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'Locking' dendrimer conformation through metal coordination

Mark R. Rauckhorst, Paul J. Wilson, Susan A. Hatcher, Christopher M. Hadad
and Jon R. Parquette*

Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH 43210, USA

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Abstract—Chiral intramolecularly hydrogen-bonded dendrons that fold into a dynamically biased helical conformation can be 'locked' in kinetically controlled conformations by coordination to copper(II) metal centers. Covalent bonding of each pyridine-2,6-dicarboxamide repeat unit of the dendrons to a copper metal center forces this subunit to exist in only the *syn–syn* conformation and dramatically rigidifies the dendron structure. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The three-dimensional globular morphology of dendrimer macromolecules[1] makes them attractive materials in which to induce higher levels of structural order in a manner resembling the folded structures of proteins.[2] Many of the potential applications envisaged for dendrimers (e.g. enantioselective catalysts, chemical sensors, optical switches) can only be realized in materials expressing highly ordered and controllable conformations. However, the goal of inducing higher-order three-dimensional organization in chiral dendrimers[3] has been severely hampered by the conformational flexibility of most commonly studied dendrimers.[4] We have recently reported that a chiral helical secondary structure can be induced in dendrimers constructed using an AB_2 repeating unit based on 4-aminopyridine-2,6-dicarboxamide.[5] These dendrons exhibit a dynamic conformational bias for an M-type helicity relating a pair of anthranilamide termini at the second and third generations (Fig. 1). Further, the chiral bias of the dendrons is extremely sensitive to solvent quality, temperature and dendron generation. In this manuscript, we report that the secondary structure of these dendrons can be kinetically locked by metal coordination.[6]

2. Design considerations

The ability of the dendrons to exhibit a chirally biased helical secondary structure is predicated on the preference of the repeat unit to exist predominantly in the *syn–syn* conformation rather than either the higher energy *syn–anti* or *anti–anti* forms (Fig. 2).[7] The *syn–syn* conformation is lowest in energy because this conformation places the amide NH groups in close proximity to the pyridine-*N* which permits intramolecular hydrogen bonding interactions to occur and; further, this orientation of the amides minimizes the repulsive electrostatic interactions between the amide oxygens and the pyr-*N* that are present in the *anti–anti* and *syn–anti* forms.[8] This conformational preference orients the dendritic branches in a manner that induces a helical conformation relating anthranilamide groups linked through the pyridine-2,6-dicarboxamide repeat unit. At higher generations of dendrons with chiral terminal groups, this orientation causes the branches to experience putative packing interactions that lead to a chirally biased helical conformation at the periphery.[5a] However, the helical antipodes experience a dynamic equilibrium that interconverts the M and P conformations quickly relative to the NMR timescale.[9]

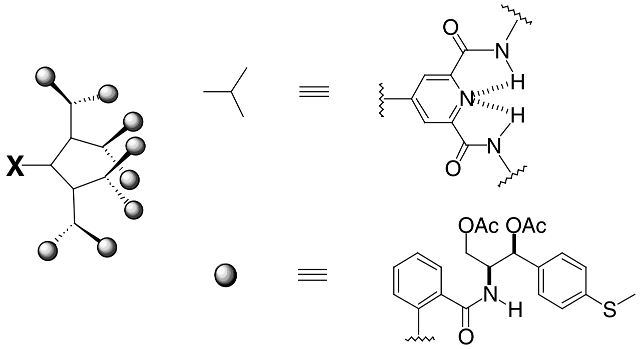

Figure 1. Schematic depiction of the helical bias of intramolecularly hydrogen-bonded dendrons.

We reasoned that the *syn–syn* conformation of the pyridine-2,6-dicarboxamide repeat unit might be destabilized relative

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Keywords: dendrimer conformation; *syn–syn* conformation; copper(II) metal centers.

* Corresponding author. Tel.: +1-614-292-5886; fax: +1-614-292-1685; e-mail: parquett@chemistry.ohio-state.edu

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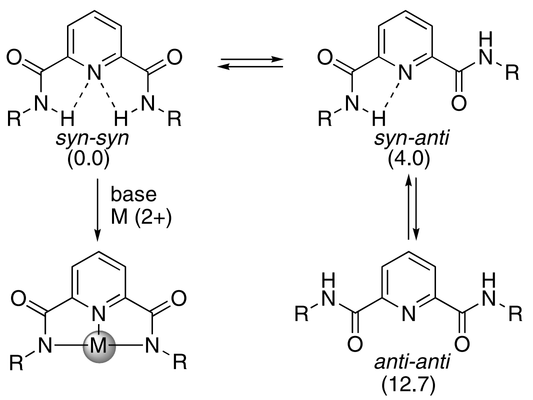


