The continuous FPTase activity assay is based on the enhancement of fluorescence and the accompanying shift to lower wavelength emission maximum of certain fluorophores, like dansyl, upon change from a polar to nonpolar molecular environment.[8] We designed an acceptor peptide substrate with an environmentally sensitive fluorescence probe positioned proximally to the reaction center. Substrate pentapeptide *N*-dansyl-GCVLS (Ds-GCVLS) and expected product *N*-dansyl-G[*S*-farnesyl-C]VLS (Ds-G[f-C]VLS) were synthesized by standard methods,[9,10] and the purified peptide derivatives were characterized analytically.[11] Incubation of Ds-GCVLS with recombinant human FPTase (hFPTase) and FPP results in a time-dependent increase in fluorescence at 505 nm with excitation at 340 nm (Figure 1, curve A). Covalent attachment of the farnesyl moiety to the cysteine thiol of Ds-GCVLS places the nonpolar, hydrophobic group near to the dansyl moiety, altering (intramolecularly) the local chemical environment of the reporter group and causing a dramatic change in its fluorescence properties. Fluorescence emission spectra taken before addition of enzyme (Figure 1, curve B) and after complete conversion to product (Figure 1, curve C) show a decrease of the emission maximum wavelength from 565 to 515 nm together with a 13-fold enhancement of fluorescence intensity at 505 nm (see difference curve D). Spectra of authentic product Ds-G[f-C]VLS and of product resulting from FPTase catalysis using Ds-GCVLS as substrate are superimposable (not shown). Fluorescence enhancement and shift of the emission maximum depend upon the relative distance and chemical nature of the residue side chains between the cysteine group and the N-terminal dansyl group[12] as well as upon the detergent content in the buffer.[13]

Using Ds-GCVLS as substrate, FPTase follows Michaelis-Menten kinetics, with k_{cat}(Ds-GCVLS) = 0.5 s^{-1} and K_M(Ds-GCVLS) = 1.4 μM. The value K_M(FPP) = 30 nM in the presence of Ds-GCVLS is the same as that determined previously using Ras as substrate.[14] The time-dependent change in fluorescence (reaction velocity) is linearly dependent upon enzyme concentration. As a mimic of the normal Ras substrate, Ds-GCVLS can also be used to evaluate FPTase inhibitors. CIFM is a competitive inhibitor of Ds-GCVLS binding with K_i(CIFM) = 9 nM, which agrees with results found using Ras as acceptor substrate.[14]

To our knowledge, this is the first continuous fluorescence assay that monitors the progress of a transferase or ligase type of reaction. Here, the fluorescence enhancement results from the change in local chemical environment that occurs upon covalent attachment of two substrates. Other continuous fluorescence assays have been devised for hydrolases, lyases (proteases, lipases, phosphatases, etc.), or isomerases, where the reporter group changes its fluorescence properties after the parent substrate has been cleaved or isomerized.[15] In addition to simplifying enzyme mechanistic studies, the assay, adapted to a 96-well plate format, will facilitate high-volume drug-screening efforts. Monitoring a product-associated change in the local molecular environment of a fluorescence reporter group should be applicable to other enzymes that catalyze hydrophobic postttranslational modifications, such as geranylgeranyl, palmitoyl, and *N*-myristoyl transferases.

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Supplementary Material Available: Experimental details for the synthesis of Ds-GCVLS and Ds-G[f-C]VLS and plot showing the inhibition of hFPTase by peptide CIFM (3 pages). Ordering information is given on any current masthead page.

(7) Reiss, Y.; Seabra, M. C.; Goldstein, J. L.; Brown, M. S. *Methods: Companion Methods Enzymol.* **1990**, *1*, 241-245.

(8) Lakowicz, J. P. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.

(9) Dansylated peptides were prepared using standard *t*-Boc solid-phase methods using an ABI 430A peptide synthesizer. Cleavage and purification of the dansylated peptides from the PAM resin was achieved by HF hydrolysis and reverse-phase (C_{18}) HPLC, respectively (see supplementary material for details).

(10) Peptide farnesylation was achieved by treating the cysteinyl thiol with farnesyl bromide (1 equiv, 0.02 M) and diisopropylethylamine (3 equiv, 0.06 M) in DMF at 20 °C. Farnesylated peptides were purified by reverse-phase HPLC (see supplementary material for details).

(11) Compounds were characterized by ^{1}H NMR, high-resolution fast atom bombardment mass spectrometry, and elemental analysis (see supplementary material for details).

