

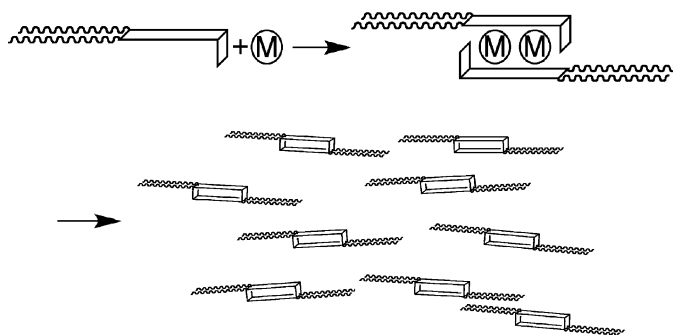
Synthesis and Stereochemistry of Long-Chain Quinoxaline Metallocyclophanes

Mark J. Howard,[†] Fenton R. Heitzler,^{*,‡,§} and Sandra I. G. Dias[‡]

Chemical Laboratory, University of Kent, Canterbury, Kent, UK CT2 7NH, and Department of Biosciences, University of Kent, Canterbury, Kent, UK CT2 7NJ

fentonh@ualberta.ca

Received October 16, 2007



Condensation of 1,2-diamino-4,5-bis(*n*-alkoxy)arenes with an oligopyridyl-type α -diketone afforded a series of long-chain pyridine–quinoxaline hybrids. These were evaluated for their ability to self-assemble with tetrahedral Cu(I) and Ag(I) to form dimeric, double-decker amphiphillic complexes having a flattened metallocyclophane topology. Detailed NOESY and T_1 relaxation time experimentation showed that the configuration of the dicopper(I) complexes corresponds to inversion (*meso*) symmetry, which leads to an extended molecular shape, wherein the alkoxy chains of the individual ligand components lie on opposite sides of the metallocyclophane core, as opposed to the same side. Preliminary measurements show that the disilver(I) complexes having $^{12}\text{C}_{12}\text{H}_{25}$ and $^{12}\text{C}_{18}\text{H}_{37}$ chains exhibit reversible melting processes and undergo two endothermic transitions each, at 189/237 and 59/80 °C, respectively.

Introduction

A face-to-face, π,π -stacked packing arrangement of arenes is a key feature of organic materials for molecular electronics applications.^{1–5} This geometry permits efficient intermolecular overlap of parallel π -orbitals, which in turn facilitates one- and two-dimensional charge carrier transport.^{4–6} Long-range, hierarchical ordering on this basis may lead to electronic delocal-

ization along the stacking direction.⁷ This affords optical and electronic device functionality for photocopiers, laser printers, solar cells, organic light-emitting diodes, and field effect transistors.^{8,9} The strategies employed by synthetic chemists to achieve this ordering include expansion of π -conjugated surfaces in extended arenes,^{1,5,10} chalcogen–chalcogen interactions between main group heteroatoms,^{3,11} hydrogen-bonded net-

[†] Department of Biosciences.

[‡] Chemical Laboratory.

[§] Current address: Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta T6G 2G2, Canada; Fax: +1-780 492-8231.

(1) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048.

(2) Facchetti, A.; Yoon, M. H.; Marks, T. J. *Adv. Mat.* **2005**, *17*, 1705–1725.

(3) Kobayashi, K.; Masu, H.; Shuto, A.; Yamaguchi, K. *Chem. Mat.* **2005**, *17*, 6666–6673.

(4) Moon, H.; Zeis, R.; Borkent, E. J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322–15323.

(5) Wu, J. S.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747.

(6) Curtis, M. D.; Cao, J.; Kampf, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 4318–4328.

(7) Kastler, M.; Pisula, W.; Laquai, F.; Kumar, A.; Davies, R. J.; Balushev, S.; Garcia-Gutierrez, M. C.; Wasserfallen, D.; Butt, H. J.; Riekel, C.; Wegner, G.; Müllen, K. *Adv. Mat.* **2006**, *18*, 2255–2259; Don Park, Y.; Lim, J. A.; Lee, H. S.; Cho, K. *Mater. Today* **2007**, *10*, 46–54; Hoebe, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. *J. Chem. Rev.* **2005**, *105*, 1491–1546.

(8) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832–4887; Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83–109.

(9) Pucci, D.; Barberio, G.; Bellusci, A.; Crispini, A.; Donnio, B.; Giorgini, L.; Ghedini, M.; La Deda, M.; Szerb, E. D. *Chem. Eur. J.* **2006**, *12*, 6738–6747.

works,¹² self-assembly of metallocyclophanes¹³ or other positively charged coordination complexes,¹⁴ as well as long-range association of amphiphilic molecules in solvophobic environments.¹⁵

The design of columnar liquid crystal arrays along the preceding lines necessitates a combination of intercore attraction and hydrophobic contacts between aliphatic chains¹⁶ to achieve a molecular face-on orientation. The alkyl residues guarantee a minimal spacing between the columns, such that interactions between neighboring molecules within the same column are much stronger than between neighboring columns.¹⁷ Metallochromes potentially unite the luminescent, charge-transport and electrochemical properties of metal-containing compounds with the order and mobility of the liquid crystalline state.¹⁸ Our previous work showed that quinoxaline–pyridine hybrids like **1**, **2**¹, and related compounds^{19–21} self-assemble in the presence of appropriate metal ions into π -stacked, double-decker complexes [**1**₂Cu₂][PF₆]₂ and [**2**¹₂Cu₂][PF₆]₂ in which inter- and intramolecular stacking separations are identical.²² This is significant, since the charge-transport or luminescent properties of copper(I) and silver(I) complexes are appropriate for photonic-based applications.²³ Also, we anticipate that the extension of this self-assembly motif will lead to long alkyl chain substituted mesogenic dicopper(I) complexes—in spite of the tetrahedral ligand field of those metal centers.⁹