Figure 2. Conformational preference of pyridine-2,6-dicarboxamide ($R=C_6H_5$). Relative energies (kcal/mol) predicted by AM1 are shown in parentheses.[8]

to the *syn–anti* forms in the dendrons especially at the focal and internal positions as a consequence of the steric bulk of the dendritic branches linked through the repeat unit. This perturbation in conformational equilibria would partially denature the dendrons resulting in a more conformationally dynamic and less stable secondary structure. Therefore, it was envisaged that replacing the non-covalent intramolecular hydrogen-bonding interactions of the pyridine-2,6-dicarboxamide unit with covalent bonding to a divalent metal[10] would enforce the *syn–syn* conformation and rigidify the dendron secondary structure.[6]

3. Metal coordination/characterization

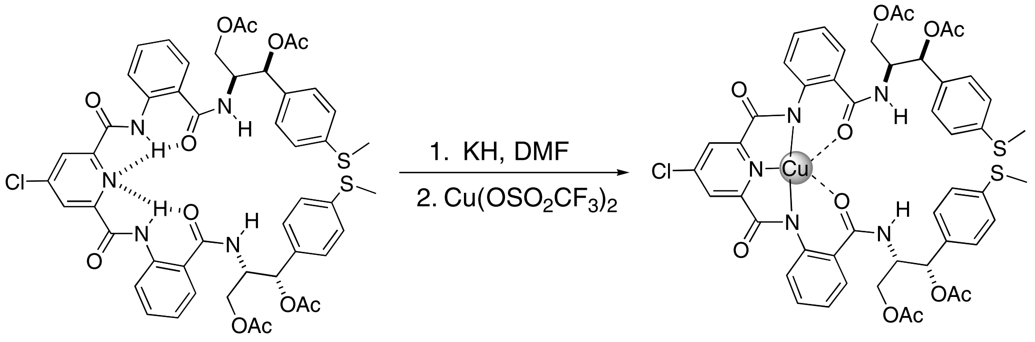
Double deprotonation of the pyridyl diamide followed by coordination to a divalent metal center provides a planar tridentate chelate that maintains a rigidly locked *syn–syn* diamide conformation.[10] Accordingly, treatment of the dendrons with excess KH in DMF followed by 1.2, 3.2 or 7.2 equiv. of $Cu(OSO_2CF_3)_2$ afforded copper-chelated dendrons with one ([G1]–Cu, **1**, 81%), three ([G2]–Cu_3, **2**, 70%) or seven ([G3]–Cu_7, **3**, 50%) coppers, respectively (Scheme 1, Fig. 3). The deprotonation/metallation of dendrons **2** and **3** most likely occurs sequentially rather than to generate a multianionic structure that undergoes metallation all at once. The complexes were dark green materials that, fortuitously, could be purified using silica gel chromatography to homogeneity as verified by HPLC analysis (Fig. 4).

Although the paramagnetic nature of the Cu^{II} complexes precluded characterization by NMR, elemental composition was determined by combustion analysis and electrospray ionization mass spectral analysis. Initial efforts to determine the molecular weight of the dentritic copper complexes by MALDI-TOF spectrometry were severely hampered by the tendency of the complexes to absorb the laser energy which resulted in complicated, ambiguous mass spectral data due to significant decomposition of the sample. Consequently, electrospray ionization from a solution of CH_3OH/THF (1:1) (NaCl) was employed to circumvent these problems (Fig. 5). The spectra were slightly complicated by the sequential loss of acetic acid ($C_2H_4O_2$) and the tendency to form methanol adducts. For example, the first generation dendritic complex (G1–Cu, **1**) exhibited an $[M+Na]^+$ peak at $m/e=1081.20$ (Calcd 1081.16) supportive of the structure of the complex. However, a relatively intense peak at m/e 1021.14 (Calcd 1021.14) associated with the loss of one acetic acid unit $[M+Na-C_2H_4O_2]^+$ was also observed. Similarly, a peak at $m/e=961.11$ associated with the loss of two acetic acid molecules $(M+Na-2(C_2H_4O_2))^+$ (Calcd 961.11) was also observed. Similar peaks associated with the loss of acetic acid were observed in **2** and **3**. In **3**, methanol adducts were also observed.