(12) CVLS is the naturally occurring C-terminal sequence for Harvey-Ras.[16] To optimize the sensitivity of the assay, a number of other N-dansylated peptides were synthesized [note: the factor by which fluorescence intensity was increased upon conversion of substrate to product follows each substrate in parentheses]: Ds-CVIM (7), Ds-CVLS (5), Ds-GCVLS (13), Ds-KCVLS (5), Ds-GKCVLS (10), and Ds-SKCVLS (4).

(13) Fluorescence is extremely sensitive to solvent conditions. For example, reactions in Tris-HCl yielded higher fluorescence enhancements than in HEPES. The fluorescence of product compared to substrate increased with increasing detergent (octyl-β-D-glucopyranoside) content, up to a concentration of 0.6% (w/v) detergent. However, at concentrations above 0.2% (w/v) detergent, the enzyme activity appeared to decrease.

(14) Pompliano, D. L.; Rands, E.; Schaber, M. D.; Mosser, S. D.; Anthony, N. J.; Gibbs, J. B. *Biochemistry* **1992**, *31*, 3800-3807.

(15) For example: (a) Matayoshi, E. D.; Wang, G. T.; Krafft, G. A.; Erickson, J. *Science* **1990**, *247*, 954-958. (b) Garcia-Echeverria, C.; Kofron, J. L.; Kuzmic, P.; Kishore, V.; Rich, D. H. *J. Am. Chem. Soc.* **1992**, *114*, 2758-2759. (c) Shashidhar, M. S.; Volwerk, J. J.; Keana, J. F. W.; Griffith, O. H. *Anal. Biochem.* **1991**, *198*, 10-14.

(16) Capon, D. J.; Chen, E. Y.; Levinson, A. D.; Seeburg, P. H.; Goeddel, D. V. *Nature (London)* **1983**, *302*, 33-37.

Kedarcidin, a New Chromoprotein Antitumor Antibiotic: Structure Elucidation of Kedarcidin Chromophore

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In the course of our fermentation lead discovery program, we have discovered a number of cytotoxic antitumor antibiotics which belong to the enediyne class.[1,2] Kedarcidin is a new chromoprotein antitumor antibiotic discovered during our search for new lead substances.[3] As with the known chromoprotein neocarzinostatin (NCS),[4] the antitumor activity of kedarcidin is due primarily to the chromophore. The structure determination of kedarcidin chromophore is disclosed herein.

Kedarcidin was recovered from broth filtrate by adsorption to a QAE anion exchanger, followed by gel filtration and ion exchange chromatography.[3b] The noncovalently bound chromophore was obtained by ethyl acetate extraction of concentrated aqueous chromoprotein solution, followed by silica gel vacuum liquid chromatography. The compound is a buff-colored amorphous solid

(1) (a) Golik, J.; Clardy, J.; Dubay, G.; Groenewald, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3461-3462. (b) Golik, J.; Dubay, G.; Groenewald, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3462-3464.

(2) (a) Konishi, M.; Ohkuma, H.; Matsumoto, K.; Tsuno, T.; Kamei, H.; Miyaki, T.; Oki, T.; Kawaguchi, H.; VanDuyne, G. D.; Clardy, J. *J. Antibiot.* **1989**, *42*, 1449-1452. (b) Konishi, M.; Ohkuma, H.; Tsuno, T.; Oki, T.; VanDuyne, G. D.; Clardy, J. *J. Am. Chem. Soc.* **1990**, *112*, 3715-3716.

(3) (a) Lam, K. S.; Hesler, G. A.; Gustavson, D. R.; Crosswell, A. R.; Veitch, J. M.; Forenza, S.; Tomita, K. *J. Antibiot.* **1991**, *44*, 472-478. (b) Hofstead, S. J.; Matson, J. A.; Malacko, A. R.; Marquardt, H. *J. Antibiot.* **1992**, *45*, 1250-1254.

(4) (a) Goldberg, I. H. *Acc. Chem. Res.* **1991**, *24*, 191-198. (b) Edo, K.; Mizugaki, M.; Koide, Y.; Seto, H.; Furihata, K.; Otake, N.; Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331-334. (c) Hensons, O. D.; Goldberg, I. H. *J. Antibiot.* **1989**, *42*, 761-768. (d) Hensons, O. D.; Giner, J.-L.; Goldberg, I. H. *J. Am. Chem. Soc.* **1989**, *111*, 3295-3299. (e) Myers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212-7214.