These goals must take into account metallocyclophane diastereomerism; in principle, our metallocyclophanes may exist as either a *C*₂-symmetric or Δ , Λ / Λ , Δ -*meso*-configurational isomers.¹⁹ (Figure 1). Depending on the size of the alkoxy groups tethered to the heteroarene core, drastic differences in the molecular dimensions and dipoles of the metallocyclophane dication may exist. Distinguishing the diastereomers, or even identifying a dynamically equilibrating mixture thereof, usually depends on X-ray single-crystal determination, when crystalline

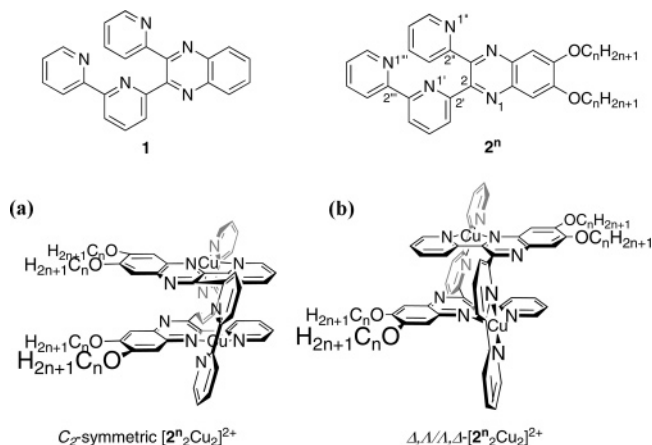


FIGURE 1. Previous (**1**) and current (**2**ⁿ) metallocyclophane ligands, as well as the [**2**ⁿ₂Cu₂]²⁺dications according to (a) *C*₂- and (b) inversion (*meso*) symmetry.

material is available and shows the *C*₂-symmetric form to be preferred in the solid state.^{20,22} In solution, ¹H and ¹³C NMR spectroscopy indicate the aromatic shifts of both forms to be coincident at all temperatures.¹⁹ In this report, we consequently document the synthesis of such long-chain ligands and their metallocyclophane complexes, in addition to assignment of their solution-state stereochemistry, and provide an initial description of their thermotropic behavior.

Results and Discussion

The preparation of the target molecules necessitated 1,2-diamino-4,5-bis(*n*-alkoxy) arenes **3**ⁿ (*n* = 6, 12, and 18), and Scheme 1 reports their syntheses. Thus, alkylation of catechol with the corresponding alkyl bromides either in (a) acetone with a catalytic amount of KI or (b) 2-butanone and dibenzo-18-crown-6 ether as catalyst afforded the diethers in respectable yields (Table 1). The nitration of **3**ⁿ, using nitric acid/acetic acid in dichloromethane, efficiently provided the matching dinitro-ethers **4**ⁿ (*n* = 6, 12, and 18; see Table 2). The reduction of **4**ⁿ to the diamino diethers **5**ⁿ (*n* = 6, 12, and 18), availed itself of hydrazine hydrate and 5% palladium on charcoal. In agreement with findings from the literature,^{24,25} the diamines

TABLE 1. Yields of Catechol Diethers **3**ⁿ According to Synthetic Method^a

	<i>n</i> = 6 (%)	<i>n</i> = 12 (%)	<i>n</i> = 18 (%)
method a	64	22	5
method b	—	57	79

^a See Scheme 1 for details of synthetic method.

TABLE 2. Yields of Dinitrodiethers **4**ⁿ and Oligopyridine–quinoxaline Diethers **2**ⁿ^a

	<i>n</i> = 6 (%)	<i>n</i> = 12 (%)	<i>n</i> = 18 (%)
4 ⁿ	75	73	80
2 ⁿ	71	74	37

^a See Scheme 1 for reaction details.

(24) Ong, C. W.; Liao, S. C.; Chang, T. H.; Hsu, H. F. *J. Org. Chem.* **2004**, *69*, 3181–3185.

(25) Antonisse, M. M. G.; Snellink-Ruel, B. H. M.; Yigit, I.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Org. Chem.* **1997**, *62*, 9034–9038.

(10) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028–8029; Zhu, S. S.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12568–12577.

(11) Briseno, A. L.; Miao, Q.; Ling, M. M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576–15577; Mas-Torrent, M.; Rovira, C. *J. Mater. Chem.* **2006**, *16*, 433–436.

(12) Sokolov, A. N.; Friscic, T.; MacGillivray, L. R. *J. Am. Chem. Soc.* **2006**, *128*, 2806–2807; Gearba, R. I.; Lehmann, M.; Levin, J.; Ivanov, D. A.; Koch, M. H. J.; Barbera, J.; Debije, M. G.; Piris, J.; Geerts, Y. H. *Adv. Mater.* **2003**, *15*, 1614–1618; Schenning, A. P. H. J.; Jonkhøj, P.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 409–416; Lin, C. H.; Tour, J. *J. Org. Chem.* **2002**, *67*, 7761–7768.

