evidence for positive cooperativity among the metal binding sites in **1**-Cu$_3$.

Thus, metal-binding properties of **1** and the high symmetry of **1**-Cu$_3$ illustrate a high degree of control over the degree and regularity of molecular entwinement. In combination with an appropriate macrocyclization method, the stage is set for the directed synthesis of complex topological stereoisomers of high symmetry, specifically, a molecular trefoil knot.[36]

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[32] Crystal structure analysis of **1**-Cu$_3$: Bruker CCD SMART diffractometer, sealed tube, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, Ω scans, temperature 213(2) K, cell determination with 317 reflections ($1.1 < \Theta < 19.3°$). Data collection, data reduction, Lorentz and polarization corrections using SMART and SAINT, absorption correction by SABABS, solution by direct methods, remaining non-H atoms by LS − ΔF syntheses, refinement against F^2 (SHELXL) with all H atoms included in idealized positions, all Cu, O, and F atoms refined anisotropically. Structure solution, refinements, graphics, and tables calculations performed with SHELXTL/PC. **1**: $C_{132}H_{90}B_3Cu_3F_{12}N_{12}O_6$, M_r 2391.21, monoclinic, space group $P2_1/c$ (no. 14), $a = 24.879(2)$, $b = 14.4764(12)$, $c = 37.097(3)$ Å, $\beta = 102.912(1)°$, $V = 13023(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.220$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.558$ mm^{-1}, crystal dimensions ca. $0.15 \times 0.06 \times 0.06$ mm^3, $2\theta_{max} = 38.6°$, 37667 reflections measured, 9851 unique reflections($R_{int} = 0.149$), 770 parameters, 3 restraints, $R_1(wR_2) = 0.1163$ (0.2624) for 5498 reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-148313. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Tetranuclear Copper(I)-Biphenanthroline Gridwork: Violation of the Principle of Maximal Donor Coordination Caused by Intercalation and CH-to-N Forces[**]

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The amelioration of "hot spots" in a molecule through specific molecular association is a general chemical principle, which has been recently highlighted as a driving force for "supramolecular" reactions.[1] The instability of unpaired radicals, uncoordinated metal ions and ligands, and unasso-

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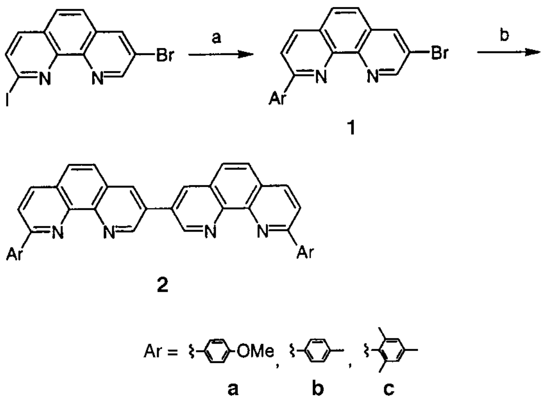
ciated hydrogen bond acceptors and donors attest to the generality of such chemical assembly phenomena. From such empirical wisdom, “rules” were developed for supramolecular design, such as the principle of maximum coordination, in which it is assumed that a metal ion with a defined ligand field will associate with enough donor atoms to satisfy that field, and that no donor atoms will be left uncoordinated.[2, 3] Though trivial for monodentate ligands, this principle has provided a rationalization for the structures found in several metal-coordination arrays.[4–10] A signal example in this area has been the molecular grids,[11] wherein *n* rods of *m* bidentate ligands coordinate $(n \times m)/2$ tetrahedral metal ions.[3, 11–13] The stoichiometry in such complexes is uniformly $L_nM_{(n\times m)/2}$, for example, a 2 × 2 grid from a bisbipyridine rod (Scheme 1).[14] The regularity of this composition has evoked the idea of algorithmic or programmed molecular association.[15, 16] Despite the appeal of such imagery, the diversity of association forces in chemistry complicates the molecular algorithm to an extent where the analogy between modern computer scripts and supramolecular design is unwarranted. To this point, we present a simple metal–ligand combination that highlights the limitations of such “programs”.

