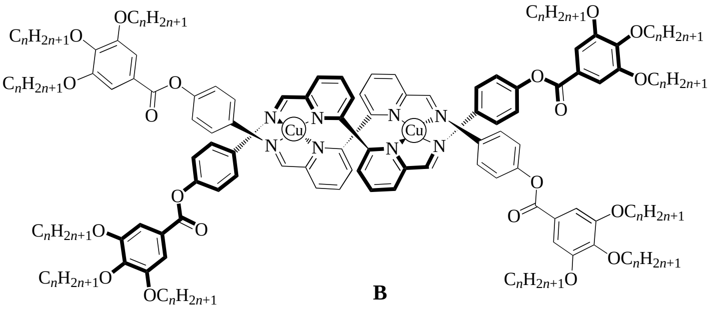
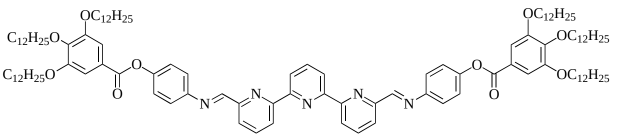


A

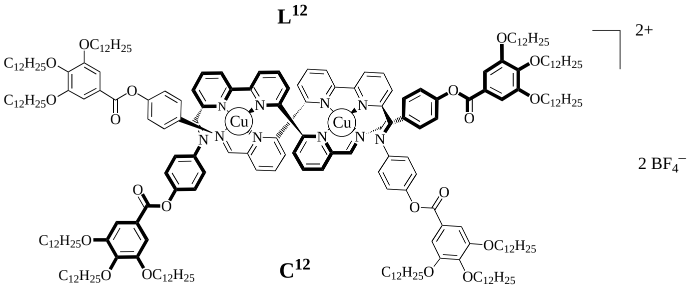


B

Ligands $\mathbf{L}^n$ ($n = 8$, 12, 16) were synthesized in excellent yield by an acid-catalyzed reaction of the pivotal 6,6″-diformyl-2,2′:6′,6″-terpyridine[8] with the appropriate polyfunctionalized aniline. The ligands self-associate in the presence of $[Cu(CH_3CN)_4][BF_4]$ to afford dark-brown, air-stable, binuclear metallohelicates $\mathbf{C}^n$ in almost quantitative yield. All new compounds were fully characterized by NMR spectroscopy and by electrospray mass spectrometry (ES-MS); for example, the ES-MS spectrum of $\mathbf{C}^{12}$ exhibits peaks at m/z 3785.3 $[\mathbf{C}^{12} - BF_4]^+$ and 1849.1 $[\mathbf{C}^{12} - 2BF_4]^{2+}$.



$\mathbf{L}^{12}$



$\mathbf{C}^{12}$

Complexation of copper(I) by $\mathbf{L}^{12}$ induces an upfield shift of about 0.31 ppm for the ^{1}H NMR signal of the imine proton while the wavenumber of the $\nu_{N=C}$ stretching vibration increases by circa 40 cm^{-1}. Cation binding also affects other regions of the ^{1}H NMR spectra, the most notable being the upfield shifts of the three doublets belonging to those protons attached to the pyridine rings *ortho* to the imine group ($\Delta\delta = 0.78$) and to the exocyclic C–C bond ($\Delta\delta = 0.66$ (terminal rings) and 0.43 (central ring)). Furthermore, the AB quartet belonging to the bridging N-phenyl-O moiety is shifted upfield by 0.48 ppm. These various spectral perturbations, together with the ES-MS results, are consistent with two polytopic ligands wrapping around two copper(I) cations in such a way that each metal center is coordinated to three pyridine nitrogen atoms and one imino nitrogen atom, leaving a vacant imine group on each ligand. This arrangement forces the above-mentioned protons to reside within the shielding region exerted by the complementary ligand. Only a single imine resonance is observed in solution, however, such that the complex must be in a state of dynamic fluctuation whereby the two coordinated terpy ligands glide across the metal centers.[9] This internal flexibility might be of extreme importance in controlling the morphology of the metal complex and we note that recent studies have established that certain conformationally unlocked complexes form chiral microdomains within columnar mesophases.[10] Indeed, the binuclear copper(I) complexes, being equipped with a chiral helical shell and extended paraffinic tails, possess the necessary functionalities by which to assemble into mesophases. Ligands $\mathbf{L}^8$ and $\mathbf{L}^{16}$ also formed helicoidal dinuclear copper(I) complexes featuring similar spectroscopic behaviour.

