Stabilization of Nondiscoid Columnar Liquid Crystals: Studies of Unsymmetrical Copper Bis-β-diketonates

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A series of copper(bis-β-diketonate) complexes are reported which display columnar liquid-crystal phases with a hexagonal disordered structure (D_{hd}). The complexes do not have the disc-shape characteristic of most D_{hd} materials, but produce a disc shape by forming dimers with 90° rotations between nearest neighbors. In the liquid-crystalline state this dimerized nature produces short-range rotational correlations. Three side-chain copper bis-β-diketonates with a single phenyl substituent, **2**, are not liquid crystalline, and it was found that an extension of the mesogenic core is necessary to introduce liquid crystallinity. The simple phenyl analogues, **3a**, are monotropic, and the addition of electron-withdrawing substituents to the phenyl moiety, **3b**−**d**, results in a stabilization of the mesophase. These substituents produce favorable dipolar interactions which stabilize the mesophase. Consistent with this explanation, electron-donating substituents are not effective at stabilizing the mesophase. Substitution of the complex with thiophene groups rather than phenyls, **4**, produces stable mesophases with greatly lowered melting and clearing points. This latter result indicates that thiophene substitution provides dispersive forces which destabilize the crystal phase. Thiophene substitution may provide a general method for reducing transition temperatures in metallomesogens.

Introduction

The ability to control intermolecular interactions is central to the design of molecule-based materials with cooperative properties (e.g., magnetism, conductivity). This ability is particularly important in the field of metallomesogens,[1] wherein an effective extrapolation of the unique properties of the transition metals to produce materials with novel bulk properties requires delicate tuning of the intermetallic contacts. We have been developing general systematic approaches for the control of the average intermolecular interactions in metallomesogens.[2,3] One approach, which is the subject of the work reported herein, has been to design discotic (columnar) liquid crystals based upon molecules which have a partial disk shape.[2,4,5] In the systems of interest, the molecules produce disk shapes by assembling into dimerized structures which then can project a disk shape. As shown schematically in Figure 1, depending on their shape, the molecules tend to assemble with 180° correlations (type 1) or with 90° correlations (type 2). It is important to note that the structures are dynamic, and due to the liquid nature of the mesophase these rotational organizations exhibit only short-range order. It is critical for the formation of a stable mesophase that pairs of molecules complement each other to produce a disc shape. For example, homologous complexes with type 1 and type 2 structures can both display the same side-chain density, the same core size, the same temperature range of liquid crystallinity, and the same lattice constant in their mesophase. However, if the molecules do not complement each other, their liquid-crystal phases are not miscible.[2d]

These correlated columnar phases are similar to polar smectics which organize with antiparallel correlations as a result of dipolar forces.[6] These types of smectic phases are known as antiphases, and thus we refer to type 1 phases as discotic antiphases.[2c,d] However, the correlated columnar materials investigated in our laboratory are different from the smectic antiphases in that they do not display a dominant dipole. This aspect has led us to attribute the special organizations to molecular shape factors. Hence, although dipoles can play a role, they are not dominant. We note that other columnar phases based upon nondiscoid molecules have been reported to be stabilized by the organization of dipoles.[7] We previously demonstrated both types 1 and 2 bimetallomesogen systems and found both to display the same

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(1) For reviews on metallomesogens see: (a) Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375. (b) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215. (c) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993**, *93*, 861. (d) Bruce, D. W. In *Inorganic Materials*, Bruce, D. W.; O'Hare, D., Eds.; John Wiley and Sons: New York, 1992; Chapter 8.

(2) (a) Serrette, A. G.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 8879. (b) Lai, C. K.; Serrette, A. G.; Swager, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 7949. (c) Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 101. (d) Serrette, A. G.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 2252.

(3) Zheng, H.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067.

(4) Liquid crystalline metal bis(β-diketonates) have been extensively reviewed.[1] There have been other reports of nondiscoid metal bis(β-diketonates) which display columnar phases. (a) Barberá, J.; Cativiela, C.; Serrano, J. L.; Zurbano, M. M. *Adv. Mater.* **1991**, *3*, 602. (b) Atencio, R.; Barberá, J.; Cativiela, C.; Lahoz, F. J.; Serrano, J. L.; Zurbano, *J. Am. Chem. Soc.* **1994**, *116*, 11558. (c) Ohta, K.; Takenata, O.; Hasebe, H.; Morizumi, Y.; Fujimoto, T.; Yamamoto, I. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 135. (d) Ohta, K.; Morizumi, Y.; Akimoto, H.; Takenata, O.; Fujimoto, T.; Yamamoto, I. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 143.