Among bidentate ligands, 1,10-phenanthroline is renowned for the generality of its stable metal complexes.[17, 18] In particular, copper(I) and silver(I) form stable tetrahedral complexes with 1,10-phenanthroline.[19, 20] Rods of 3,8-linked oligophenanthrolines should therefore provide excellent scaffolds for the creation of molecular grids. Recent methods in phenanthroline halogenation provided a route to a series of 2-aryl-8-bromo-1,10-phenanthrolines **1a–c**,[21] which, through reductive homocoupling mediated by nickel(0),[22] formed the 2,2′-diaryl-8,8′-bis-1,10-phenanthrolines (Scheme 2) (**2a–c**).

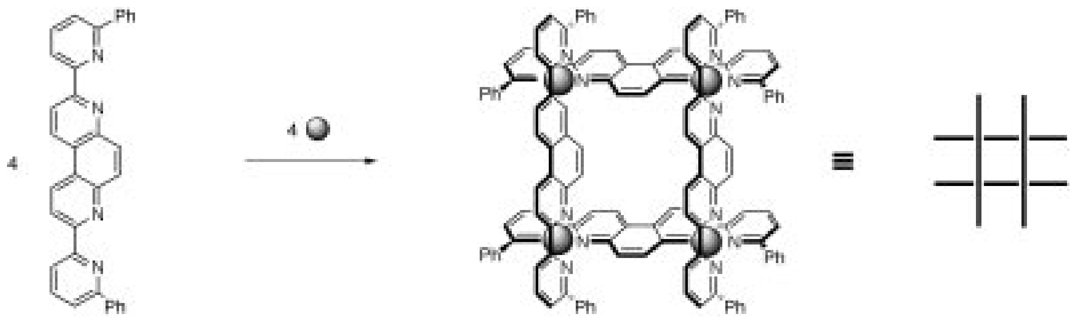
Combination of a suspension of **2a** in acetonitrile with copper(I) or silver(I) produces a red (**3a**-Cu) or colorless (**3a**-Ag) homogeneous solution, respectively. In each case, all the signals in the ^{1}H and ^{13}C NMR spectra are sharp and can be assigned to two sets of phenanthroline resonances in a ratio of 2:1. Such spectra imply that there are two different kinds of environments for the biphenanthroline rods in the complex but that each rod is symmetric about its midpoint. Variations in counterion, molecular equivalents, or solvents have little effect on the spectra. No single M_nL_n molecular grid, weave, or cycle has the symmetry necessary to account for the complexity and relative amounts of the specific signals seen in these spectra, even with consideration of dynamic processes. Persistence of the general spectral qualities and precise 2:1 ratio seriously restricts the likelihood of multiple species in equilibrium. Electrospray mass spectrometry provides a crucial clue to solve the mystery of the structure in solution; the molecular ion corresponds to the formula $M^{+}_{4}L_{6}A^{-}_{4}$, in violation of the $L_nM_{(n+m)/2}$ rule!



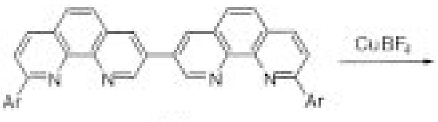
Scheme 2. a) Arylboronic acid, $[Pd(PPh_3)_4]$, $Ba(OH)_2$, 1,2-dimethoxyethane, H_2O, reflux; b) $NiCl_2 \cdot 6H_2O$, PPh_3, Zn, DMF, 50 °C.

Even the clarification of molecular stoichiometry does not provide an immediate solution to this “structural algorithm.” The principle of maximum coordination might seduce one to search for hexacoordinate solutions if not for the sacrilegious sound of octahedral copper(I)! Ultimately, crystal structure analysis brought this chemical regression to self-consistency: **3a**-Cu is a 3 × 3 molecular grid possessing 4 ligands coordinatively bonded to metal ions in the form of a molecular square (host) with 2 additional ligands filling the interstitial spaces (guest) (Figure 1).[23] Given this unanticipated “output,” a closer inspection of the molecular program seems warranted.