(13) Nohra, B.; Graule, S.; Lescop, C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 3520–3521; Huang, P. H.; Lin, J. T.; Yeh, M. C. P. *J. Organomet. Chem.* **2006**, *691*, 975–982; Dinolfo, P. H.; Coropceanu, V.; Bredas, J. L.; Hupp, J. T. *J. Am. Chem. Soc.* **2006**, *128*, 12592–12593; Ghedini, M.; Pucci, D.; Crispini, A.; Aiello, I.; Barigelli, F.; Gessi, A.; Francescangeli, O. *Appl. Organomet. Chem.* **1999**, *13*, 565–581.

(14) Zheng, S. L.; Zhang, J. P.; Wong, W. T.; Chen, X. M. *J. Am. Chem. Soc.* **2003**, *125*, 6882–6883; Gregg, D. J.; Fitchett, C. M.; Draper, S. M. *Chem. Commun.* **2006**, 3090–3092.

(15) Che, Y.; Datar, A.; Balakrishnan, K.; Zang, L. *J. Am. Chem. Soc.* **2007**, *129*, 7234–7235.

(16) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals*; Taylor and Francis: London, 1997.

(17) Kumar, S. *Liq. Cryst.* **2004**, *31*, 1037–1059.

(18) Binnemans, K. *Chem. Rev.* **2005**, *105*, 4148–4204.

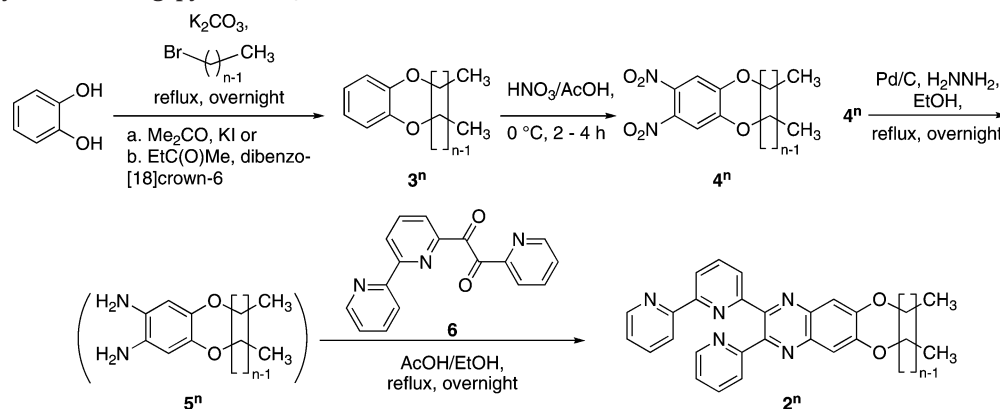
(19) Cragg, P. J.; Heitzler, F. R.; Howard, M. J.; Prokes, I.; Weyhermüller, T. *Chem. Commun.* **2004**, 280–281.

(20) Bark, T.; Weyhermüller, T.; Heitzler, F. *Chem. Commun.* **1998**, 1475–1476.

(21) Heitzler, F.; Weyhermüller, T. *J. Chem. Soc., Dalton Trans.* **1997**, 3653–3654.

(22) Heitzler, F.; Dias, S. I. G.; Neuburger, M. *Eur. J. Inorg. Chem.* **2004**, 685–688.

(23) Xu, Z. T. *Coord. Chem. Rev.* **2006**, *250*, 2745–2757.

SCHEME 1. Synthesis of Oligopyridine–Quinoxaline Diethers **2ⁿ**, **2¹²**, and **2¹⁸**

5⁶ and **5¹²** and, by analogy, **5¹⁸** are air-sensitive materials; thus, they were used immediately upon preparation, and merely preliminary characterization is reported. Subsequently, condensation of **5ⁿ** with α -diketone²⁶ **6** in acetic acid/ethanol produced **2ⁿ** ($n = 6, 12$, and 18) in moderate to good yields (Table 2). The results of ¹H- and ¹³C NMR, IR, UV–vis, and EI-MS spectroscopic characterization of **2ⁿ** are in accord with their anticipated structures. In all cases, **2ⁿ** displayed clean melting points; no secondary endothermic processes were observed.

Treatment of **2ⁿ** with one equivalent of copper(I)tetrakis-(acetonitrile) hexafluorophosphate in degassed methanol and at ambient temperature gave purple- or brown-colored solutions, from which the complexes were deposited in quantitative yields. The results of these materials' combustion analyses bespoke a 1:1 metal/ligand ratio, and their ESI-MS spectra contained peaks corresponding to successive loss of two PF₆[−] ions or one metal center; these findings agreed with their formulation as [2ⁿ₂Cu₂][PF₆]₂. The solubility of these complexes in polar solvents expectedly drops with increasing alkyl chain length of **2ⁿ**;

[2¹⁸₂Cu₂][PF₆]₂ is very poorly soluble in acetonitrile (proton NMR spectra of this compound were only suitable after overnight data collection).