The unique coordination of these intricate complexes was unambigously confirmed by a crystallographic structural determination of the parent complex, in which the trialkoxybenzoate termini are replaced by methoxy groups (Figure 1 a). The packing of this compound, projected along the *xy* plane, has the molecules aligned in parallel rows and arranged in single layers of thickness $b/2 = 11.5$ Å surrounded by the methoxy groups and separated by the BF_4^- ions (Figures 1 b and 1 c). Evidently, this packing is auspicious for the formation of lamellar mesophases when alkyl chains are inserted between the layers, provided here by judicious tailoring of the ligands.

The thermotropic polymorphism of $\mathbf{C}^{12}$ was analyzed by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The DSC profiles, recorded on heating from 0 to 200 °C, show two peaks, each corresponding to a first-order phase transition. The crystal melts at 115 °C[11] into a liquid-crystalline material and transforms to an isotropic liquid at 187 °C ($\Delta H = 2.6$ J g^{-1}). The liquid-crystalline phase does not revert back to the crystal upon cooling to room temperature. Optical textures, observed on slow cooling from the isotropic melt (crossed droplets turning into micellar rods and coalescing into a fine Schlieren texture), indicate that the liquid crystal has a biaxial smectic structure.

Definitive structural information for the liquid-crystalline phase was sought from X-ray diffraction (XRD) studies. The observed patterns (Figure 2) indicate an unusual macroscopic organization wherein individual molecules align to form a columnar liquid crystal with a lamellar morphology, similar to what we found for an *ortho*-metallated palladium complex.[12] Hints of such supramolecular organization have been suggested by Levelut et al.[13] and Lattermann et al.[14] for charge transfer assemblies and azamacrocyclic compounds, respectively. Four notable aspects of the structure are as follows. a) The diffuse band at 4.5 Å (marked A in Figure 2) confirms that the alkyl chains are segregated from the aromatic cores and have a liquidlike conformation. b) The presence of two sharp equidistant reflections, indexed as (001) and (002), shows the molecules to be arranged in regularly spaced layers

