carried out prior to addition of the next polyelectrolyte to ensure removal of the nonadsorbed polyelectrolyte.

SEM measurements were conducted with a Zeiss DSM 40 instrument operated at an accelerated voltage of 15 kV. After the required number of polyelectrolyte layers were deposited, the MF core was removed by exposure to an aqueous solution of low pH. Samples were prepared by applying a drop of the shell solution to PEI-coated glass. After allowing the shells to settle the slides were extensively rinsed in Millipore water and then dried under a gentle stream of nitrogen.

The TEM specimens were fixed with gluteraldehyde, OsO_4, and $K_2Cr_2O_7$, and dehydrated in ethanol/acetone. The samples were embedded in Epon 812/Araldite M resin and polymerized in an oven for two days.[15] Thin sections (80 – 100 nm) were cut with a Reichert ultratome, and stained with uranyl acetate and lead citrate. Measurements were performed on a JEOL 100 B electron microscope.

The AFM images were obtained with a Digital Instruments Nanoscope IIIa in the tapping mode. Samples were prepared by applying a drop of the shell solution to PEI-coated glass. After allowing the shells to settle the slides were extensively rinsed in Millipore water and then dried under a gentle stream of nitrogen.

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Cation-Induced Macroscopic Ordering of Non-Mesomorphic Modules—A New Application for Metallohelicates**

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A major goal in the emerging field of supramolecular chemistry is to relate local molecular architecture to the macroscopic ordering of the system. Such large-scale organization is probably essential for the construction of practical devices from molecular units.[1–3] Despite this realization, little genuine progress has been made with regard to the integration of local order into large-scale multidimensional arrays.[4] In marked contrast, tremendous advances have been made in the construction of exotic supermolecules by stepwise acretion of simple building blocks.[5, 6]

We now present a strategy that exploits a metallohelicate, assembled from non-mesomorphic but lipid-like organic strands, to promote formation of a liquid crystalline state at ambient temperature. The key element of this approach lies with the helix that provides rigidity and polarizability to counterbalance the flexibility and nonpolarizability of the paraffinic chains (amphiphilic character). This subtle balance between organized and chaotic domains controls the fate of the mesomorphic material. This system, the first liquid crystalline metallohelicate, illustrates the tremendous organ-

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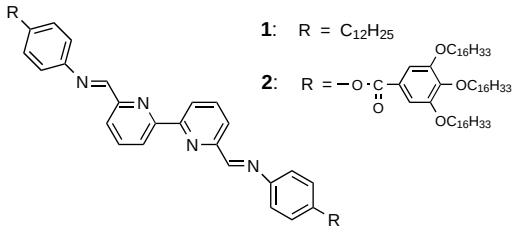
izational ability of copper(I) cations. It is, in fact, remarkable that the cation is able to induce order at both molecular and supramolecular levels, considering the large volume and structural disorder inherent in the nondiscoidal ligand. This point is well illustrated by comparison of the molar volumes calculated for the ligand ($V_m = 1356\ cm^3\,mol^{-1}$) and the cation ($V_m = 2.2\ cm^3\,mol^{-1}$).[7]

Our recent discovery[8] that a stable copper(I) helicate with bridging diiminobipyridine subunits is formed selectively and quantitatively by a cooperative process has prompted exploration of other polycatenar iminobipyridine ligands as building blocks. These nondiscoidal units are the key element by which the local molecular architecture (double helix) is incorporated into an organized macroscopic ensemble. Ligands **1** and **2** were synthesized in 90 and 99% yield, respectively, by reaction of 6,6′-diformyl-2,2′-bipyridine[9] with



the corresponding aniline derivative[10] in the presence of trace amounts of acid. As expected, both ligands self-associate in the presence of $[Cu(CH_3CN)_4]BF_4$[11] to afford deep-green, air-stable materials in excellent yield. These products were identified as the corresponding dinuclear copper(I) complexes with the formulae $[Cu_2(\mathbf{1})_2](BF_4)_2$ (**3**) and $[Cu_2(\mathbf{2})_2](BF_4)_2$ (**4**).

On the basis of mass spectrometry and elemental analysis, it was concluded that these dinuclear copper(I) complexes were not contaminated with mononuclear or slipped polymeric structures (**3**: positive ion FAB-MS: *m*/*z* 1611.8 $[M^+ - BF_4]$, 1524.8 $[M^+ - 2BF_4]$; **4**: MALDI TOF-MS: 4388 $[M]$, 4301 $[M - BF_4]$, 4214 $[M - 2BF_4]$). The well-defined ^1H and ^{13}C NMR spectra of both complexes (Figure 1) reveal that the ligands are equivalent and symmetric about the center. In both complexes, the imine H signal is shifted upfield by $\Delta\delta = 0.3$ due to direct involvement of the nitrogen atom in the coordination sphere of the copper ion. This situation was confirmed by solid-state and solution-phase FT-IR studies which showed a shift of the imino stretching vibration by about 40 cm^{-1} versus the free ligand.