The aromatic regions of these compounds' ¹H NMR spectra are presented in Figure 2. Whereas only [2¹²₂Cu₂][PF₆]₂ has been completely assigned using two-dimensional methods, the aromatic shifts from [2⁶₂Cu₂][PF₆]₂ and [2¹⁸₂Cu₂][PF₆]₂ closely correspond to those of the dodecyl-substituted complex as well as related compounds.^{19,20,22} Their spectra also display the shielding effects that are particular to this family of dicopper-(I) metallocyclophanes:^{19,20,22} the protons adjacent to the alkoxy substitution points (H-5 and H-8) appear ~0.7 ppm upfield, relative to the bare ligands, and the resonance of H-3'' on the stacked pyridine ring is shielded from an edge-on interaction with the 2,6'-bipyridyl group of the same ligand equivalent. The –OCH₂– methylene protons exhibit diastereotopic splitting, as is to be expected from their proximity to stereogenic, tetrahedral Cu(I) centers. Hence, there is no real uncertainty regarding the

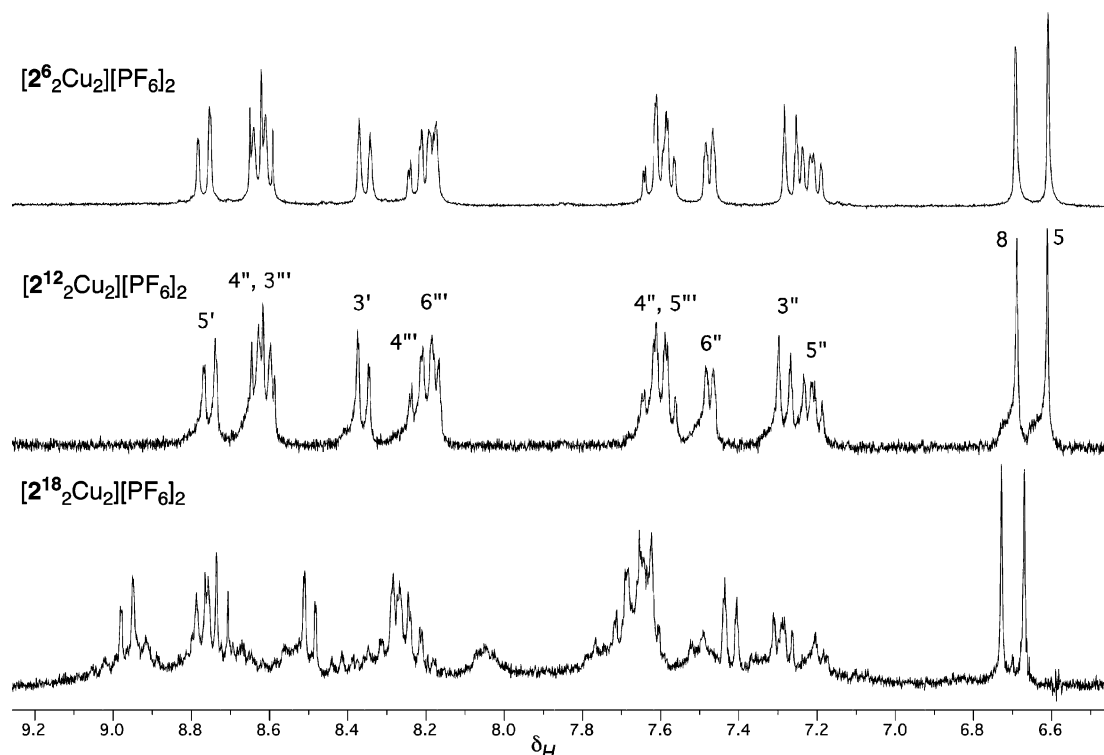


FIGURE 2. Overlap plot of ¹H NMR spectra of [2ⁿ₂Cu₂][PF₆]₂ ($n = 6, 12$, and 18); recorded at 270 MHz in acetonitrile-*d*₃.