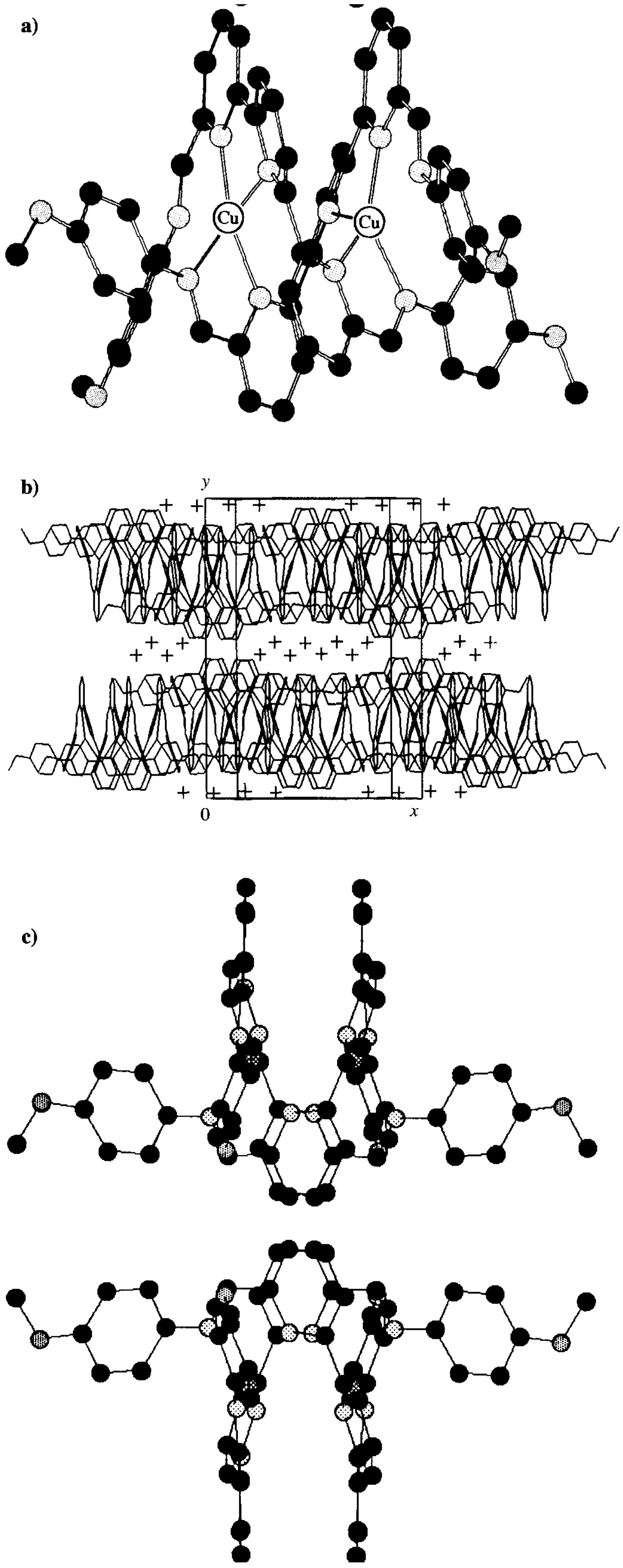


Figure 1. a) X-ray crystal structure of the copper(I) terpyridine helicate prepared from a terpy–anisole ligand[9]; b) crystal packing of the same dinuclear copper(I) complex projected along the *xy* plane. For the sake of clarity the BF_4^- ions are represented as +; c) view of two molecules of this complex projected along the *xy* plane. The BF_4^- ions located between these molecules have been omitted for clarity.

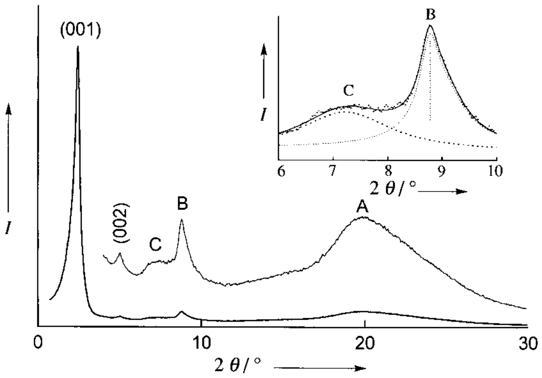


Figure 2. Powder X-ray diffraction pattern of complex $\mathbf{C}^{12}$ in the liquid-crystal state ($T = 100\,°C$). For clarity, the intensity at Bragg angles $2\theta > 3°$ is multiplied tenfold. The intensity I is reported in arbitrary units. Inset: expanded representation of peaks B and C.

for which the lamellar period $d = 35.5$ Å corresponds to the length of one individual helicate (Figure 3). c) The bands B and C (Figure 2) are related to the internal structure of the aromatic sublayers with the respective spacings of 10.1 and 12.2 Å due to the lateral dimensions of the helicate core. The sharpness of B ($\Delta(2\theta) \approx 0.4°$) shows that the lateral packing of