From the crystal structure of $(\mathbf{3a}\text{-Cu})^{4+} \cdot 4BF_4^{-}$, we see two striking elements of molecular complementarity: 1) the grid spacing between host biphenanthroline rods is about 7.5 Å on average and therefore well accommodates an additional rod as an aromatic guest by intercalation; 2) the “uncoordinated” nitrogen atoms of the guest biphenanthrolines are positioned within van der Waals contacts of one set of C9,C9′ hydrogen atoms of the host scaffold. Effects that account for the stability of the complex must include primarily dispersive and to a lesser extent electrostatic interactions among the π clouds (“π stacking”).[24–31] Coincidentally, a complimentary electrostatic interaction between the hydrogen atoms of C9 on the scaffold and the nitrogen atoms of the guest exists. Some would herald the proximity of aromatic hydrogen atoms and phenanthroline nitrogen atoms as



Scheme 1. Simple 2 × 2 grid a la Baxter et al. ● = Cu^{I}.



2a

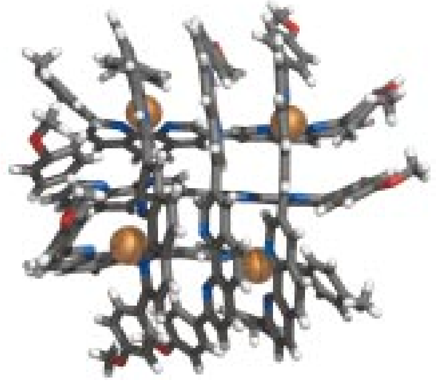


Figure 1. X-ray structure of the host–guest 3 × 3 grid **3a**-Cu.

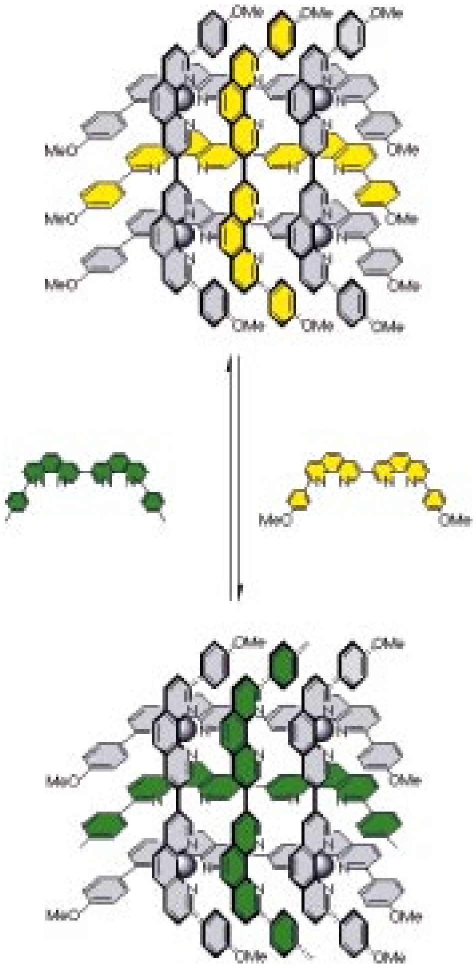
evidence for CH–N hydrogen bonds;[32, 33] however, it should be kept in mind that the molecular complex is an equilibrium structure that balances all molecular forces. Thus, if attraction among the π systems was great enough, the energy benefit of intercalation could force the proximity of nitrogen and hydrogen even at the energy cost of local repulsive interactions.[34]

Variation in the aryl substitutent affords us some control over this grid motif. Whereas the simple electronic perturbation of swapping anisyl for tolyl leads to a similar 3 × 3 grid complex, **3b**-Cu, the steric/conformational perturbation of the mesityl group does not produce a grid architecture. The mesityl groups twist out of the plane of the biphenanthroline ligand and jut their *ortho* methyl groups into the interstitial spaces, precluding intercalation by another ligand and leading to an instability of the grid architecture. Thus, it is not simply that a “stable” 2 × 2 grid is formed and the guests then fit in,[14] but rather there must be a cooperativity between the host and guest components that gives **3**-Cu its unique supramolecular structure.