4. Conformational analysis

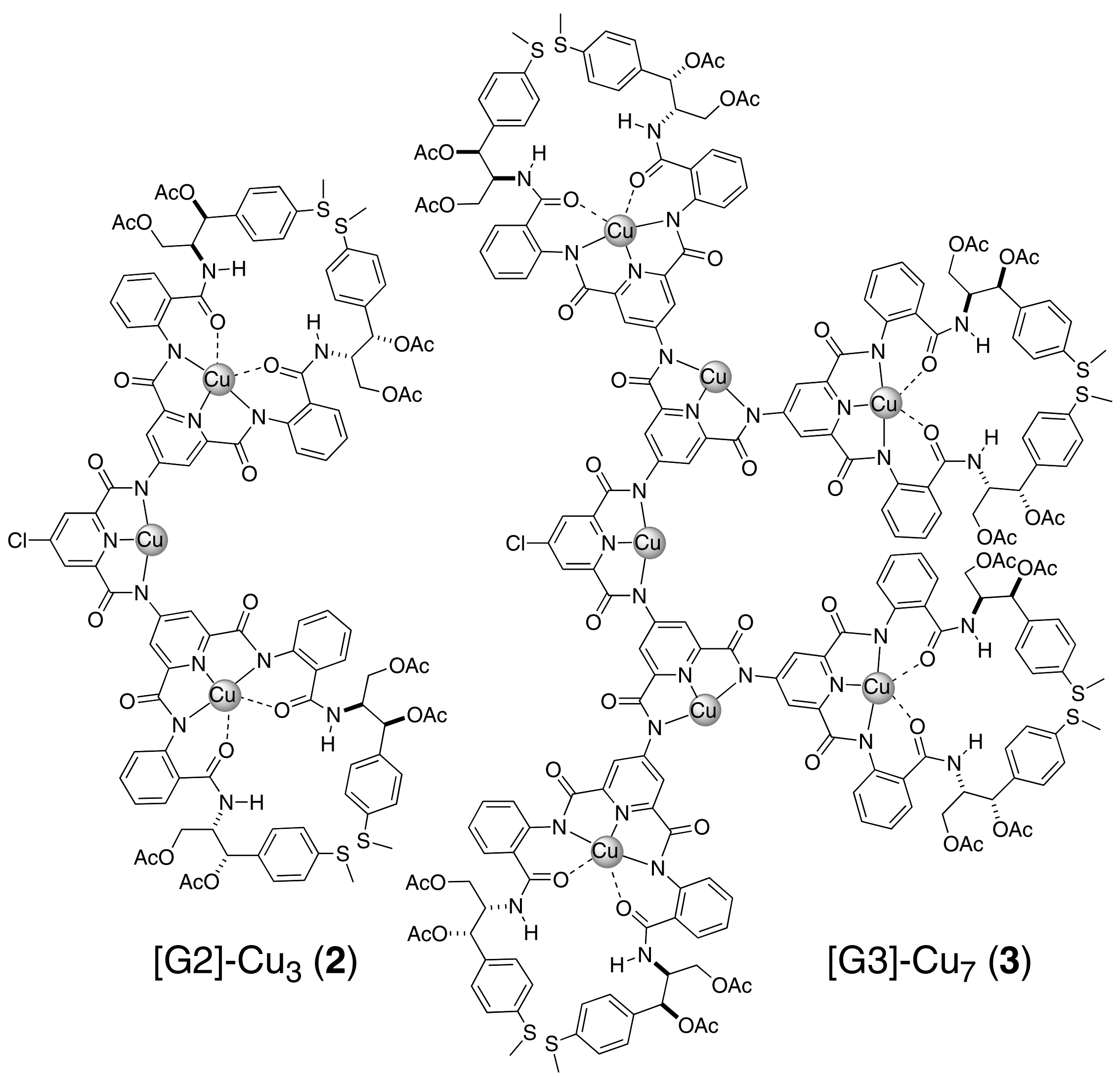
4.1. Time-dependent density functional calculations: determination of electric transition moments

In previous studies of the parent dendrons,[11] the sense of the helical conformational bias relating a pair of anthranilamide termini was determined by inspection of the excitonic couplet centered at 316 nm in the circular dichroism (CD) spectra. This couplet reflects the excitonic mixing of the $\pi\rightarrow\pi^*$ transitions of adjacent anthranilamide chromophores at the periphery. However, the electronic spectra of dendrons **1**–**3** are significantly perturbed by the presence of the coordinated copper atoms. Therefore, to facilitate interpretation of the UV and CD spectra, time-dependent density-functional theory (TDDFT) methods[12] were applied to the copper(II) complex of 2,6-bis-[(2-methylcarbamoylphenyl)-carbamoyl]pyridine (**4**) to determine the direction of the electric transition moments in this model substructure (Fig. 6). Prior to performing the TDDFT electronic structure calculations, the geometry of this complex was optimized



[G1]-Cu (**1**)

Scheme 1. Coordination of Cu^{II} to dendron.



[G2]-Cu$_3$ (**2**)

[G3]-Cu$_7$ (**3**)

Figure 3. Second and third generation dendrons coordinated to three and seven copper(II) centers, respectively.