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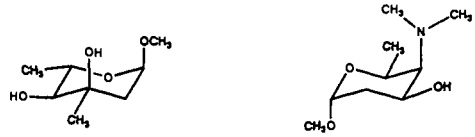
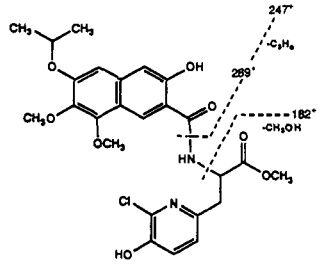
(SiO_2 TLC, R_f 0.29, benzene–methanol, 9:2 v/v). The purification was guided by the *Escherichia coli* SOS chromotest.[5] The high potency in tumor models (HCT-116 cell line IC_{50} 0.4 ng/mL; iv implanted P388 leukemia T/C 214 at 0.25 mg/kg/dose) led us to suspect an enediyne. Its molecular formula was established as $C_{53}H_{60}N_3O_{16}Cl$ by HRFABMS ($[M + H]^+$ m/z 1030.3708, calcd 1030.3740). The UV spectrum [λ_{max} (MeOH) 256, 316 nm (log ϵ 4.78, 4.16)] was indicative of aromatic functionality with extended conjugation. The IR spectrum had bands characteristic of hydroxyl, ester, amide, and significantly, alkyne groups.[6]

The chromophore of kedarcidin is very unstable in solution. The compound was readily degraded when subjected to acidic methanolysis (4.6 M HCl in methanol). Three products were isolated and characterized: methyl α-L-mycaroside (**1**), the methyl α-glycoside of the novel amino sugar kedarosamine (**2**), and the 2′-chloroazatyrosyl naphthoamide fragment (**3**). The structure of **2** was determined by X-ray crystallographic analysis of a *p*-bromobenzoate derivative.[7]



(1)

(2)



(3)

Compound **3** displayed a UV spectrum similar to that of the parent chromophore: λ_{max} (MeOH) 256, 292, 318 nm (log ϵ 4.78, 4.10, 4.05). The molecular formula of $C_{25}H_{27}N_2O_8Cl$ was established by HRFABMS ($[M + H]^+$ m/z 519.1529, calcd 519.1534). Major fragment ions were observed at m/z 289, 247, and 182. HRFABMS established the m/z 289.1078 fragment ion as $C_{16}H_{17}O_5$, the tetrasubstituted 2-naphthoic acid unit as shown (**3**). A key ion at m/z 182.0010, established as $C_8H_5NO_2Cl$, is due to the 2′-chloroazatyrosine fragment with loss of methanol. The ^1H NMR spectrum indicated resonances consistent with a carbomethoxyl group and a phenolic group, neither of which was present in the parent chromophore, suggesting a prior double linkage of this fragment to a $C_{14}H_8O$ central core. Additional proof for the 2′-chloroazatyrosine methyl ester portion resulted from comparison of heteronuclear NMR data with that of synthetic 2-chloro-3-hydroxy-6-methylpyridine.[8] Although the antibiotic azatyrosine (L-β-(5-hydroxy-2-pyridyl)alanine)[9] has been previously obtained from *Streptomyces*, the kedarcidin chromophore is the first known example of a natural product containing this moiety as a structural fragment.

In the mass spectrum of the parent kedarcidin chromophore, the base peak m/z 158 is due to facile cleavage of the amino sugar

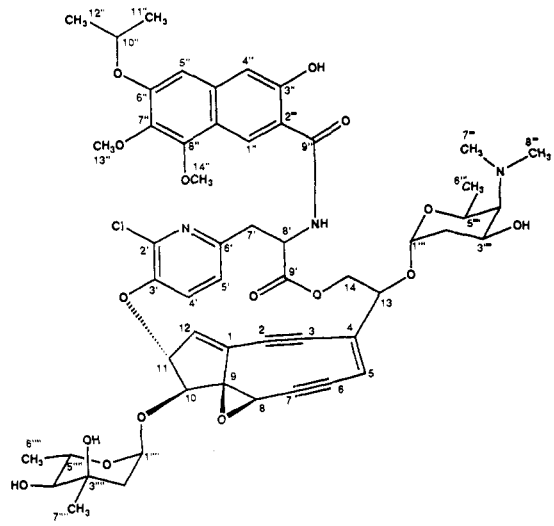


Figure 1.