The most striking effect of complexation is found for the signals of atoms H3 and H3′ (*ortho* to the exocyclic bipyridine C–C bond), which are shifted downfield by $\delta = 1.9$ in **3** and 1.3 in **4**. This shift arises because each ligand wraps around the two copper(I) cations, with the iminopyridine fragment chelated in a *cis* fashion and the two pyridine units twisted about the central exocyclic C–C bond (i.e., 40° in complex **3**[12]). This process forces H3 and H3′ to reside within the shielding region exerted by the iminophenyl ring of the complementary ligand. Less significant shifts are observed for other H atoms of the bipyridine and phenyl fragments attached to the imine. The unique mode of coordination of this α,α'-imino-substituted bipyridine is confirmed by the

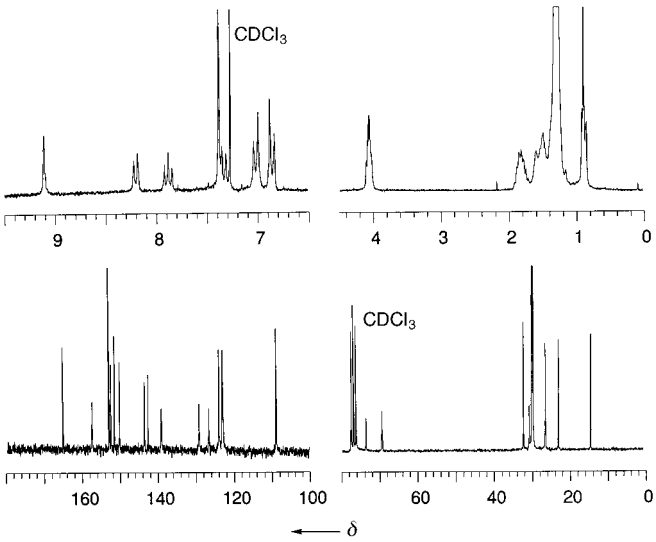


Figure 1. NMR spectra of complex **4** in $CDCl_3$. Top: ^1H NMR (200 MHz); bottom: $^{13}C\{^1H\}$ NMR (50.3 MHz). The aromatic regions of the spectra (left) have been multiplied by four versus the aliphatic regions (right).

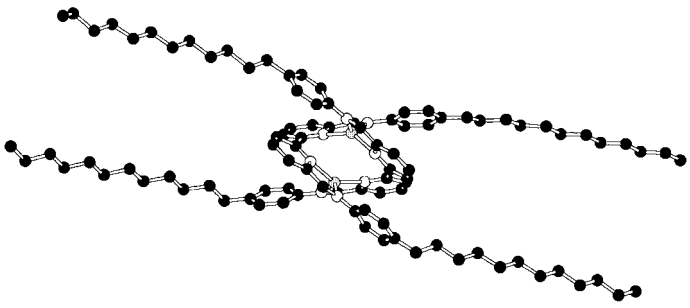
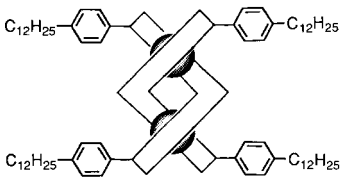
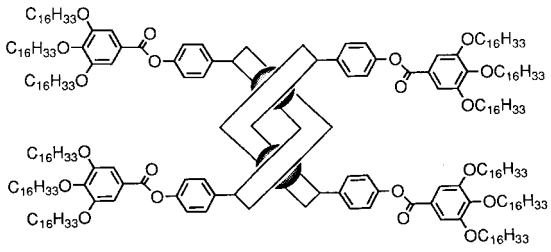


Figure 2. The structure of the cation in **3** in the crystal.

crystallographic structure of **3**[12] (Figure 2), where the central unit is not chelating but adopts a bridging coordination mode (see structure formulae of **3** and **4**).