(5) Serrette, A. G.; Swager, T. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2342−5.

(6) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals; Textures and Structures*; Leonard Hill Publishers: Glasgow, 1984, pp 143−149.

(7) Paulus, W.; Ringsdorf, H.; Diele, S.; Pelzl, G. *Liq. Cryst.* **1991**, *9*, 807.

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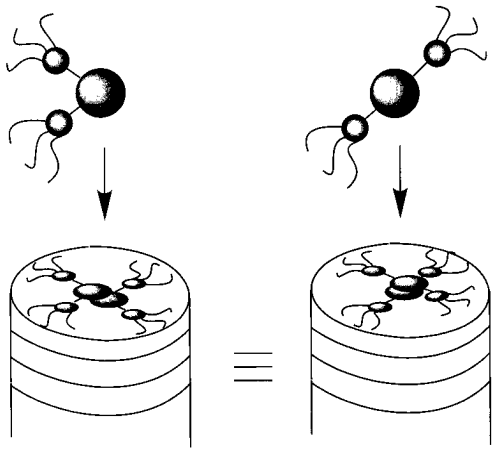
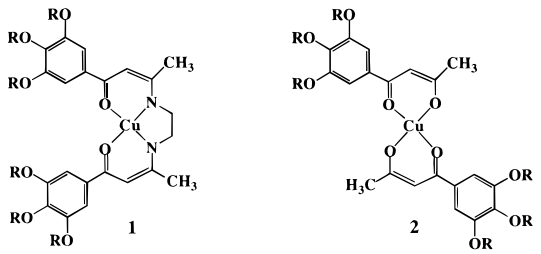


Figure 1. Schematic representation of the assembly of nondiscoid molecules into correlated columnar liquid-crystalline phases which have similar attributes.

liquid-crystal attributes but to lack miscibility.[2b,d] We have also investigated analogous metal bis(β-diketonate) complexes **1** and **2** (type 1 and 2 systems, respectively)



and find that although **1** displays well-behaved liquid crystallinity with good thermodynamic stability,[2c] **2** did not appear to be liquid crystalline.[8] In this paper we describe complexes related to **2** wherein an extension of the mesogenic core and the addition of dipoles have been used to stabilize liquid crystallinity.

Results and Discussion

Given the lack of liquid crystallinity observed for **2** and the fact that the related bimetallo bis-β-triketonates which have larger cores are liquid crystalline,[2b,d] we have pursued copper bis-β-diketonate liquid crystals with expanded mesogenic cores. This was accomplished by substitution of the methyl group of **2** for aromatic groups to provide compounds **3** and **4.** The synthesis of all of the compounds was accomplished by previously reported procedures[3] involving a base-induced condensation between a methyl ketone and ester. The thermodynamic and structural characterization of the liquid-crystalline analogues are summarized in Tables 1−3. In accord with what we have observed in other square-planar correlated columnar phases[2b−d] (both types 1 and 2), we find that the liquid-crystal phases of **3** and **4** exhibit exclusively disordered hexagonal columnar phases (D_{hd}). All structural assignments were made by using both a polarizing microscope and X-ray diffraction (Table 2). Our optical results are typical of D_{hd} materials, and samples displayed areas of uniform extinction,

(8) We have found similar behavior in vanadyl analogues of **2**. Zheng, H.; Carroll, P. J.; Swager, T. M. *Liq. Cryst.* **1993**, *14*, 1421.