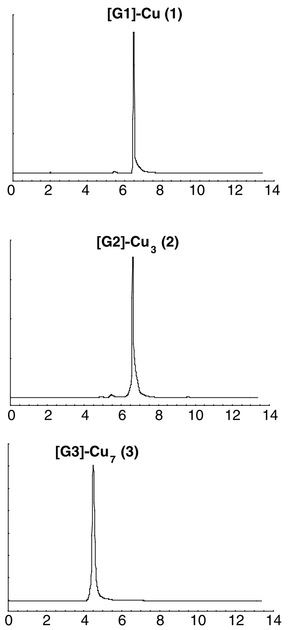


Figure 4. HPLC Analysis of copper-chelated dendrons (3% CH_3OH/CH_2Cl_2, SiO_2 column).

with Gaussian98[13] using the unrestricted B3LYP functional[14] and the 6-311G* basis set for Cu and the 3-21G basis set for all other atoms.[15] The starting geometry for the optimization was created by modifying the X-ray crystal structure, reported by Borovik, of the copper(II) complex of 2,6-bis-[{(2-(acetylphenyl)-carbamoylphenyl}-carbamoyl]-pyridine.[10b] The TDDFT-B3LYP electronic structure calculation was carried out on this optimized geometry using the same basis sets.

The calculated UV spectrum, shown in Figure 6, indicates several transitions with maxima at 356 and 386 nm and is in qualitative agreement with experiment. The dominant transitions for these two intense peaks are listed in Table 1, and the corresponding α-orbital plots are shown in Figure 7. The transitions are significant mixtures of excitations from various occupied orbitals to unoccupied orbitals. Inspection of the excitations that contribute to these absorption maxima indicates that both transitions are dominated by $\pi \rightarrow \pi^*$ excitations that promote an electron from a π molecular orbital of an anthranilamide group to a π^* orbital of the pyridine ring. Therefore, the electric transition dipole moments run approximately along the axis containing the anthranilamide and pyridine chromophores

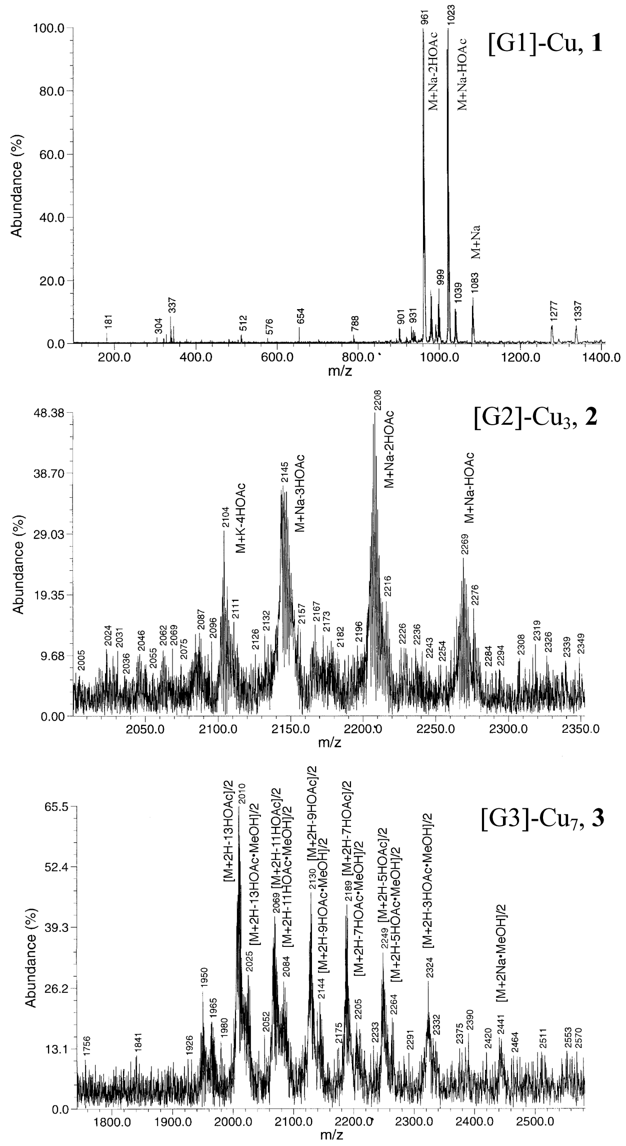


Figure 5. Electrospray mass spectra of metallated dendrons **1**–**3**.

as shown in Figure 8. The experimental UV spectra of the dendrons shown in Figures 9 and 10 displayed a broad absorption in the range of 300–375 nm with an estimated maximum at approximately 340 nm which probably represents both calculated maxima from the TDDFT calculation.