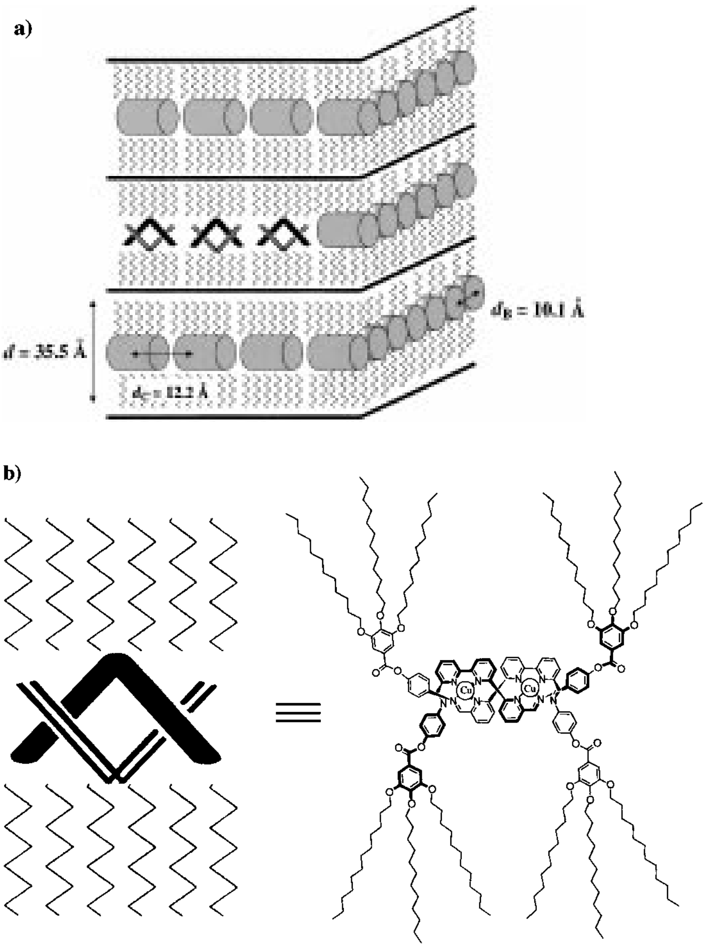


Figure 3. a) Schematic front and lateral view of the smectic layering. The rigid helicate cores (shown schematically (see b) and as gray cylinders) are arranged in single layers separated by the molten alkyl chains (wavy lines). b) Schematic representation of the terpy-based metallohelicate.

molecular rows inside the aromatic sublayers extends over some 22 rows whereas the width of C ($\Delta(2\theta)\approx 2.0^{\circ}$) indicates loose packing inside the rows that is restricted to 3.5 repeat units. d) The absence of (10l) reflections and, significantly, the presence of a wide-angle wing to band B show that the layers are not positionally correlated in three-dimensional space. Therefore, the liquid-crystalline phase has a genuine smectic structure (Figure 3) and resembles that of linear DNA stretched across a lipid bilayer.[15] In fact, the structural similarity between the smectic liquid-crystalline phase and the oriented DNA molecule is striking. From the one-dimensional positional order inside the layers and long-range orientational order of the rows across the layers, as revealed by the optical texture, the structure can be categorized into the class of hexatic smectic liquid crystals.[16] We consider that local segregation of the polar helicate from the paraffinic chains creates an interface that facilitates adoption of a nondiscoidal liquid-crystalline phase. This seems to be viable to obtain new types of self-organized assemblies of nanoscopic dimensions.