3



4

When observed under a polarizing optical microscope and analyzed by differential scanning calorimetry (DSC), ligands **1** and **2** and complex **3** appear non-mesomorphic with well-defined melting points. In **3** we assume that the balance between the aromatic core and the paraffinic chains is not

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favorable for the formation of mesophases. The polymorphic behavior of complex **4** was investigated as a function of temperature by DSC and polarizing optical microscopy. The DSC thermograms were measured by heating and subsequent cooling over the range 0 to 200 °C and revealed the presence of two sharp peaks indicative of reversible first-order phase transitions. The peak at 25 °C ($\Delta H \approx 132$ kJ mol^{-1}) is related to the appearance of a liquid crystalline phase, while the peak at 181 °C ($\Delta H \approx 3.1$ kJ mol^{-1}) is due to melting into an isotropic liquid. The optical textures observed upon slow cooling of the isotropic melt (Figure 3, top) clearly show the existence of a

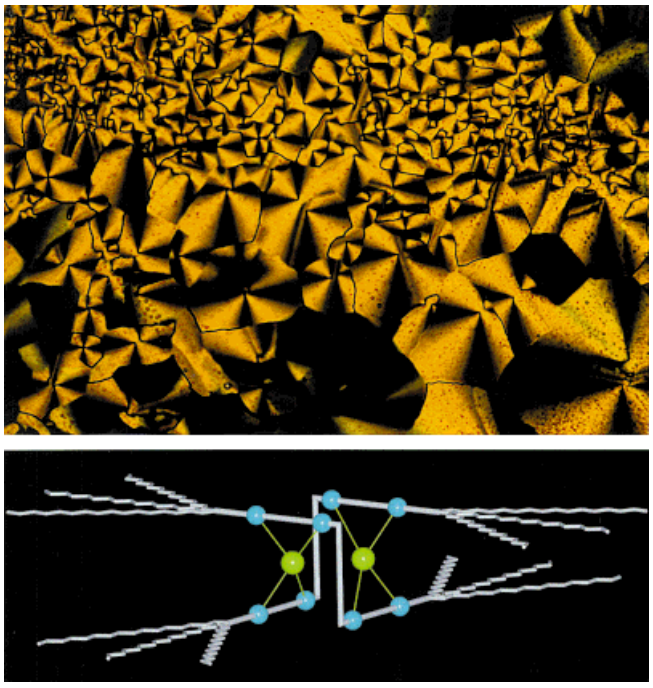


Figure 3. Top: Optical textures of complex **4** observed with a polarizing microscope on slow cooling from the isotropic melt: pseudo-focal-conic texture at 100 °C. Bottom: Schematic view of an isolated molecule of **4**. Nitrogen: blue, copper: green.

viscous columnar phase (appearance of a pseudo-focal-conic texture which turns into a classical texture). These observations may be summarized as follows:

$$\text{crystal} \overset{25\,^\circ\text{C}\ (132\ \text{kJ mol}^{-1})}{\rightleftharpoons} \text{columnar} \overset{181\,^\circ\text{C}\ (3.1\ \text{kJ mol}^{-1})}{\rightleftharpoons} \text{isotopic}$$

The columnar nature of the liquid crystalline phase was confirmed by X-ray diffraction. The presence of a diffuse band at 4.6 Å (Figure 4) indicates that the alkyl chains adopt a liquidlike conformation. The diffuse band at 10 Å corresponds to the height of the rigid organometallic cores, as estimated by molecular modeling of the crystal packing and subsequently confirmed by crystallographic study of single crystals of complex **3** (Figure 2).[12]

A schematic representation of the cation in **4** is given in the lower part of Figure 3. The cores are stacked on top of each other in a disordered fashion to form columns. However, the presence of two sharp reflections at 39.2 and 21.8 Å shows that, although disordered within the columns, the molecules are nevertheless arranged periodically at the macroscopic