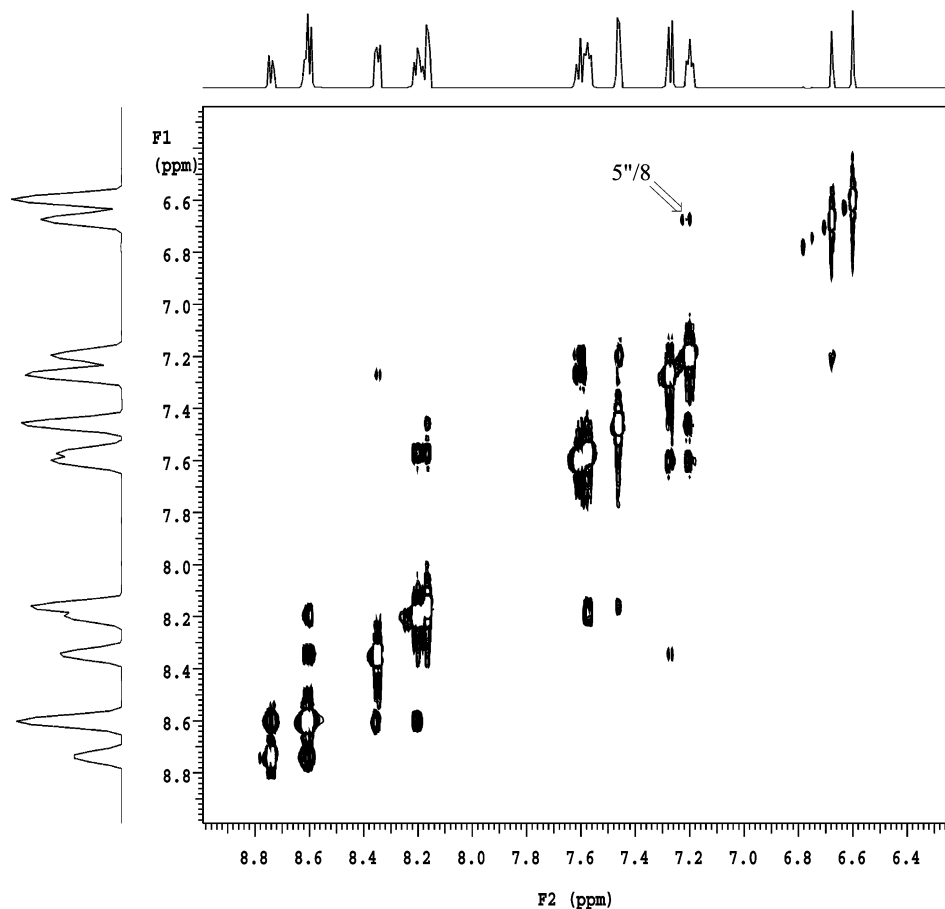


FIGURE 3. NOESY spectrum of $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ (CD_3CN , 600 MHz; mixing time of 2 s).

existence of the metallocyclophane cores in all three compounds. The aromatic shifts of these complexes display no concentration dependence.

Examination of molecular models indicates that the lengths of $\Delta,\Delta/\Delta,\Delta$ - and $\Delta,\Delta/\Delta,\Delta$ -configurations for $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ should be ~ 23 and 44 Å, respectively. To investigate these configurational preferences, two-dimensional NOE correlation experiments were carried out on $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ (Figure 3). Numerous *short-range, through-space interactions* are evident between the flanking 2,2'-bipyridyl groups and the pyridyl quinoxaline “decks” of $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$; these are anticipated to be present in either of the two conceivable dimeric complex stereochemistries. However, these studies also revealed a close contact between H-5'' of the solitary “deck” pyridyl ring and H-8 on the quinoxaline ring, and this is only consistent with *meso*- $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ (cf. Figure 1).

Another important difference between the structures of the $\Delta,\Delta/\Delta,\Delta$ - and $\Delta,\Delta/\Delta,\Delta$ -configurations for $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ relates to the location of methylene protons on the alkoxy chain of the ligand relative to the principal (short) axis. In a hypothetical $\Delta,\Delta/\Delta,\Delta$ -configuration, the methylene protons adjacent to the alkoxy-chain termini are at opposite ends to the complex dication as those next to the metallocyclophane core. In the $\Delta,\Delta/\Delta,\Delta$ -configuration, the latter set of protons are instead adjacent to the center of mass and the principal axis (Figure 1). Thus, the rates of anisotropic tumbling—and thus spin–lattice relaxation times (T_1)—for both sets of protons should be *similar* for a $\Delta,\Delta/\Delta,\Delta$ -configuration and *dissimilar* for a $\Delta,\Delta/\Delta,\Delta$ -configuration.^{19,27} We therefore determined ^1H T_1

relaxation times of $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ using the inversion–recovery method at 600 MHz. The values thereby obtained indicated a significant difference between the opposite ends of the dodecyloxy chains, which is consistent with $\Delta,\Delta/\Delta,\Delta$ - $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$ (Figure 4). This consistency stems from the anisotropic structure of this complex, which allows a visual estimate for the T_1 values of the methylene protons. We would expect an increase in T_1 with distance from the principal axis of rotation passing through the long axis of the molecule, and this is indeed what is observed following resonance assignment.

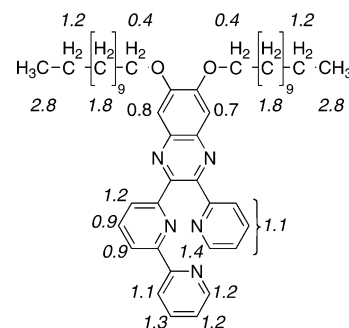


FIGURE 4. Assignment of ^1H T_1 relaxation times (s) for $[2^{12}_2\text{Cu}_2][\text{PF}_6]_2$, determined at 600 MHz in acetonitrile- d_3 .

For preparation of the silver complexes of 2^n , $[2^n\text{Ag}_2][\text{BF}_4]_2$, ($n = 6, 12$, and 18) treatment of the ligands with one equivalent of silver tetrafluoroborate in methanol and at ambient temperature gave yellow-colored solutions, which upon standing

deposited the solid complexes in quantitative yields. The ^1H NMR spectra of these materials displayed only greatly exchange-broadened chemical shifts and were therefore of little use in assigning their structures. However, their IR spectra uniformly showed absorptions at $\nu \approx 1058\text{ cm}^{-1}$ from the B–F stretch of BF_4^- . As well, their ESI-MS spectra were dominated by fragmentation to form the $[\text{2}^n\text{Ag}_2(\text{BF}_4)]^+$, $[\text{2}^n\text{Ag}_2]^+$, and $[\text{2}^n\text{-Ag}]^+$ ions, and their combustion analyses furthermore support dimeric structures.