Table 1. Phase Behavior of Complexes 3a−3f[a]

3a ($n = 8$)	K 71.3 (14.8) D_{hd} *b* 35.4 (0.05) I
3a ($n = 12$)	K 81.7 (11.8) D_{hd} *b* 45.6 (0.19) I
3a ($n = 14$)	K 87.8 (7.57) D_{hd} *b* 49.7 (2.45) I
3b ($n = 4$)	K 155.4 (6.87) / 135.4 (7.62) I
3b ($n = 6$)	K 77.4 (9.83) D_{hd} 138.0 (0.72) / 134.8 (0.75) I
3b ($n = 8$)	K 67.6 (27.8) D_{hd} 140.1 (1.39) / 135.8 (1.30) I
3b ($n = 10$)	K 62.5 (5.97) D_{hd} 130 (<0.01) / 125 (<0.01) I
3b ($n = 12$)	K 60.3 (12.1) D_{hd} 115.3 (0.18) / 107.9 (0.17) I
3b ($n = 14$)	K 38.5 (10.9) / 28.3 (5.57) D_{hd} 101.4 (0.075) / 88.1 (0.11) I
3c	K 114.0 (26.1) / 85.6 (29.6) D_{hd} 128.6 (0.88) / 124.6 (0.86) I
3d	K 80.5 (13.4) / 33.0 (17.8) D_{hd} 107.6 (0.32) / 103.9 (0.28) I
3e	K 77.6 (23.9) D_{hd} 82.8 (0.37) / 66.0 (0.13) I
3f	K 112.1 (0.38) / 106.7 (0.46) K 127.5 (15.0) / 117.7 (15.7) I

[a] Transition temperatures (°C) were taken as the maxima of the DSC peaks and are given above or below the arrows. Transition enthalpies (kcal/mol) are given in the parentheses. [b] Transition not observed. Crystallization takes place slowly over time.

Table 2. Variable-Temperature XRD Data for Complexes 3a−e and 4 ($n = 12$)

compound	mesophase	lattice constant (Å)	obsd (calcd) spacing (Å)	Miller indices
3a ($n = 12$)	D_{hd} at 52 °C	$a = 29.42$	25.48	(100)
3b ($n = 6$)	D_{hd} at 109 °C	$a = 23.96$	20.75	(100)
3b ($n = 8$)	D_{hd} at 118 °C	$a = 26.62$	23.05 (23.05)	(100)
			13.33 (13.31)	(110)
3b ($n = 10$)	D_{hd} at 92 °C	$a = 29.94$	25.93	(100)
3b ($n = 12$)	D_{hd} at 92 °C	$a = 31.05$	26.89 (26.89)	(100)
			15.54 (15.52)	(110)
			13.46 (13.45)	(200)
3b ($n = 14$)	D_{hd} at 63 °C	$a = 33.53$	29.04 (29.04)	(100)
			16.80 (16.77)	(110)
			14.53 (14.52)	(200)
3c	D_{hd} at 105 °C	$a = 30.76$	26.64 (26.64)	(100)
			15.29 (15.38)	(110)
3d	D_{hd} at 83 °C	$a = 30.48$	26.40 (26.40)	(100)
			15.24 (15.21)	(110)
			13.21 (13.20)	(200)
3e	D_{hd} at 74 °C	$a = 29.94$	25.93	(100)
4 ($n = 8$)	D_{hd} at 65 °C	$a = 25.40$	22.01	(100)
4 ($n = 10$)	D_{hd} at 65 °C	$a = 27.49$	23.81	(100)
4 ($n = 12$)	D_{hd} at 65 °C	$a = 30.20$	26.16 (26.16)	(100)
			15.14 (15.10)	(110)
			13.15 (13.08)	(200)

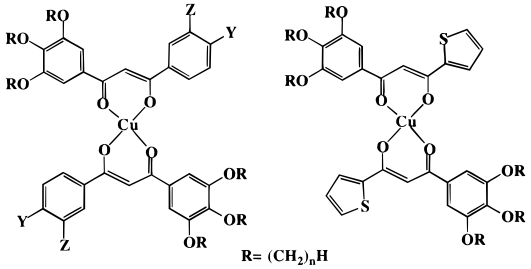
linear birefringent defects, and fan textures.[9] The X-ray results in all cases gave a single intense low-angle peak

(9) For reviews on discotics see: (a) Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen H. T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121. (b) Billard, J. In *Liquid Crystals of One- and Two-Dimensional Order*; Springer Series in Chemical Physics, Berlin, 1980; p 383. (c) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57 and references therein.