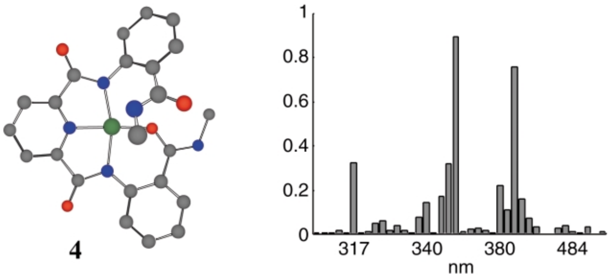


Figure 6. TDDFT-calculated UV spectrum (right) of 2,6-bis-[(2-methylcarbamoylphenyl)carbamoyl]-pyridine (**4**) (left, DFT-optimized geometry).

Table 1. Dominant TD-DFT (B3LYP(3-21G,6-311G*)) MO→MO transitions for the 386 and 356 nm transitions for **4**

λ (nm)	Osc. Str.	MO→MO Transition	Weight
386.7	0.0759	126α→128α	0.42
		127α→129α	−0.33
		124β→127β	0.27
		125β→127β	0.45
		125β→129β	−0.22
		126β→129β	−0.29
356.1	0.0898	125α→129α	0.39
		126α→129α	0.55
		125β→129β	0.50
		126β→130β	0.32

Using the B3LYP(3-21G,6-311G*) optimized geometry. Only transitions with an absolute weighting factor of greater than 0.2 are listed.

4.2. Circular dichroism

The CD spectrum of [G1]–Cu shows a bisignet couplet with a positive Cotton effect (CE) at 339 nm, a negative CE at 378 nm and a zero-crossing at 350 nm corresponding to negative chirality as defined by Nakanishi and Harada (Fig. 9(A)).[16] Therefore, the helicity relating the anthranilamide terminal groups can be assigned as M chirality as shown in Figure 8. It is noteworthy that although the second and third generation dendrons exhibited an M helical bias prior to coordination to copper(II), the helicity of the first generation dendron was unbiased in contrast to the corresponding copper(II) complex. Furthermore, the CD spectra of [G1]–Cu (**1**) are insensitive to solvent quality and to temperature up to 60°C in CH_3CN and 110°C in bis(2-butoxyethyl)ether indicating that a very rigid M-type helical conformation is produced upon coordination to copper(II). This conformational behavior is consistent with our recent observation that a related pyridine-2,6-diamide system exhibited a low barrier to helical interconversion (12.3 kcal/mol)[17] wherein coordination of the pyridyl diamide to a zinc atom rendered the system atropisomeric.[18]

The CD spectrum of the first sample of [G2]–Cu_3 (**2**) (sample 1) that was prepared is shown in Figure 9(B). Surprisingly, subsequent samples prepared in an apparently identical fashion afforded a significantly different CD spectrum labelled as 'sample 2'. Both samples were homogeneous by HPLC analysis and afforded identical

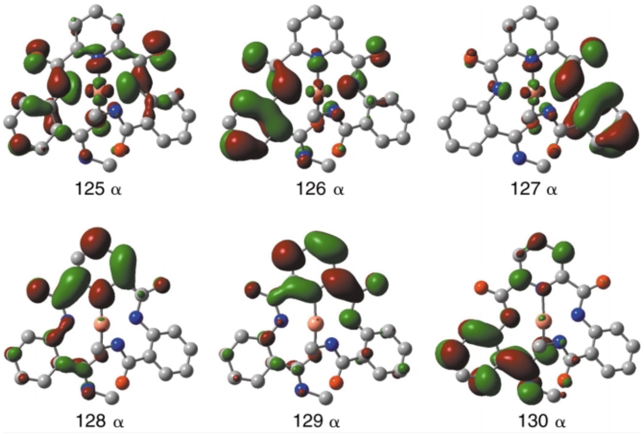


Figure 7. Molecular orbital plots for complex **4** (alpha electrons).

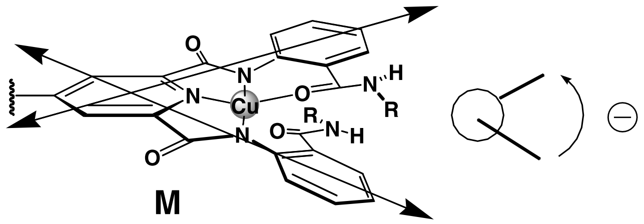


Figure 8. Calculated direction of electric transition moment in **4**.