A preliminary survey of all complexes' thermotropic behavior was undertaken using differential scanning calorimetry. For the dicopper(I) complexes, $[\text{2}^6\text{Cu}_2][\text{PF}_6]_2$ decomposed directly from the solid state before melting (Table 3). On the other hand, both

TABLE 3. Phase Transition Temperatures and Phase Transition Enthalpies of Dicopper(I) and Disilver(I) Metallomesogens

	$T_{\text{melt}}\text{ (}^\circ\text{C)}$	$T_{\text{decomp}}\text{ (}^\circ\text{C)}$	$\Delta H\text{ (kJ mol}^{-1}\text{)}$
$[\text{2}^6\text{Cu}_2][\text{PF}_6]_2$		214	
$[\text{2}^{12}\text{Cu}_2][\text{PF}_6]_2$	135	~ 207	
$[\text{2}^{18}\text{Cu}_2][\text{PF}_6]_2$	113	~ 160	
$[\text{2}^6\text{Ag}_2][\text{BF}_4]_2$		134	
$[\text{2}^{12}\text{Ag}_2][\text{BF}_4]_2$	189	> 250	–22.34
	237		–12.16
$[\text{2}^{18}\text{Ag}_2][\text{BF}_4]_2$	59	> 140	–35.89
	80		–20.98

$[\text{2}^{12}\text{Cu}_2][\text{PF}_6]_2$ and $[\text{2}^{18}\text{Cu}_2][\text{PF}_6]_2$ reversibly melted and solidified below their decomposition temperatures. Among the disilver(I) complexes, $[\text{2}^6\text{Ag}_2][\text{BF}_4]_2$ decomposed upon heating. Intriguingly, $[\text{2}^{12}\text{Ag}_2][\text{BF}_4]_2$ and $[\text{2}^{18}\text{Ag}_2][\text{BF}_4]_2$ each underwent two endothermic transitions before forming isotropic phases, and these processes are likewise reversible. Currently, we are not yet able to conclusively classify these intermediate states according to traditional mesogen descriptors. However, the overwhelming majority of silver(I)-containing mesogens adapt either linear or bent geometries about the metal,^{28,29} with few exceptions.²⁹ Since our substances likely have tetrahedral ligand fields, it is therefore not obvious that their states should be comparable to those earlier substances.

Conclusions

The synthesis of quinoxaline–pyridine hybrids disubstituted with long-chain alkoxy ethers has been demonstrated in three cases. These compounds self-assemble with tetrahedral metals, to form double-decker, hydrophobic metallocyclophanes. The molecular symmetry of the dicopper(I) metallocyclophanes, and by inference, that of their disilver(I) homologues, is characterized by inversion symmetry, which results in the alkoxy chains lying on opposite sides of the metallocyclophane core. Formation of a chiral (racemic) configuration, where the alkoxy chains lie on the same side of the core, is apparently thwarted by steric interactions between the alkoxy chains. We shall be reporting

on the consequences of this phenomenon on the mesogenic behavior of these, and other metallocyclophanes, in due course.

Experimental Section

1,2-Bis-dodecyloxy-benzene (3^{12}). Catechol (5.00 g, 45.4 mmol), anhydrous K_2CO_3 (25.1 g, 182 mmol), 1-bromododecane (24.0 mL, 100 mmol), and dibenzo-18-crown-6 (0.5 g) in 2-butanone (250 mL) were heated overnight under reflux and N_2 . The mixture was filtered hot and the solvent evaporated at reduced pressure. Recrystallization (MeOH) afforded 3^{12} as a white solid in 57% yield (11.6 g, 25.9 mmol). Mp $43\text{ }^\circ\text{C}$ (lit.:³⁰ $45\text{--}46\text{ }^\circ\text{C}$); Calcd for $\text{C}_{30}\text{H}_{54}\text{O}_2$: C, 80.65; H, 12.18. Found: C, 80.56; H, 12.38; EI-MS (70 eV): m/z 446 ($[\text{M}]^+$, 10%); 110 ($[\text{M} - \text{C}_{24}\text{H}_{48}]^+$, 100%); IR (KBr): 2918 (s, ArC–H), 2848 (C–H), 1593 (w, C=C), 1512 (m, C=C), 1256 (s, C–O–C), 730 (m, C–H) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz): δ 6.88 (s, 4H), 3.98 (t, $J = 6.6$, 6.9 Hz, 4H), 1.80 (m, 4H), 1.26 (m, 36H), 0.88 (t, $J = 6.3$, 6.9 Hz, 6H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 149.3 (2C, C), 121.0 (2C, CH), 114.2 (2C, CH), 69.3 (2C, CH_2), 31.9 (2C, CH_2), 29.7 (2C, CH_2), 29.4 (10C, CH_2), 29.3 (2C, CH_2), 26.1 (2C, CH_2), 22.7 (2C, CH_2), 14.1 (2C, CH_3).

1,2-Bis-dodecyloxy-4,5-dinitro-benzene (4^{12}). HNO_3 (3.5 mL, 69%) and fuming HNO_3 (30 mL) were added to a solution of benzene derivative 3^{12} (4.50 g, 10.1 mmol) in AcOH (30 mL) over 2 h at $0\text{ }^\circ\text{C}$. The resulting orange solution was stirred for another 2 h at ambient temperature. The mixture was poured over an ice–water mixture (1.5 L), the precipitate was collected by vacuum filtration and washed with H_2O . Recrystallization (EtOH) afforded 4^{12} as a yellow solid in 73% yield (3.93 g, 7.32 mmol). Mp $80\text{ }^\circ\text{C}$ (lit.:²⁴ $81\text{--}82\text{ }^\circ\text{C}$); Calcd for $\text{C}_{30}\text{H}_{52}\text{N}_2\text{O}_6$: C, 67.13; H, 9.76; N, 5.22; Found: C, 68.58; H, 10.04; N, 5.18; EI-MS (70 eV): m/z 537 ($[\text{M}]^+$, 10%), 201 ($[\text{M} - \text{C}_{24}\text{H}_{48}]^+$, 30%); IR (KBr): 3068 (w, ArC–H), 2918 (s, C–H), 1586 (m, C=C), 1537 (s, N=O), 1372 (s, NO_2), 1230 (s, C–O–C), 871 (C–N), 751 (m, C–H), 664 (w, C–H) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz): δ 7.29 (s, 2H), 4.09 (t, $J = 6.3$, 6.6 Hz, 4H), 1.87 (m, 4H), 1.26 (m, 36H), 0.88 (t, $J = 6.6$, 7.1 Hz, 6H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 151.7 (2C, C), 136.4 (2C, C), 107.8 (2C, CH), 70.2 (2C, CH_2), 31.9 (2C, CH_2), 29.6 (2C, CH_2), 29.5 (2C, CH_2), 29.4 (2C, CH_2), 29.3 (2C, CH_2), 29.2 (4C, CH_2), 28.7 (2C, CH_2), 25.8 (2C, CH_2), 22.7 (2C, CH_2), 14.1 (2C, CH_3).