Table 3. Phase Behavior of Complexes 4 (n = 4, 6, 8, 10, 12, 14, 16)[a]

4 (n = 4)	K $\underset{99.5\ (1.17)}{\overset{107.5\ (1.34)}{\rightleftharpoons}}$ K $\underset{130.0\ (31.4)}{\overset{174.1\ (34.4)}{\rightleftharpoons}}$ I
4 (n = 6)	K $\xrightarrow{33.4\ (23.2)}$ K $\underset{90.7\ (48.2)}{\overset{112.2\ (52.6)}{\rightleftharpoons}}$ I
4 (n = 8)	K $\xrightarrow{34.1\ (10.4)}$ D_{hd} $\underset{58.4\ (1.30)}{\overset{64.1\ (1.59)}{\rightleftharpoons}}$ I
4 (n = 10)	K $\xrightarrow{34.1\ (10.2)}$ D_{hd} $\underset{62.7\ (-1.47)}{\overset{68.8\ (1.63)}{\rightleftharpoons}}$ I
4 (n = 12)	K $\underset{8.1\ (54.9)}{\overset{37.8\ (70.1)}{\rightleftharpoons}}$ D_{hd} $\underset{71.8\ (1.64)}{\overset{77.0\ (1.89)}{\rightleftharpoons}}$ I
4 (n = 14)	K $\underset{23.9\ (74.5)}{\overset{79.5\ (113.8)}{\rightleftharpoons}}$ I
4 (n = 16)	K $\underset{45.4\ (176.9)}{\overset{85.6\ (177.9)}{\rightleftharpoons}}$ I

indicative of the (100) reflection of a hexagonal lattice, and in most cases we observed additional low-angle peaks indexing to (110) and (200) reflections. At wide angle, we observe halos due to scattering from short-range correlations between molten cores and side chains.



	Y	Z	n
3a	H	H	8,12,14
3b	F	H	4,6,8,10,12,14
3c	CF_3	H	12
3d	H	F	12
3e	OCH_3	H	12
3f	$N(CH_3)_2$	H	12

4 n=4,6,8,10,12,14,16

Our initial attempts at stabilizing the liquid-crystal phase by the addition of a simple phenyl group met with limited success, and three such derivatives **3a** (n = 8, 12, 14) exhibited monotropic behavior. The data in Table 1 show that increased side-chain length in **3a** stabilizes the crystal phase and increases the isotropic transition temperature. Encouraged by this result, we decided to investigate related compounds with substituted phenyls. Ideal substituents produce increased dipolar interactions which balance the dispersive forces and stabilize the mesophase. Since the β-diketonate group is best considered to be electron rich, the addition of electron-withdrawing groups to the phenyl groups should produce the largest dipolar effect. Although the added dipoles can create an attractive force, the rotational dynamics of the added groups also provide dispersive forces, and in a most favorable situation these forces will principally destabilize crystal phases.

Fluorine substitution generally produces minimal steric effects relative to the hydrogen derivatives but results in large dipolar differences. Para-fluorine substitution to produce **3b** results in a dramatic stabilization of the mesophase with all analogues except the C_4-substituted complexes which display enantiotropic behavior. Indicative of enhanced dipolar interactions between the cores, higher clearing temperatures are observed for all of the derivatives of **3b** relative to their homologues in series **3a**. The magnitude of the stabilization is side-chain dependent, and the isotropic point for the **3b** (n = 8) is ≈ 70° higher than **3a** (n = 8). With increasing side-chain length, the clearing temperatures decrease, and for **3b** (n = 14) the isotropic phase is ≈13° higher than **3a** (n = 14). This dependence suggests that the dipolar interactions depend upon intermolecular rotational correlations which decrease with increasing side-chain length. It is also interesting to note that the fluorine groups destabilize the crystal phases of all **3b** complexes relative to the parent phenyl analogues. This result suggests that the added polar character of the fluorine groups cannot be favorably organized in the crystal phase.

To better understand the large effect of para-fluorine substitution observed for **3b**, we investigated an additional complex, **3c** (n = 12). The p-trifluoromethyl group in **3c** is more electron withdrawing than the fluorine group of **3b**, and we observe a similar mesophase stabilization for **3c** relative to **3b** (n = 12) as illustrated by an increased isotropic point. However, the crystal phase of **3c** is also stabilized and transforms to a liquid crystal at 114 °C, a temperature 54°C higher than that observed for **3b**. Hence, the net result is a lower range of liquid crystallinity for **3c** as compared with **3b** (i.e., 14.6° vs 55.0°, respectively). Meta-fluorine substitution in **3d** also produced a stable mesophase. In this case, the lack of conjugation with the β-diketonate should provide a more localized effect which may be responsible for the slightly lower isotropic transition of **3d** as compared to **3b**. Meta substitution may also produce different dispersive effects than observed for **3b**. This is due to the fact that in **3b** the fluorine group is coincident with the phenyl's axis of rotation, whereas in **3d** the meta substitution will restrict rotation by increasing the dipolar interactions between neighboring groups. This latter effect partially accounts for the higher temperature of the (ca. 20 °C) crystal-to-mesophase transition for **3d** as compared to **3b**.