kedarosamine (HRFABMS m/z 158.1178, $C_8H_{16}NO_2$). In the NMR spectrum (DMSO-d_6), a small ^1H–^1H coupling (J = 3.2 Hz) between the anomeric proton (δ 5.11) and the adjacent axial methylene proton (δ 1.74) indicated α-linkage. A weak ion at m/z 886.2940 ($C_{46}H_{49}N_3O_{13}Cl$) due to cleavage of the mycarose was also observed. The α-linkage was again apparent from the ^1H–^1H coupling constant (J = 4.2 Hz) between the anomeric proton (δ 4.81) and the adjacent axial methylene proton (δ 2.05). Major ions were present at m/z 289 and 247 as in compound **3**. The above data indicates that the kedarosamine and mycarose units are each linked by a single bond to the central core structure, while the naphthoic acid group is linked to a 2′-chloroazatyrosyl unit which bridges the $C_{14}H_8O$ central core.

The structure elucidation of the central core portion was subsequently solved through chemical reduction[10] and low-temperature 2D NMR experiments. Degradation of the chromophore was minimized when using CD_3CN–DMSO-d_6 (1:1)[11] as an NMR solvent at 0 °C, allowing for extended COLOC and NOE experiments. We have proposed the 8,9-epoxybicyclo[7.3.0]dodecadienediyne system as the core portion of the structure (Figure 1). The presence of an epoxide fused to the 8 and 9 positions of the enediyne system was supported by a large coupling constant (J_{C-H} = 194 Hz) between C-8 (δ 49.9) and its attached proton (δ 4.30). This proton (δ 4.30) displayed a significant NOE interaction with the two ortho protons H-4′ and H-5′ (δ 8.05, 7.22) on the pyridine ring, indicating that these two protons reside on the same face of the dodecadienediyne ring system and establishing the relative stereochemistry of the epoxide. Three quaternary carbon signals at δ 88.2, 99.9 (degenerate), and 104.0 were assigned to alkyne carbons C-6, C-2, C-3, and C-7, respectively. The ^1H–^1H coupling constant (J = 3.1 Hz) between the two cyclopentenyl methines H-10 (δ 4.34) and H-11 (δ 5.44) was indicative of trans-substitution, as in the NCS chromophore.[4b,e] The relative stereochemistry of the enediyne core was established from ^1H–^1H coupling constants and NOE data. The absolute stereochemistry has not been fully determined. The similarity of the C_{14} dienediyne carbon skeleton in NCS chromophore suggests a common biogenetic origin.[4d]

The kedarcidin chromophore is an interesting example of a bioreductively activated DNA-damaging antitumor agent. Preliminary DNA cleavage studies reveal an unusually high degree of sequence specificity. Full details[10] on the structure elucidation and mechanism of action will appear in a forthcoming article.

(5) (a) Quillardet, P.; Huisman, O.; D'Ari, R.; Hofnung, M. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 5971–5975. (b) Mamber, S. W.; Okasinski, W. G.; Pinter, C. D.; Tunac, J. B. *Mutation Res.* **1986**, *171*, 83–90.

(6) IR bands at ν_{max} (KBr) 3432, 2976, 2934, 2188, 1742, 1656, 1622 cm^{-1}.

(7) Leet, J. E.; Golik, J.; Hofstead, S. J.; Matson, J. A.; Lee, A.; Clardy, J. *Tetrahedron Lett.*, submitted for publication.

(8) Weis, C. D. *J. Heterocycl. Chem.* **1976**, *13*, 145–147.

(9) Inouye, S.; Shomura, T.; Tsuruoka, T.; Ogawa, Y.; Watanabe, H.; Yoshida, J.; Niida, T. *Chem. Pharm. Bull.* **1975**, *23*, 2669–2677.

(10) Leet, J. E.; Schroeder, D. R.; Hofstead, S. J.; Golik, J.; Colson, K. L.; Huang, S.; Klohr, S. E.; Lee, M. S.; Doyle, T. W.; Matson, J. A. Manuscript in preparation.

(11) DMSO-d_6 shifts reported in text. Using CD_3CN–DMSO-d_6 (1:1) shifted ^1H values by +0.1 ppm and ^{13}C values by +2 ppm from DMSO-d_6 values.

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Supplementary Material Available: Tables of ^{13}C and ^{1}H NMR chemical shifts and ^{1}H NMR NOE data and summaries of MS and IR data for kedarcidin chromophore (Figure 1), tables of ^{13}C and ^{1}H NMR data for methyl α-L-mycaroside (**1**), the methyl α- and β-glycosides of kedarosamine (**2**), and the 2'-chloroazatyrosyl naphthoamide fragment (**3**), computer-generated drawing of the X-ray structure of the 3-*p*-bromobenzoate derivative of the methyl β-glycoside of kedarosamine with atom numbering scheme, and crystallographic parameters (19 pages). Ordering information is given on any current masthead page.