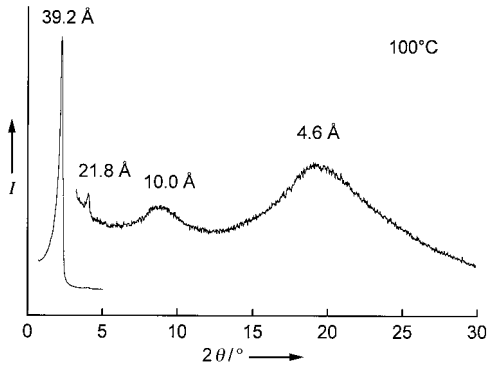
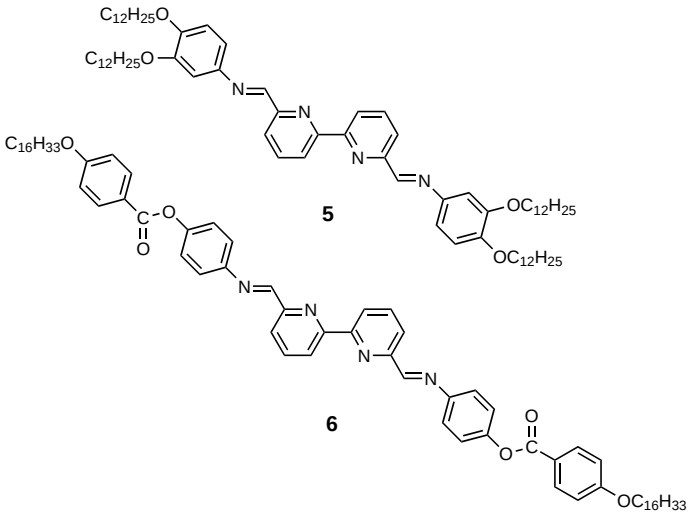


Figure 4. Typical X-ray diffraction patterns of **4** in the columnar phase at 100 °C. Intensity I in arbitrary units.

level. It is important to note that the measured Bragg spacings are in a noncrystallographic ratio ($\sqrt{3.2}$) which indicates the existence of a two-dimensional crystal lattice. The structure of the liquid crystalline phase appears, therefore, to consist of columns of rigid cores surrounded by molten alkyl chains and laterally packed in a two-dimensional lattice of rectangular or oblique symmetry. From the dimensions of the rigid organometallic cores ($8 \times 8 \times 10$ Å; Figure 3, bottom), it is possible to calculate the area around the aromatic cores covered by the twelve alkyl chains of each complex molecule: $4 \times (8 \times 10) = 320$ Å^2, which corresponds to a molecular area of $320/12 \approx 27$ Å^2 per alkyl chain.

The realization that α,α'-diimino-substituted 2,2′-bipyridine nondiscoidal ligands form stable copper(I) helicates that display liquid crystalline behavior opens the door to several broad and fruitful areas of supramolecular chemistry. While numerous examples of copper(I) helicates are known, it has proved extremely difficult to assemble such structures into organized assemblies. It is necessary to select the number, length, and nature of the lipid-like chains with great care. In most cases non-mesomorphic metallohelicates are formed, and it is clear that there is a high barrier to arranging the metallohelicate into ordered columns (ligands **1**, **5**, and **6** were greatly inferior to **2**). Thermotropic liquid crystalline bipyridine ligands are known,[13] but despite considerable effort expended on the development of bipyridine-based metal-



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lomesogens only a few examples have been reported so far.[14] In this respect, the onset of liquid crystalline behavior can be seen as a result of a fine balance between order (helix) and chaos (alkyl chains). Optimization of this balance will produce a low-temperature metallomesogen. As shown here and previously observed in many cases,[2] the use of a discoidal ligand is not mandatory for the generation of columnar mesophases.

The initial step in the overall process is the formation of a stable metallohelicate, and is itself a challenge in view of the bulky alkyl chains that complicate the gathering of the ligands around the cations. The helix provides essential rigidity that favors subsequent stacking of the aromatic cores. While it is unclear if a helicate is a prerequisite for liquid crystalline behavior, it is clear that some kind of ordered central structure is essential for macroscopic ordering. The pivotal role of the central metal cation cannot be overstated in such systems. The combination of properties (color, polarizability, and magnetism) within the self-assembled supermolecule is quite unique and provides new opportunities for the future application of liquid crystals that are addressable by weak magnetic or optical fields. We are currently exploring the properties of other fascinating multinuclear complexes constructed with terpyridines, naphtyridines, pyridine-substituted diazines, pyrazines, and anthyridines to gain further insights into the chemistry and material science properties of these challenging systems.