To further confirm the origin of the stabilization in these materials, we investigated other compounds with electron-donating groups on the phenyl group, **3e** and **3f**. Compound **3e** with a p-methoxy group displays limited mesophase stability. The initial crystal phase transforms to the D_h phase at 77.6 °C and the isotropic transition is 82.8 °C. This complex was observed to undergo larger supercooling (16.8 °C at 10 °C/min) than is typical for a well-behaved liquid crystal. Although the origin of the supercooling is unclear, one possibility is that the D_{hd} phase is kinetically accessible but not thermodynamically stable, and the more stable crystal phase is not observed due to unfavorable kinetics. We have also investigated **3f** which has the highly electron-donating p-dimethylamino group. For this case, we find no mesomorphic behavior, and the compound undergoes a crystal-to-isotropic transition at 127.5 °C.

The deleterious effect of electron-donating groups is not universal, and we have found that replacement of the phenyl with an electron-donating thiophene group can result in stable mesophases. Thiophene analogues of classic phenylene-based liquid crystals have attractive properties which include high polarizabilities and greatly

reduced transition temperatures.[10] As a result, we have investigated a series of copper bis-β-diketonate analogues **4** ($n = 4, 6, 8, 10, 12, 14, 16$) wherein the phenyl has been replaced by a thiophene. As shown in Table 3, derivatives with intermediate side-chain lengths display stable D_{hd} phases. The dominate effect of the thiophene substituent has been to reduce the melting and clearing temperatures. Compounds **4** ($n = 8, 10, 12$) have relatively low clearing transitions, and the mesophases are indefinitely stable at room temperature. The ability of thiophene substitution to produce stable liquid crystallinity appears to originate with a destabilization of the crystal phase since the clearing transitions are at lower temperatures than those of the phenyl derivatives.

Summary

We have synthesized copper bis(β-diketonate) complexes with nondiscoid structures which display D_{hd} phases. The shape of the compounds produces 90° correlations between nearest-neighbor molecules. We have found that liquid crystallinity is stabilized by the addition of electron-withdrawing substituents to the phenyl groups, **3b**−**d**. This substitution produces favorable intermolecular dipolar interactions, and electron-donating groups were found to be ineffective at stabilizing liquid crystallinity. Thiophene substitution can produce enantiotropic mesomorphism at lower temperatures. The mode of action of the thiophene is principally dispersive and destabilizes the crystal phases.

Experimental Section

General Methods. The 1,2,3-trialkoxy methyl benzoate ester derivatives were synthesized by using literature procedures.[11] ^{1}H and ^{13}C NMR spectra were measured on a Bruker AC-250. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), and m (multiplet). Infrared spectra were recorded on a Perkin-Elmer 1760-X FTIR using Nujol mull methods and polystyrene as a standard. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 240C elemental analyzer, and analysis results are given in Table 4. DSC investigations were carried out on a Perkin-Elmer DSC-7. Optical microscopy was carried out on a Leica polarizing microscope in combination with a Mettler FP 80HT/FP 82HT hot stage. X-ray diffraction studies were carried out on samples in capillary tubes with an INEL diffractometer with a 2 kW Cu Kα X-ray source fitted with an INEL CPS-120 position-sensitive detector and a home-built oven. The temperature was controlled by a Minco CT 137 temperature controller. The detector was calibrated using mica and silicon standards which were obtained from the National Bureau of Standards (NBS). Benzophenone, 4-fluorobenzophenone, 3-fluorobenzophenone, 4-(trifluoromethyl)benzophenone, 4-methoxybenzophenone, thiophene methyl ketone, and 4-(dimethylamino)benzophenone are commercially available and were used without purification.