Discotic Bimetallomesogens: Building Blocks for the Formation of New Columnar Arrangements of Transition Metals

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Liquid crystals incorporating transition metal complexes as their core groups (mesogens) promise to dramatically increase the range of properties currently exhibited by mesomorphic materials.[1] The development of bimetallic mesogens is an important step to the realization of the true potential of inorganic liquid crystals since these mesogens can exhibit ferromagnetism[2] and/or mixed oxidation states,[3] properties key to the formation of magnetic and conductive materials, respectively. However, this aspect of inorganic liquid crystals has been somewhat limited, and only a few bimetallic liquid crystals have been described.[1,4] We report herein our results on the development of new discotic dicopper liquid crystalline complexes and the use of molecular shape to create novel columnar superstructures.

We have synthesized and characterized a number of dicopper complexes[5] as shown in Scheme I. These complexes melt to give birefringent fluid phases with columnar superstructures as is often observed for disc-shaped molecules.[6] Although the monomeric structures of **II** and **IIIa,b** do not exhibit the disc-like shape which is typically a precondition for the formation of a columnar mesophase, dimeric structures of **II** and **IIIa,b** can display a disc-like shape similar to that of **I** if nearest neighbors in the columns are correlated, such as is shown in Scheme I. The columnar liquid crystalline phases of **I**, **II**, and **IIIa,b** are stable over a wide temperature range, but the stability of these phases is very sensitive to the number of side chains and to electronic effects. For example, liquid crystallinity is totally suppressed in derivatives of **I** and **II** substituted by 3,4-dialkoxyphenyl groups instead of 3,4,5-trialkoxyphenyls. Similar modification of **IIIa,b** still results in mesomorphism, although optical textures are suggestive of smectic phases rather than columnar phases. Substitution of the terminal methyl group of **II** for a trifluoromethyl group also destroys the liquid crystallinity by increasing the melting point. Presumably the increased affinity of the more electron-poor copper centers for axial ligands increases dative interactions between the neighboring complexes.

DSC analysis of **I** shows a large enthalpy (5–25 kcal/mol) for the crystal-to-liquid crystal transition at lower temperature (50–100 °C) and a low enthalpy (0.5–2.3 kcal/mol) for the liquid crystal-to-isotropic transition at higher temperatures (150–225 °C). The width of the temperature range of mesomorphism is roughly side chain independent at about 120 °C, and the melting and clearing points both decrease as the side chain length increases. The textures of **I** viewed under a polarizing microscope are best described as mosaic with wedge- and leaf-shaped disclinations. This texture combined with analysis of the directional nature of extinction brushes indicates a tilted rectangular columnar structure.[7] X-ray diffraction (Figure 1) confirms that the columns pack in a rectangular array with liquid-like order within the columns (i.e., D_{rd}). For **I** (n = 8) the distortion away from a hexagonal lattice is large,[7b,8] **a** = 57.0 Å and b = 27.1 Å, and for **I** (n = 10) we have found a lower distortion, a = 55.6 Å and b = 30.3 Å.

Many of the **II** and **IIIa,b** derivatives exhibit relatively high clearing points (200–250 °C) which are accompanied by some decomposition. However, a reduction of clearing points with increasing side chain lengths results in stable isotropic phases for **II** ($n \geq 10$) and **IIIb** (n = 14). DSC analysis reveals a very wide temperature range of mesomorphism (100–150 °C), which is constant for different derivatives of **II** and **IIIa**, with **IIIb** showing more complex behavior. The combined enthalpies of the crystal-to-crystal and/or crystal-to-liquid crystal transitions are large (10–20 kcal/mol), and the liquid crystal-to-isotropic transitions are of low enthalpy (0.5–1.2 kcal/mol). When cooled from their isotropic phases, **II** and **IIIa,b** display textures which are a mixture of pseudo focal conics and mosaic regions with linear birefringent defects, suggesting hexagonal columnar structures.[6] As is shown in Figure 1, X-ray diffraction of the mesophases of **II** and **IIIb** confirms a hexagonal columnar arrangement with liquid-like order in the columns (i.e., D_{hd}). The identical d-spacing of the (100) peaks supports the idea that dimerization of **II** and **IIIa,b** produces a similar shape (Scheme I). Hence, **IIIa,b** exhibits a novel antiparallel correlation within the columns (i.e., a D_{hd} antiphase), which results in a structure whereby nonequivalent metal centers stack in an alternating fashion. Indeed a crystal structure determination on **IIIb** (n = 6) shows such an alternating antiparallel columnar arrangement.[9] Although the lattice parameters of the

† Office of Naval Research Young Investigator, 1992–1995.