1,2-Diamino-4,5-bis-dodecyloxy-benzene (5^{12}). Hydrazine monohydrate (1.0 mL, 20 mmol) and palladium on carbon (0.2 g, 5%) were added to a suspension of the dinitroarene 4^{12} (0.30 g, 0.55 mmol) in EtOH (50 mL). The mixture was heated overnight under reflux and N_2 . The hot solution was filtered through Celite and under N_2 to give the crude product 5^{12} as a white solid in quantitative yield (0.26 g). ^1H NMR (CDCl_3 , 270 MHz): δ 6.38 (s, 2H), 3.88 (t, $J = 6.6$ Hz, 4H), 1.74 (m, 4H), 1.27 (m, 36H), 0.88 (t, $J = 6.5$, 6.9 Hz, 6H). This material was unstable in air and was used immediately upon preparation.

2-(2,6'-Bipyrid-6'-yl-6,7-bis-dodecyloxy)-3-(pyrid-2-yl)-quinoxaline (2^{12}). Diamino diether 5^{12} (0.47 g, 1.0 mmol) and AcOH (2 mL) were added to α -diketone **6** (0.03 g, 1 mmol) in EtOH (15 mL). The mixture was heated overnight under reflux and N_2 . The solution was cooled to ambient temperature, neutralized with a satd aq NaHCO_3 soln (10 mL), extracted with CH_2Cl_2 ($3 \times 20\text{ mL}$), and dried (MgSO_4), and the solvent was evaporated at atmospheric pressure. Column chromatography (EtOAc, alumina) and recrystallization (MeOH) afforded 2^{12} as white crystals in 74% yield (0.53 g, 0.74 mmol). Mp $87\text{ }^\circ\text{C}$; Calcd for $\text{C}_{47}\text{H}_{63}\text{N}_5\text{O}_2$: C, 77.33; H, 8.70; N, 9.59; Found: C, 77.21; H, 8.90; N, 9.27; EI-MS (70 eV): m/z 729 ($[\text{M}]^+$, 30%), 560 ($[\text{M} - \text{C}_{12}\text{H}_{25}]^+$, 50%), 392 ($[\text{M} - \text{C}_{24}\text{H}_{50}]^+$, 100%); IR (KBr): 2918 (ArC–H), 2848 (C–H), 1563 (m, C=N), 1496 (s, C=C), 1223 (s, C–O–C), 780 (m, C–H), 745 (m, C–H) cm^{-1} ; UV (CH_3CN): λ (log ϵ) 239 (4.48), 268

(26) Heitzler, F. R. *Synlett* **1999**, 1203–1206.

(27) Kemp, W. *NMR in Chemistry: A Multinuclear Introduction*; MacMillan: London, 1986.

(28) Tolochko, B. P.; Chernov, S. V.; Nikitenko, S. G.; Whitcomb, D. R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1998**, 405, 428–434; Albeniz, A. C.; Barbera, J.; Espinet, P.; Lequerica, M. C.; Levelut, A. M.; Lopez-Marcos, F. J.; Serrano, J. L. *Eur. J. Inorg. Chem.* **2000**, 133–138; Iida, M.; Inoue, M.; Tanase, T.; Takeuchi, T.; Sugibayashi, M.; Ohta, K. *Eur. J. Inorg. Chem.* **2004**, 3920–3929; Lee, C. K.; Hsu, K. M.; Tsai, C. H.; Lai, C. K.; Lin, I. J. B. *Dalton Trans.* **2004**, 1120–1126; Bruce, D. W. *Acc. Chem. Res.* **2000**, 33, 831–840.

(29) Neve, F.; Ghedini, M.; Levelut, A. M.; Francescangeli, O. *Chem. Mater.* **1994**, 6, 70–76.

(30) Egri, J.; Halmos, J.; Rakoczi, J. *Acta Chim. Acad. Sci. Hung.* **1972**, 73, 469–473.