Ligand Synthesis. The ligands were synthesized by the condensation of the trialkoxy benzoates with the methyl ketones under the same procedures previously reported for related β-diketones.[3] For the 1-(3′,4′,5′-trialkoxyphenyl)-3-thiophenylpropane-1,3-diones, the procedure was modified slightly such that THF was used as the solvent. The isolated yields ranged from 85% to 95% for all phenyl ligands and for the thiophene-containing ligands the yields were lower (ca. 65%). Spectroscopic data for selected compounds follows.

Table 4. Elemental Analysis of Copper Bis(β-diketone) Complexes

	% carbon		% hydrogen	
complex	calcd	found	calcd	found
3a ($n = 8$)	73.23	73.96	9.30	9.54
3a ($n = 12$)	74.67	74.32	9.89	10.55
3a ($n = 14$)	75.27	75.30	10.13	9.87
3b ($n = 4$)	66.27	66.71	7.00	7.42
3b ($n = 6$)	69.11	69.50	8.08	8.55
3b ($n = 8$)	71.23	71.38	8.89	8.89
3b ($n = 10$)	72.86	73.24	9.51	9.82
3b ($n = 12$)	74.16	74.21	10.01	10.42
3b ($n = 14$)	75.22	74.01	10.41	10.72
3c ($n = 12$)	71.35	71.55	9.37	9.21
3d ($n = 12$)	74.16	74.67	10.01	9.76
3e ($n = 12$)	77.43	77.06	10.74	11.14
3f ($n = 12$)	74.80	74.88	10.42	10.63
4 ($n = 4$)	62.76	63.12	7.11	7.30
4 ($n = 6$)	66.19	66.54	8.19	8.65
4 ($n = 8$)	68.73	69.10	8.98	9.13
4 ($n = 10$)	70.68	70.82	9.59	9.85
4 ($n = 12$)	72.24	73.01	10.07	10.41
4 ($n = 14$)	73.50	74.13	10.47	10.76
4 ($n = 16$)	74.54	74.87	10.79	11.14

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-phenylpropane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.84−0.89 {m, $OCH_2(CH_2)_{10}\mathbf{CH_3}$}, 1.26−1.49 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.70−1.88 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 4.02, 4.04, 4.07 {t, $O\mathbf{CH_2}(CH_2)_{10}CH_3$}, 6.75 (s, ArCOH**CH**COAr), 7.19 (s, **ArH**), 7.43−7.53 (m, **ArH**), 7.94−7.98 (m, **ArH**) 16.99 (s, Ar**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.7, 30.3, 31.9, 69.3, 73.5, 92.7, 106.0, 127.0, 128.6, 130.5, 132.2, 135.4, 142.4, 153.1, 184.0, 186.6. Elemental anal. calcd: C 78.92, H 10.63. Found: C 79.02, H 10.96.

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-(4″-(trifluoromethyl)phenyl)propane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.83−0.88 {m, $OCH_2(CH_2)_{10}\mathbf{CH_3}$}, 1.24−1.53 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.68−1.87 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 4.01, 4.04, 4.06 {t, $O\mathbf{CH_2}(CH_2)_{10}CH_3$}, 6.73 (s, ArCOH**CH**COAr), 7.18 (s, **ArH**), 7.71, 7.74 (d, **ArH**), 8.03, 8.06 (d, **ArH**), 16.81 (s, Ar**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.6, 30.3, 31.9, 69.5, 73.6, 93.5, 106.3, 125.6, 127.3, 130.2, 133.3, 133.8, 138.6, 142.9, 153.2, 168.9, 172.8, 181.7, 187.7. Elemental anal. calcd: C 73.90, H 9.83. Found: C 74.18, H 10.40.

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-(4″-fluorophenyl)-propane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.84−0.89 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 1.25−1.48 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.69−1.87 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 4.01, 4.03, 4.06 {t, $O\mathbf{CH_2}(CH_2)_{10}CH_3$}, 6.67 (s, ArCOH**CH**COAr), 7.17 (s, **ArH**), 7.92−8.00 (m, **ArH**), 17.00 (s, Ar**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.6, 29.7, 30.3, 31.9, 69.4, 73.6, 92.4, 105.9, 106.0, 113.9, 115.5, 115.9, 130.2, 142.5, 153.1, 183.4, 186.0. Elemental anal. calcd: C 77.10, H 10.44. Found: C 77.37, H 10.18.