(1) Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375.

(2) (a) Kahn, O. *Comments Inorg. Chem.* **1984**, *3*, 105–132. (b) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834–850.

(3) (a) Creutz, C. *Prog. Inorg. Chem.* (Lippard, S. J., Ed.) **1983**, *30*, 1. (b) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

(4) Three structural types of bimetallomesogens have been reported. For bimetallic compounds with bridging carboxylates and dithiocarboxylates, see: (a) Cayton, R. H.; Chisholm, M. H.; Darrington, F. D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1481. (b) Giroud-Godqin, A. M.; Marchon, J. C.; Guillon, D.; Skoulios, A. *J. Phys. Chem.* **1986**, *90*, 5502. (c) Barbera, J.; Esteruelas, M. A.; Levelut, A. M.; Oro, L. A.; Serrano, J. L.; Sola, E. *Inorg. Chem.* **1992**, *31*, 732. (d) Ohta, K.; Ema, H.; Yamamoto, I.; Matsuzaki, K. *Liq. Cryst.* **1988**, *3*, 1671. For cyclometalated dimeric palladium complexes, see: (e) Ghedini, M.; Longeri, M.; Bartolino, R. *Mol. Cryst. Liq. Cryst.* **1982**, *84*, 207. (f) Rox, M. B.; Ruiz, N.; Serrano, J. L.; Espinet, P. *Liq. Cryst.* **1991**, *9*, 77. Dimeric copper phthalocyanines were very recently reported: (g) Lelievre, D.; Bosio, L.; Simon, J.; Andre', J. J.; Bensebaa, F. *J. Am. Chem. Soc.* **1992**, *114*, 4475.

(5) Copper triketonate complexes have been previously investigated. (a) Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833. (b) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P.; Kuszaj, J. M. *Inorg. Chem.* **1976**, *15*, 1633. (c) Lintvedt, R. L.; Kramer, L. S. *Inorg. Chem.* **1983**, *22*, 796. (d) Lintvedt, R. L.; Rupp, K. A.; Heeg, M. J. *Inorg. Chem.* **1988**, *27*, 331. (e) Lintvedt, R. L.; Kramer, L. S.; Ranger, G.; Corfield, P. W.; Glick, M. D. *Inorg. Chem.* **1983**, *22*, 3580. (f) Lintvedt, R. L.; Ranger, G.; Schoenfelner, B. A. *Inorg. Chem.* **1984**, *23*, 688. (g) Baker, D.; Dudley, C. W.; Oldham, C. *J. Chem. Soc. A* **1970**, 2608. (h) Guthrie, J. W.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1980**, *19*, 2949. (i) Wishart, J. F.; Ceccarelli, C.; Lintvedt, R. L.; Berg, J. M.; Foley, D. P.; Frey, T.; Hahn, J. E.; Hodgson, K. O.; Weis, R. *Inorg. Chem.* **1983**, *22*, 1667. (j) Lintvedt, R. L.; Tomlonovic, B.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *150*, 407.

(6) (a) Candrasekhar, S. *Advances in Liquid Crystals*; Academic Press: New York, 1982; Vol. 5, pp 47–78. (b) Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen, H. T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121. (c) Billard, J. In *Liquid Crystals of One- and Two-Dimensional Order*; Springer Series in Chemical Physics; Springer: Berlin, 1980; p 383. (d) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57.

(7) (a) Destrade, C.; Mondon-Bernaud, M. D.; Gasparoux, H.; Levelut, A. M.; Tinh, N. H. *Proc. Int. Conf. Liq. Cryst.* **1980**, 29. (b) Tinh, N. H.; Foucher, P.; Destrade, C.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 277. (c) Tinh, N. H.; Cayuela, R.; Destrade, C.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 141. (d) Destrade, C.; Tinh, N. H.; Mamlok, L.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 139.

(8) Billard, J.; Bubois, J. C.; Vaucher, C.; Levelut, A. M. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 115.

0002-7863/92/1514-7948$03.00/0