Chemical oxidation of $\mathbf{C}^{\mathbf{12}}$ with ferrocenium cations forms a mixed-valence complex $\mathbf{C}^{\mathbf{12m}}$ which was unambigously characterized by its ES-MS spectrum (pseudomolecular peaks at m/z 1892.7 $[\mathbf{C}^{\mathbf{12m}}-2\,BF_4]^{2+}$ and 1233.0 $[\mathbf{C}^{\mathbf{12m}}-3\,BF_4]^{3+}$), its EPR spectrum,[17,18] and a Gaussian-shaped intervalence charge transfer (IVCT) absorption band[19] centered at 1435 nm ($\varepsilon_{max}=48\pm10\,\text{M}^{-1}\,\text{cm}^{-1}$). Observation of this IVCT band indicates that the metal centers possess very similar coordination shells in the mixed-valence complex, while the EPR spectrum is consistent with the copper(II) center being five coordinate. These realizations are made possible by the availability of ancillary imino functions adjacent to each metal center that can coordinate to the emergent copper(II) cation and thereby stabilize the higher-valence state. Remarkably, the mixed-valence complex remains liquid crystalline over a wide temperature range but, because of the increased electronic charge, the morphology differs significantly from that described for the binuclear copper(I) complex. Indeed, the XRD studies reveal a single sharp peak at 51 Å (indicative of macroscopic order) together with a diffuse band at about 4.5 Å confirming that the alkyl chains are conformationally disordered. The absence of supplementary reflection peaks limits, at the present time, further description of the morphology of this liquid-crystalline material.

In summary, we have described an example of a liquid-crystalline metallohelicate which resists recrystallization from the melt and which forms a liquid-crystalline, mixed-valence complex. This is clear indication that multicharged (di- and tricationic) helicates can be organized under ambient conditions into large scale macroscopic arrays that retain redox activity. It should be noted that there is a precedent for forming a liquid-crystalline material from a mixed-valence Ru^{II}/Ru^{III} complex.[20] While the mesophase obtained with the Cu-terpy helicate is smectic, that of the corresponding 2,2′-bipyridine complex[4] is columnar. The two major structural differences between these polypyridine complexes might account for this structural variation: a) The extended length of the aromatic core stretches the molecule into a calamitic shape that favors a smectic arrangement; and b) fluxional motion inherent to the terpy-based metallohelicate increases the entropy of the system and favours the formation of the mesophase. It is this local fluctuation that establishes microdomains sustaining liquid-crystalline behavior at room temperature. Furthermore, the $\mathbf{C}^{n}$ helicate forms a highly unusual, smectic mesophase comprising layers of metallohelicates arranged in equidistant columns but without a third-dimensional correlation of the layers (Figure 3). Such structures are made possible by combining internal flexibility of the coordinated polytopic ligands, ancillary coordination sites to stabilize emerging redox centers, and multiple flexible side-chains. The unique properties of these liquid-crystalline complexes arise from the combination of order and mobility at the molecular level and from an adequate mismatch between the central helicoidal shell and the flexible swallow-tail-shape paraffinic tails. The principles elucidated here may certainly be applicable to other classes of molecules as well and suggest that introduction of flexible coils in self-assembled supramolecular structures might provide a novel strategy to construct multidimensional nanostructures.