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-(3″-fluorophenyl)-propane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.83−0.88 {m, $OCH_2(CH_2)_{10}\mathbf{CH_3}$}, 1.24−1.47 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.69−1.87 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 3.97−4.06 {m, $O\mathbf{CH_2}(CH_2)_{10}CH_3$}, 6.69 (s, ArCOH**CH**COAr), 7.17 (s, **ArH**), 7.21−7.27 (m, **ArH**), 7.40, 7.43, 7.45, 7.48 (dd, **ArH**), 7.63, 7.66 (d, **ArH**), 7.72, 7.75 (d, **ArH**), 16.85 (s, Ar**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.6, 30.3, 31.9, 69.4, 73.6, 93.0, 106.2, 113.8, 114.1, 118.9, 119.2, 122.6, 130.2, 137.7, 142.7, 153.1, 160.9, 164.8, 182.4, 186.9. Elemental anal. calcd: C 77.10, H 10.44, Found: C 76.85, H 11.02.

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-(4″-methoxyphenyl)propane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.83−0.88 {m, $OCH_2(CH_2)_{10}\mathbf{CH_3}$}, 1.24−1.47 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.68−1.84 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 3.87 (s, $ArO\mathbf{CH_3}$), 3.99−4.06 {m, $O\mathbf{CH_2}(CH_2)_{10}CH_3$}, 6.66 (s, ArCOH**CH**COAr), 6.95, 6.98 (d, **ArH**), 7.15 (s, **ArH**), 7.93, 7.96 (d, **ArH**), 17.10 (s, Ar**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.7, 30.3, 31.9, 55.4, 69.4, 73.6, 91.9, 105.9, 113.9, 128.0, 129.1,

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130.6, 142.2, 153.09, 163.1, 184.6, 185.0. Elemental anal. calcd: C 77.43, H 10.66. Found: C 76.54, H 11.24.

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-(4″-(dimethylamino)-phenyl)propane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.83−0.88 {m, $OCH_2(CH_2)_{10}\mathbf{CH_3}$}, 1.25−1.47 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.71−1.84 {m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 3.05 {s, $ArN\mathbf{(CH_3)_2}$}, 3.96−4.06 {m, $O\mathbf{CH_2}(CH_2)_{10}CH_3$}, 6.64 (s, ArCOH**CH**COAr), 6.67, 6.70 (d, **ArH**), 7.15 (s, **ArH**), 7.87, 7.91 (d, **ArH**), 17.30 (s, Ar**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.7, 29.7, 30.3, 31.9, 40.0, 69.1, 69.3, 73.55, 91.2, 105.7, 111.0, 122.5, 129.1, 131.0, 141.7, 153.0, 153.2, 183.3, 185.5. Elemental anal. calcd: C 77.75, H 10.94. Found: C 78.54, H 11.08.

1-(3′,4′,5′-Tridodecenoxyphenyl)-3-thiophenyl-propane-1,3-dione: ^{1}H NMR ($CDCl_3$) 0.85 {t, $OCH_2(CH_2)_{10}\mathbf{CH_3}$}, 1.18−1.60 {m, $OCH_2CH_2\mathbf{(CH_2)_9}CH_3$}, 1.83 (m, $OCH_2\mathbf{CH_2}(CH_2)_9CH_3$}, 4.2 (t, $O\mathbf{CH_2}$), 6.55 (s, ArCOH**CH**COTh), 7.10 (s, **ArH**), 7.15 (d, **ThH**), 7.60 (d, **ThH**), 7.80 (d, **ThH**), 17.01 (s, Th**COH**CHCOAr). ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 26.1, 29.4, 29.6, 29.7, 30.3, 31.9, 69.4, 73.6, 92.6, 105.7, 107.7, 128.2, 129.4, 130.0, 132.2, 142.0, 142.3, 153.1, 181.7, 181.8, Elemental anal. calcd: C 75.19, H 10.49. Found: C 75.55 H 10.81.

Copper Complexes. These compounds were synthesized and purified using procedures reported previously for related complexes.[3] The yields of the compounds where near quantitative in most cases. All of the compounds were judged to be pure by elemental analysis and by the sharp DSC peaks observed for the phase transitions. The slight differences between the experimental and calculated values for the longer side-chain analogues is the result of small amounts of trapped solvent.

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