(4.44), 370 (4.14) nm; ^1H NMR (CDCl_3 , 270 MHz): δ 8.76 (br d, $J^{6''-5''} = 4.9$ Hz; 1H; H6''), 8.59–8.65 (m, 4H, H4'', H3'''), 8.36 (dd, $J^{3'-5''} = 0.8$, $J^{3'-4''} = 7.5$ Hz; 2H, H3'), 8.16–8.24 (m, 4H, H4''', H6'''), 7.56–7.66 (m, 4H, H4'', H5'''), 7.47 (br d, $J^{6''-5''} = 6.6$ Hz, 2H, H6''), 7.29 (d, $J^{3''-4''} = 8.1$ Hz, 2H, H3''), 7.19–7.26 (m, 2H, H5''), 6.69 (s, 2H, H8), 6.61 (s, 2H, H5), 3.96–4.02 (m, 8H, H2''', H2''''), 3.70–3.79 (m, 4H, H1'''', H1'''''), 3.54–3.60 (m, 4H, H1'''', H1'''''), 1.20–1.40 (m, 72 H), 0.82–0.94 (m, 12H); ^{13}C NMR (CDCl_3 , 67.5 MHz): δ 159.0 (1C, C), 156.4 (1C, C), 155.8 (1C, C), 154.4 (1C, C), 153.3 (1C, C), 150.1 (1C, C), 149.1 (1C, C), 148.8 (1C, CH), 148.8 (1C, CH), 138.4 (2C, C), 137.7 (1C, C), 136.3 (1C, CH), 136.1 (2C, CH), 124.1 (1C, CH), 123.8 (1C, CH), 123.5 (1C, CH), 122.3 (1C, CH), 120.8 (1C, CH), 119.9 (1C, CH), 107.4 (1C, CH), 107.2 (1C, CH), 69.2 (2C, CH₂), 31.9 (2C, CH₂), 29.6 (6C, CH₂), 29.3 (4C, CH₂), 28.8 (4C, CH₂), 26.0 (2C, CH₂), 22.6 (2C, CH₂), 14.1 (2C, CH₃).

[$^{12}_2\text{Cu}_2$][PF₆]₂. To a solution of quinoxaline **2**¹² (0.020 g, 0.027 mmol) in degassed MeOH (5 mL) under N₂ was added [Cu(MeCN)₄][PF₆] (0.010 g, 0.027 mmol). The solution was stirred at ambient temperature, and after 5 min a solid precipitated. After 1 h the purple precipitate was collected by vacuum filtration, washed with MeOH and dried under vacuum (P₄O₁₀). The product [**2**¹²₂-Cu₂][PF₆]₂ was obtained in 93% yield. Calcd for C₉₄H₁₂₆-Cu₂F₁₂N₁₀O₄P₂: C, 60.14; H, 6.76; N, 7.46. Found: C, 60.01; H, 6.80; N, 7.36; ESI-MS: m/z 993 ([**2**¹²₂Cu]⁺, 5%), 792 ([**2**¹²₂Cu₂]²⁺, 25%), 730.8 ([**2**¹² - H]⁺, 100%); IR (KBr): 2920 (s, ArC–H), 2851 (m, C–H), 1596 (w, C=N), 1497 (s, C=C), 1222 (s, C–O–C), 841 (s, P–F), 780 (w, C–H), 557 (m, F–P–F) cm⁻¹; UV–vis (CH₃CN): λ (log ϵ) 241 (4.99), 281 (4.80), 381 (4.47), 483 (3.85), 582 (3.74) nm; ^1H NMR (CD₃CN, 270 MHz): δ 8.75 (d, $J^{5'-4'} =$

8.2 Hz, 2H, H5'/H3'), 8.62 (m, 4H, H4', H3'''), 8.37 (d, $J^{3'-4'} =$ 7.4 Hz, 2H, H3'/H5'), 8.23 (m, 4H, H4''', H6'''), 7.60 (m, 4H, H4'', H5'''), 7.48 (br d, $J^{6''-5''} = 5.9$ Hz, 2H, H6''), 7.29 (m, 4H, H5'', H3''), 6.68 (s, 2H, H5/H8), 6.60 (s, 2H, H8/H5), 3.99 (t, 8H, H1''', H1''''') 3.72 (m, 2H, H2'''''), 3.57 (m, 2H, H2'''''), 2.13 (m, 4H, H2'''''), 1.28 (m, 72H, H3'''''/H11''''', H3'''''/H11'''''), 0.87 (m, 12H, H12''''', H12''''').

[$^{12}_2\text{Ag}_2$][BF₄]₂. A solution of quinoxaline **2**¹² (0.020 g, 0.027 mmol) in degassed MeOH (2 mL) under N₂ was treated with solid AgBF₄ (0.005 g, 0.03 mmol). The yellow solution was stirred for 1 h, and the precipitated yellow solid was collected by vacuum filtration, washed with MeOH, and dried under vacuum (P₄O₁₀). Calcd for C₉₄H₁₂₆Ag₂B₂F₈N₁₀O₄: C, 61.05; H, 6.87; N, 7.57; Found: C, 60.35; H, 6.87; N, 7.55; ESI-MS: m/z 1568 ([**2**¹²₂Ag]⁺, 15%), 838 ([**2**¹²₂Ag₂]²⁺, 90%); IR (KBr): 2923 (s, ArC–H), 2852 (s, C–H), 1592 (m, C=N), 1497 (s, C=C), 1224 (s, C–O–C), 1058 (s, B–F), 776 (m, C–H) cm⁻¹; UV–vis (CH₃CN): λ (log ϵ) 234 (6.09), 272 (6.01), 372 (5.74) nm.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support (Grant R/R09138) and Mr. K. Howland (Biosciences, University of Kent) for technical assistance.

Supporting Information Available: Standard conditions, remaining detailed synthetic procedures, spectroscopic characterization, and $^1\text{H}/^{13}\text{C}$ NMR spectra of selected compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO7021839