Experimental Section

Ligand $\mathbf{L}^{\mathbf{12}}$: A Schlenk tube was successively charged with 6,6″-diformyl-2,2′:6′,6″-terpyridine (0.035 g, 0.120 mmol), 4-[3,4,5-tri(dodecyloxy)benzoyloxy)]aniline (0.186 g, 0.243 mmol), EtOH (10 mL) and acetic acid (1 drop). At 80 °C, complete solubilisation occurs and the solution was heated for 4 h. After cooling to room temperature, the precipitate was filtered, washed with EtOH (3 × 10 mL) and afforded 0.172 g of $\mathbf{L}^{\mathbf{12}}$ (80 % yield). M.p. 77–79 °C; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=300$ nm ($62\,400\,\text{M}^{-1}\,\text{cm}^{-1}$); ^1H NMR (200.1 MHz, $CDCl_3$, 25 °C): $\delta=8.78$ (s, 2H, H-imine), 8.73 (d, $^3J(H,H)=7.7$ Hz, 2H), 8.62 (d, $^3J(H,H)=8.0$ Hz, 2H), 8.31 (d, $^3J(H,H)=8.0$ Hz, 2H), 8.03 (m, 3H), 7.37 (q_{AB} + s, 12H), 4.07 (m, 12H, OCH_2), 1.8 (m, 12H, CH_2), 1.5 (m, 12H, CH_2), 1.27 (br s, 96H, CH_2), 0.88 (m, 18H, CH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta=165.17$ (C=O), 161.32 (C=N), 156.17, 155.08, 154.23, 153.09, 149.89, 148.74, 143.21, 138.14, 137.61, 123.91, 122.63, 122.31, 121.72, 121.46, 115.76, 108.71 (aromatic), 73.69 (OCH_2), 69.39 (OCH_2), 32.03 (CH_2), 30.45 (CH_2), 29.80 (CH_2), 29.74 (CH_2), 29.68 (CH_2), 29.50 (CH_2), 29.47 (CH_2), 29.42 (CH_2), 26.19 (CH_2), 22.80 (CH_2), 14.20 (CH_3); IR (KBr): $\tilde{\nu}=2925$ (s), 2855 (w), 1732 (m, ester), 1629 (w, imine), 1576 (m), 1500 (m), 1464 (w), 1432 (m), 1385 (w), 1338 (s), 1192 (s), 1116 (s), 1003 (w), 958 (w), 863 cm^{-1} (w); FAB^+-MS (*meta*-nitrobenzylalcohol matrix): m/z [%]: 1785 (80) $[M+H]^+$, 1022 (20) $[M-NC_6H_4OCOC_6H_2(OC_{12}H_{25})_3]$, 259 (25) $[M-2(NC_6H_4OCOC_6H_2(OC_{12}H_{25})_3)]$; elemental analysis calcd for $C_{115}H_{173}N_5O_{10}$ ($M_r=1785.689$): C 77.35, H 9.77, N 3.92; found: C 77.10, H 9.45, N 3.62.

Dicopper(I)complex $\mathbf{C}^{\mathbf{12}}$: A solution of $[Cu(CH_3CN)_4][BF_4]$ (0.022 g, 0.069 mmol) in anhydrous CH_3CN (10 mL) was transferred by cannula to a stirred solution of $\mathbf{L}^{\mathbf{12}}$ (0.120 g, 0.067 mmol) in anhydrous CH_2Cl_2 (15 mL) at 20 °C. The solution was kept under an atmosphere of argon. After stirring for 2 h the solution was filtered over celite and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/MeOH giving 0.125 g (97 % yield) of a dark-brown powder. UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=278$ (115 200), 450 (6600), 500 nm ($5600\,\text{M}^{-1}\,\text{cm}^{-1}$); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta=8.45$ (s, 4H, H-imine), 7.93 (m, 18H), 7.37 (s, 8H), 6.92 (q_{AB}, $J_{AB}=8.9$ Hz, 16H), 4.06 (m, 24H), 1.80 (m, 24H), 1.49 (m, 24H), 1.26 (br s, 192H), 0.87 (m, 36H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta=165.05$ (C=O), 156.47 (C=N), 153.07, 152.52, 152.04, 151.42, 150.65, 144.39, 143.39, 139.50, 127.01, 125.85, 124.18, 123.15, 122.91, 108.63 (aromatic), 73.61 (OCH_2), 69.34 (OCH_2), 31.90 (CH_2), 30.36 (CH_2), 29.63 (CH_2), 29.36 (CH_2), 29.13 (CH_2), 26.13 (CH_2), 26.07 (CH_2), 22.67 (CH_2), 14.07 (CH_3); IR (KBr): $\tilde{\nu}=2925$ (s), 2855 (s), 1731 (m, ester), 1588 (m, imine), 1501 (m), 1463 (w), 1433 (m), 1384 (w), 1336 (s), 1190 (s), 1112 (s), 952 (w), 866 cm^{-1} (w); ES-MS (CH_2Cl_2): m/z: 3785.3 $[M-BF_4]^+$, 1849.1 $[M-2\,BF_4]^{2+}$; elemental analysis calcd for $C_{230}H_{346}N_{10}O_{20}Cu_2B_2F_8$ ($M_r=3872.078$): C 71.35, H 9.01, N 3.62; found: C 71.19, H 8.68, N 3.44.