elemental analyses, electrospray ionization mass spectra. The dendrons displayed similarly broad EPR spectra in the solid state; however, it was not possible to determine the coordination geometry of the complexes. Further, the CD spectra of each sample were relatively solvent and temperature insensitive up to 110°C in *bis*(2-butoxyethyl)ether. We postulated that one or both of the samples were kinetically locked in conformations that did not represent an energy minimum. To test this hypothesis, sample 2 was heated to 170°C for 60 min in *bis*(2-butoxyethyl)ether followed by slow cooling prior to recording the CD spectrum in the same solvent at −20°C. However, this annealing process produced no significant change in the spectrum. In contrast, heating sample 1 at 170°C for 30 min, then slow cooling, produced a CD spectrum at −20°C identical to that observed for sample 2. This observation strongly suggests that sample 2 exists in a thermodynamically stable conformation whereas sample 1 is kinetically locked in a higher energy conformation. Although it is not possible to unambiguously rule out the presence of metal chelates involving the peripheral amide groups, this coordination mode is unlikely given the reports of Borovik on the structure of similar pyridyl-2,6-diamides having terminal amides.[10a] Further, samples 1 and 2 exhibit identical electrospray ionization mass spectra and were homogenous by HPLC. To our knowledge, this represents the first demonstration of an ability to trap kinetically controlled conformational states in a dendrimer system and is very unusual in synthetic linear polymers.[19]

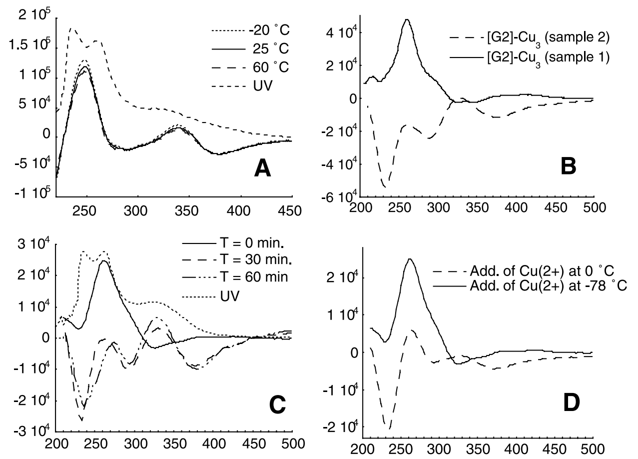


Figure 9. Circular dichroism studies of [G1]–Cu (**1**) and [G2]–Cu$_3$ (**2**). (A) [G1]–Cu (**1**) in CH$_3$CN as a function of temperature, (B) two separate samples of [G2]–Cu$_3$ (**2**) in CH$_3$CN at 25°C, (C) spectra of [G2]–Cu$_3$ (**2**) (sample 1) in *bis*(2-butoxyethyl)ether at −20°C after heating to 170°C in the same solvent, (D) [G2]–Cu$_3$ (**2**) samples prepared by coordinating to copper triflate at 0°C or −78°C measured in CH$_3$CN at 25°C.

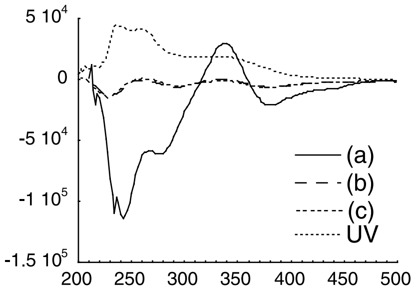


Figure 10. Circular dichroism studies of [G3]–Cu$_7$ (**3**) in *bis*(2-butoxyethyl)ether. [G3]–Cu$_7$ (**3**) samples prepared by coordinating to copper(II) triflate at (a) −42°C or (b) 0°C. (c) Spectrum after heating [G3]–Cu$_7$ (**3**) shown in (a) to 170°C for 60 min prior to recording the CD spectrum.

Reasoning that the conformation becomes locked upon coordination to copper(II), the dendrons were treated with KH at room temperature, then treated with copper(II) triflate at either −78 or 0°C. The complex formed by coordination at −78°C exhibited an identical spectrum to the 'kinetic' complex (sample 1), whereas coordination at 0°C produced a spectrum similar to that observed for sample 2. The CD spectrum displayed a couplet at 350 nm slightly lower in amplitude than observed for the sample equilibrated at 170°C (Fig. 8(C)), thereby indicating that coordination at 0°C produces a complex with a conformation that does not quite represent an energy minimum. Similar to [G1]–Cu (**1**), the thermodynamic conformation exhibits an M-type helical bias relating the peripheral anthranilamides. [G3]–Cu$_7$ (**3**) exhibits very similar conformational behavior to [G2]–Cu$_3$ (**2**). For example, coordinating copper(II) to the deprotonated dendron at either −42°C[20] (a) or 0°C (b) produces quite different CD spectra (Fig. 9). Further, heating the sample produced at −42–170°C for 60 min, then slow cooling, prior to recording the CD spectra affords a spectrum identical to the sample produced by coordination to copper(II) at 0°C. However, the CD spectra of the equilibrated sample had relatively low intensity. Therefore, the conformational preference of this sample could not be determined unambiguously. Nevertheless, these observations in addition to the temperature and solvent insensitivity of the CD spectra up to 60°C are consistent with the presence of rigid structures that do not experience dynamic conformational equilibria at this temperature in contrast to the highly dynamic conformations exhibited by the parent dendrons lacking the copper(II) atoms.