Several additional questions are raised by this simple system: What is the nature of complex stability? Is the free ligand the best guest for the host grid? What is the mechanism/time scale for grid formation? Access to two related complexes, **3a**-Cu and **3b**-Cu, provided some avenues to investigate. High-temperature NMR spectra (150 °C) of the pure complexes show no coalescence of the signals and set a lower limit on exchange barrier of host and guest ligands to about 20 kcal mol^{-1}. In contrast, a mixture of **3a**-Cu and **3b**-Cu could not be prepared fast enough to preclude scrambling of the guest ligands. Thus, the barrier to exchange could not be higher than 25 kcal mol^{-1}.

The previous two studies focused on complex to complex exchange, but one can also probe the exchange between free ligand and the guest site of the complex (Scheme 3). Addition of free **2b** to a solution of **3a**-Cu results in rapid exchange of guest followed by a slower incorporation into the host sites. By supporting the complex on alumina and passing a solution of free ligand over the stationary complex, a pure “mixed” host–guest complex could be formed—with either **2b** intercalated in place of **2a** in **3a**-Cu or **2a** intercalated in place of **2b** in **3b**-Cu—and then isolated by stripping the complex quickly from the alumina.

The dynamics of the guest-exchange process were studied in more detail by spin saturation transfer spectroscopy. In the spectrum of a solution of ligand **2a** and complex **3a**-Cu, the methyl protons of **2a** are irradiated and the transfer of magnetization is found only in the guest site of **3a**-Cu. Quantitative measure of the amount of magnetization transferred and the relaxation time of the protons led to a rate of exchange.[35] Assuming a disassociative mechanism with the first step rate limiting, the rate measured is for the unimolecular disassociation of the guest ligand from **3a**-Cu. From the rate data measured over a 20 degree range, a free energy of activation around 21 kcal mol^{-1} could be deduced and a crude partitioning indicates that at room temperature about 75% of the energy barrier is enthalpic (ca. 15 kcal mol^{-1}). Notably, the entropy for the disassociation is positive and large (ca. 20 cal K^{-1} mol^{-1}). This unusual entropy hints at a novel solvation effect akin to the hydrophobic effect in water; the disassociated guest and host exposes a significantly larger combined surface area for solvation and cavitation than the host–guest supramolecule.



Scheme 3. Exchange reaction of guest ligands.

In conclusion, the concept of an accessible and controllable molecular program, even within the limited arena of metal coordination structures, seems premature. If one wants to "program" in the "machine language" of molecules, (s)he will receive the greatest insight from the firm fundamentals of thermodynamics and kinetics as opposed to distractions of sirenous supramolecular slogans.

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Synthesis and Fluorescence Properties of Manisyl-Substituted Terpyridine, Bipyridine, and Phenanthroline**

Jon C. Loren and Jay S. Siegel*

Cation affinity, solubility, and spectroscopy (e.g. fluorescence) are three characteristic physical properties of oligopyridine-based heterocycles (2,2′:6′,2″-terpyridines, 2,2′-bipyridines, and 1,10-phenanthrolines, in the following simply designated as terpyridines, bipyridines, and 1,10-phenanthrolines) that one would like to control through a simple synthesis scheme from common building blocks.[1] In particular, aryl-substituted heterocycles of this family have a rich history in metal coordination chemistry.[2, 3] Their conjugated backbones make them attractive chromophores and molecular "antennae";[4–7] however, the larger and fused analogues typically suffer from poor solubility and inefficient chemical syntheses. Among aryl substituents, *p*-anisyl (4-methoxyphenyl) has been extensively used where further structural elaboration was desired,[8–10] and mesityl has been noted for endowing superior solubility features.

A hybrid of these two aryl motifs, 4-methoxy-2,6-dimethylphenyl or "manisyl", offers both characteristics, but has been

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