Cu^{I}/Cu^{II} mixed-valence complex **C**$^{12\mathrm{m}}$: A solution of ferrocenium (BF_4 salt) (0.003 g, 0.01 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of **C**^{12} (0.04 g, 0.01 mmol) in anhydrous CH_2Cl_2 (10 mL) at 20 °C. After stirring for 2 h, the solvent was removed. Crystallisation from hexane afforded 0.035 g (88 % yield) of a dark-brown powder. UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (ε): 279 (137 000), 450 (6700), 500 nm (4600 $\mathrm{M^{-1}cm^{-1}}$); IR (KBr): $\tilde{\nu} = 2925$ (s), 2855 (s), 1731(m, ester), 1590 (m, imine), 1500 (m), 1465 (w), 1433 (m), 1385 (w), 1336 (s), 1190 (s), 1113 (s), 862 cm^{-1} (w); ES-MS (CH_2Cl_2): m/z: 1892.7 $[M - 2BF_4]^{2+}$, 1233.0 $[M - 3BF_4]^{3+}$; elemental analysis calcd for $C_{230}H_{346}N_{10}O_{20}Cu_2B_3F_{12} \cdot CH_2Cl_2$ ($M_r = 3958.882 + 84.933$): C 68.61, H 8.67, N 3.46; found: C 68.22, H 8.41, N 3.08.

The synthesis and characterization of additional ligands and complexes, as well as their mesomorphic behavior, will be reported in full elsewhere. Equipment used: DSC: Perkin-Elmer DSC 7, heating/cooling rate 10 K min^{-1}; POM: Leitz Orthoplan, Mettler FP 82 hot stage; XRD: Guinier focusing camera, $Cu_{K\alpha 1}$ radiation, powder samples in Lindemann capillaries, INSTEC hot-stage, INEL CPS-120 curved position-sensitive detector.

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An Expeditious Total Synthesis of the Natural Stereomeric Mixture of Stenusine Following a Possible Biogenetic Pathway**

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Dedicated to Professor Pierre Potier
on the occasion of his 65th birthday

Stenus comma (Coleoptera, Staphylinidae) is a familiar beetle encountered on the sandy banks of stagnant ponds and sluggishly flowing rivers in Eastern and Central Europe. The beetle propels itself over the water surface by an unusual biological phenomenon in which it expels an oily substance with a high spreading capacity onto the aqueous surface. Since the isolation and structure elucidation of stenusine **1** (see Scheme 1; $[\alpha]^{20}_{365} = +5.8$, $c = 0.115$ in EtOH) as the main component of the propulsion fluid and a toxic chemical substance by Schildknecht et al.,[1] numerous preparations have been developed based on racemic[2] and asymmetric[1a, 3] strategies. Finally the enantioselective syntheses of isomeric (2*S*,3*S*)-1-ethyl-3-(2-methylbutyl)piperidine and (2*S*,3*R*)-1-ethyl-3-(2-methylbutyl)piperidine by Enders, De Kimpe et al.[3a] accompanied by chiral GC for both synthetic and natural samples helped to establish that natural stenusine is a mixture of the four possible stereomers in a ratio of 43:40:13:4 = (*S*,*S*):(*S*,*R*):(*R*,*R*):(*R*,*S*) with predominance (83:17) of the two epimers with *S* configuration on the side chain.

It is unusual that an organism produces a natural compound as a mixture of two pairs of enantiomers in a particular ratio. This intriguing observation led us to reflect on the biogenetic origin of the compound. Although Schildknecht et al.[1a] suggested a terpenoid origin, the biosynthesis of stenusine has not yet been elucidated by incorporation experiments. In continuation of our research on the biomimetic synthesis of piperidine alkaloids,[4] we sought a rapid access to natural stenusine. The essence of our biogenetic postulate and strategy for synthesis is that structure **1** derives most likely from lysine and isoleucine and could be considered as the biological condensation of their metabolites, 1,2,3,4-tetrahydropyridine and aldehyde (−)-**2** (Scheme 1). The inter-

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