This preliminary work suggests the possibility of imprinting dendrimers[21] by metal coordination for applications in catalysis,[22] molecular recognition and chemical sensing. We are also currently attempting to introduce diamagnetic metals to facilitate further characterization of the conformational behavior of these and related metallodendrimeric systems.

5. Experimental

5.1. General experimental

Potassium hydride (2.2 equiv. (for **1**), 6.2 equiv. (for **2**), or 14.2 equiv. (for **3**)) was washed with hexanes then dispersed in freshly distilled DMF (to make a 0.2 M solution of dendron). Dendron (1 equiv.) was then added to the suspension and stirred for 35 min at room temperature. Copper (II) triflate (1.2 equiv. (for **1**), 3.2 equiv. (for **2**), 7.2 equiv. (for **3**)) was added at the desired temperature and the solution became blue/green in color. After 1–2 h, the DMF was removed under reduced pressure and the crude complex was dissolved in dichloromethane (2 mL), washed with a pH 2 sodium sulfate buffer (0.2 M, 1 mL) then purified by flash chromatography with 25:1 dichloromethane/methanol affording the complexes as blue/green solids. Electrospray ionization mass spectra was obtained by spraying from MeOH/THF (1:1) with added NaCl.

5.1.1. [G1]–Cu (1). Mp 149°C, (dec); MS (electrospray ionization): calcd for $C_{49}H_{46}ClN_5O_{12}S_2CuNa$ (M+Na), 1081.16; obsd 1081.19. Anal. calcd C, 55.52; H, 4.37; N, 6.61. Found: C, 55.15; H, 4.66; N, 7.01. EPR ($CHCl_3$): g=2.10. UV (CH_3CN) λ_{max}=334 nm (ε 16428).

5.1.2. [G2]–Cu$_3$ (2). Mp 125°C, (dec); calcd for $C_{105}H_{94}ClN_{13}O_{26}S_4Cu_3Na-CH_3CO_2H$ (M+Na–HOAc): MS (electrospray ionization): 2267.29; obsd 2267.59. Anal. calcd C, 54.63; H, 4.10; N, 7.89. Found: C, 54.36; H, 4.41; N, 8.13. EPR ($CHCl_3$): g=2.11. UV (CH_3CN) λ_{max}=334 nm (ε 42084).

5.1.3. [G3]–Cu$_7$ (3). Mp 196°C, (dec); calcd for $C_{212}H_{184}ClCu_7N_{29}O_{49}S_8$ [(M+2H)−3HOAc+CH$_3$OH]: 2325.30; obsd 2325.13. Anal. calcd C, 54.26; H, 3.97; N, 8.46. Found: C, 54.40; H, 4.25; N, 7.95. EPR ($CHCl_3$): g=2.10. UV (CH_3CN) λ_{max}=334 nm (ε 50420).