Experimental Section

Ligand **2**: A Schlenk tube was successively charged with 6,6′-diformyl-2,2′-bipyridine (0.015 g, 0.07 mmol), 4-(3,4,5-tri(hexadecyloxy)benzoyloxy)aniline (0.137 g, 0.14 mmol), EtOH (15 mL), and acetic acid (1 drop). During heating for 6 h at 80 °C, the ligand precipitated. After the reaction mixture was cooled to room temperature, the white solid was filtered off and washed with EtOH (3 × 15 mL). Yield: 0.143 g of **2** (99 %). M.p. 102–104 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 228 (72400), 280 (54400), 301 nm (55200 $M^{-1}cm^{-1}$); ^1H NMR (200.1 MHz, $CDCl_3$, 25 °C): δ = 8.76 (s, 2H; imine H), 8.62 (dd, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 2H; H3, H3′), 8.31 (d, ^3J = 6.7 Hz, 2H; H5, H5′), 8.00 (t, ^3J = 7.7 Hz, 2H; H4, H4′), 7.43 (s, 4H), 7.34 (AB system, J_{AB} = 8.7 Hz, $\Delta\nu$ = 27.1 Hz, 8H), 4.07 (m, 12H; OCH_2), 1.81 (m, 12H; CH_2), 1.48 (m, 12H; CH_2), 1.27 (s, 144H; CH_2), 0.88 (t, ^3J = 6.3 Hz, 18H; CH_3); IR (CaF_2 cell, CH_2Cl_2): $\tilde{\nu}$ = 2919 (s), 2849 (m), 1725 (m), 1629 (w), 1587 (w), 1498 (w), 1465 (w), 1432 (w), 1384 (w), 1334 (m), 1289 (w), 1196 (s), 1120 cm^{-1} (s); positive ion FAB-MS (thioglycerol matrix): *m/z* (%): 2043(20) [M^+], 1801(7) [$M^+ - OC_{16}H_{33}$], 1560(27) [$M^+ - 2OC_{16}H_{33}$], 1202(15) [$M^+ - OCOC_6H_2(sOC_{16}H_{33})_3$], 360(23) [$M^+ - 2(O\text{-}COC_6H_2(OC_{16}H_{33})_3$]; elemental analysis calcd for $C_{134}H_{218}N_4O_{10}$: C 78.69, H 10.74, N 2.74; found: C 78.51, H 10.46, N 2.64.

Helicate **4**: A solution of $[Cu(CH_3CN)_4]BF_4$ (0.016 g, 0.051 mmol) in CH_3CN (10 mL) was transferred through a cannula to a stirred solution of **2** (0.100 g, 0.049 mmol) in CH_2Cl_2 (15 mL) at room temperature and under argon. During the addition, the color of the solution turned deep green, indicating fast Cu^I complexation. The mixture was heated at about 60 °C for 5 min and then stirred for 2 h at room temperature. The solution was filtered over celite and evaporated to dryness. The residue was recrystallized in CH_2Cl_2/Et_2O to give 0.087 g of **4** (81 % yield). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 227 (140800), 280 (96600), 314 (113300), 452 (sh, 5700), 600 nm (sh, 2200 $M^{-1}cm^{-1}$); ^1H NMR (200.1 MHz, $CDCl_3$, 25 °C): δ = 9.11 (s, 4H; imine H), 8.20 (d, ^3J = 7.5 Hz, 4H; H5, H5′), 7.88 (t, ^3J = 7.8 Hz, 4H; H4, H4′), 7.38 (s, 8H), 7.33 (d, ^3J = 7.8 Hz, 4H; H3, H3′), 6.93 (AB system, J_{AB} = 8.6 Hz, $\Delta\tilde{\nu}$ = 30.8 Hz, 16H), 4.07 (m, 24H; OCH_2), 1.81 (m, 24H, CH_2), 1.49 (m, 24H, CH_2), 1.26 (s, 288H, CH_2), 0.88 (m, 36H; CH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 165.3 (C=O), 157.6 (C=N), 153.1, 152.6, 151.7, 150.3, 143.7, 142.7, 139.2, 129.2, 124.0, 123.1, 122.9, 108.8, 77.0 (OCH_2), 69.5 (OCH_2), 31.9 (OCH_2CH_2), 30.4 (OCH_2CH_2), 29.7 (CH_2), 29.4 (CH_2), 26.1 (CH_2), 22.6 (CH_2), 14.0 (CH_3); IR (CaF_2 cell, CH_2Cl_2): $\tilde{\nu}$ = 3046 (w), 2926 (s), 2854 (m), 1729 (m), 1589 (w), 1499 (w), 1463 (w), 1429 (w), 1384 (w), 1336 (m), 1189 (s), 1062 cm^{-1} (m); elemental analysis calcd for $C_{268}H_{436}B_2Cu_2F_8N_8O_{20}$: C 73.31, H 10.01, N 2.55; found: C 73.00, H 9.74, N 2.19.

Differential scanning calorimetry: Perkin-Elmer DSC 7, heating/cooling rate of 10 °C min^{-1}. Polarizing optical microscope: Leitz Orthoplan, Mettler FP 82 hot stage. X-ray diffraction: Guinier camera, $Cu_{K\alpha 1}$ radiation, powder samples in Lindemann capillaries, INSTEC hot stage, INEL CPS-120 detector.

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