Acknowledgements

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References

1. (a) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 1996. (b) In *Dendrimers. Topics in Current Chemistry*; Vogtle, F., Ed.; Springer: New York, 1998; Vol. 197. (c) In *Dendrimers II: Architecture, Nanostructure and Supramolecular Chemistry. Topics in Current Chemistry*; Vogtle, F., Ed.; Springer: New York, 2000; Vol. 210. (d) In *Dendrimers III: Design, Dimension, Function. Topics in Current Chemistry*; Vogtle, F., Ed.; Springer: New York, 2001; Vol. 212. (e) Grayson, S. M.; Frechet, J. M. *J. Chem. Rev.* **2001**, *101*, 3819. (f) Tomalia, D. A.; Frechet, J. M. J. *J. Polym. Sci., A* **2002**, *40*, 2719–2728.
2. (a) Barron, A. E.; Zuckermann, R. N. *Curr. Opin. Chem. Biol.* **1999**, *3*, 681–687. (b) Gellman, S. H. *Acc. Chem. Res.* **1998**, *31*, 173–180. (c) Karle, I. L. *J. Mol. Struct.* **1999**, *474*, 103–112. (d) Kirshenbaum, K.; Zuckermann, R. N.; Dill, K. A. *Curr. Opin. Struct. Biol.* **1999**, *9*, 530–535.
3. (a) Peerlings, H. W. I.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3*, 1563–1570. (b) Seebach, D.; Rheiner, P. B.; Greiveldinger, G.; Butz, T.; Sellner, H. *Top. Curr. Chem.* **1998**, *197*, 125–164. (c) Thomas, C. W.; Tor, Y. *Chirality* **1998**, *10*, 53–59.
4. (a) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688. (b) Wooley, K. L.; Klug, C. A.; Tasaki, K.; Schaefer, J. *J. Am. Chem. Soc.* **1997**, *119*, 53–58, and references therein.
5. (a) Recker, J.; Tomcik, D. J.; Parquette, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 10298–10307. (b) Huang, B.; Parquette, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 2689–2690. (c) Huang, B.; Parquette, J. R. *Org. Lett.* **2000**, *2*, 239–242.
6. For some examples of metallodendrimers, see: (a) Astruc, D.; Blais, J.-C.; Cloutet, E.; Djakovitch, L.; Rigaut, S.; Ruiz, J.; Sartor, V.; Valerio, C. *Top. Curr. Chem.* **2000**, *210*, 229–259. (b) Swiegers, G. F.; Malefetse, T. *J. Chem. Rev.* **2000**, *100*, 3483–3537. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (d) Stoddart, F. J.; Welton, T. *Polyhedron* **1999**, *18*, 3575–3591. (e) MacDonnell, F. M.; Kim, M.-J.; Bodige, S. *Coord. Chem. Rev.* **1999**, *185–186*, 535–549. (f) Gorman, C. *Adv. Mater.* **1998**, *10*, 295–309. (g) Constable, E. C. *Chem. Commun.* **1997**, 1073–1080. (h) Bodige, S.; Torres, A. S.; Maloney, D. J.; Tate, D.; Kinsel, G.; Walker, A.; MacDonnell, F. M. *J. Am. Chem. Soc.* **1997**, *119*, 10364–10369.
7. For X-ray crystal structures, see: (a) Newkome, G. R.; Fronczek, F. R.; Kohli, D. K. *Acta Crystallogr. B* **1981**, *37*, 2114–2117. (b) Alcock, N. W.; Moore, P.; Reader, J. C.; Roe, S. M. *J. Chem. Soc. Dalton Trans.* **1988**, 2959–2963.
8. For a computational study, see: Malone, J. F.; Murray, C. M.; Dolan, G. M.; Docherty, R.; Lavery, A. *J. Chem. Mater.* **1997**, *9*, 2983–2989.
9. Although this equilibrium is biased toward an M helical conformation, we have been unable to observe the diastereomers by ^{1}H NMR.
10. For X-ray structures of related metal complexes of the pyridine-2,6-dicarboxamide unit, see: (a) Yu, Q.; Baroni, T. E.; Liable-Sands, L.; Rheingold, A. L.; Borovik, A. S. *Tetrahedron Lett.* **1998**, *39*, 6831–6834. (b) Kawamoto, T.; Hammes, B. S.; Ostrander, R.; Rheingold, A. L.; Borovik, A. S. *Inorg. Chem.* **1998**, *37*, 3424–3427. (c) Kawamoto, T.; Hammes, B. S.; Haggerty, B.; Yap, G. P. A.; Rheingold, A. L.; Borovik, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 285–286. (d) Kawamoto, T.; Prakash, O.; Ostrander, R.; Rheingold, A. L.; Borovik, A. S. *Inorg. Chem.* **1995**, *34*, 4294–4295.
11. For a TDDFT study of the electronic transitions of the anthranilamide chromophore see Ref. 5a.
12. (a) Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991. (b) Parr, R. G.; Yang, W. *Density Functional Theory in Atoms and Molecules*; Oxford University: New York, 1989. (c) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454–464. (d) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218–8224. (e) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135–149.
13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.;

Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN98, Revision A.6, Gaussian Inc.: Pittsburgh, PA, 1998.

14. (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
15. Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.
16. Harada, N.; Nakanishi, K. O. *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.
17. Preston, A. J.; Fraenkel, G.; Chow, A.; Gallucci, J. C.; Parquette, J. R. *J. Org. Chem.* **2003**, *68*, 22–26.
18. Preston, A.J.; Parquette, J.R. Unpublished results.
19. (a) Schlitzer, D. S.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 2196–2197. (b) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449–451.
20. Coordination was performed at −42°C rather than −78°C because the deprotonated dendron solidified at −78°C.
21. For an example of a intramolecularly crosslinked dendrimer, see: Schultz, L. G.; Zhao, Y.; Zimmerman, S. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 1962–1966.
22. For a review of dendritic catalysts, see: Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828–1849.