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Discotic Liquid Crystals through Molecular Self-Assembly[†]

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Abstract: We have created self-assembled disk-like aggregates of predictable stoichiometry which form discotic liquid crystalline phases. Attempts to assemble multiple molecules of one compound radially about a second acting as a template failed, presumably owing to the existence of a stable crystalline phase of the template. This difficulty was obviated by the choice of tetrakis(*n*-alkoxy)-6(5*H*)-phenanthridinones (**1a**−**c**), which were expected to form disk-like dimers by analogy with pyridones. All three of these compounds form columnar hexagonal liquid crystalline phases as shown by DSC, POM, and X-ray diffraction experiments. Infrared measurements show that **1a**−**c** exist as hydrogen-bonded aggregates to temperatures well above their clearing points. Intercolumnar spacing and density considerations require the discotic entities to be dimers.

Liquid crystalline phases (mesophases) formed by rodlike (calamitic) molecules have been known for more than 100 years.[1] More recently mesophase formation by disklike molecules (discotics) was predicted[2] and verified.[3] Both nematic and columnar organizations are known.[4] While there are many examples of calamitic mesogens that are formed by self-assembly via hydrogen bonding,[5] there was no precedent for

columnar mesophase formation by well-defined disklike supramolecules.

Self-assembly of non-disklike molecules to form columnar mesophases was first noted for neat soaps,[6] not a discotic system. More closely related to simple discotics are examples like diisobutylsilanediol,[7] Lattermann's monoaryl esters of *cis*, *cis*-1,3,5-cyclohexanetriol,[8] and Praefcke's inositol derivatives.[9] These molecules associate to form columnar mesophases primarily owing to amphiphilic interactions including hydrogen bonding. Percec's examples of large wedge-shaped molecules, which assemble into columns in emulation of tobacco mosaic virus, are the highest development of this type of self-assembly. The "endo recognition", which builds the column cores, is

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essentially amphiphilic; while the "exo recognition", responsible for the column peripheries, is based on shape recognition.[10] In the preceding examples, the factors that determine the number of units that will constitute "one disk" in the aggregated state remain to be elucidated completely, and confident *a priori* prediction of this number is usually not possible. Percec *et al.* cited an example in which a column stratum comprises an average of 5.8 wedge-crown ether units.[10b]

Others have used association mechanisms that lead to predictable stoichiometry. Thus, Matsunaga *et al.* employed hydrogen bonding, which is directed along the column axis to stabilize columnar mesophases,[11] Lehn *et al.* reported cases of complementary base pairing,[12] and Malthête *et al.* have described a case involving carboxyl dimer formation.[13] In the latter two cases clearly defined dimers are generated and then stack to form columns. But the resulting discotic mesophases are formed by simulation of disks by *two* dimers that pack side by side, a behavior not easily predictable on the basis of molecular structure.

Our contribution, described below, provides an example of rational molecular design of self-assembled disklike supramolecules with predictable stoichiometry that, in turn, form columnar mesophases. We have used pyridone dimerization, which is extensively documented in solution and the solid state[14] and was elegantly employed by Wuest *et al.* as the basis for their construction of highly associated solids using a concept they call molecular techtonics.[14,15] To provide sufficiently large central planar cores for our discotics, we choose to study 6(5*H*)-phenanthridinones **1**. This is not expected to affect dimerization, since compound **1** itself exists as the hydrogen-bonded dimer in its crystalline state.[16]

	1	R = H
	1a	R = Ooctyl
	1b	R = Odecyl
	1c	R = Ododecyl
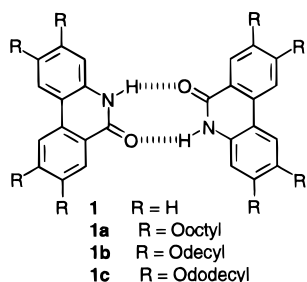
Results and Discussion

Our initial attempts to create self-assembled disks used central templates around which several molecules of a second compound were intended to assemble in radial fashion.[17] When alkoxystilbazoles[18] were mixed with trimesic acid (benzene-1,3,5-tricarboxylic acid, Figure 1) or mellitic acid (benzene-
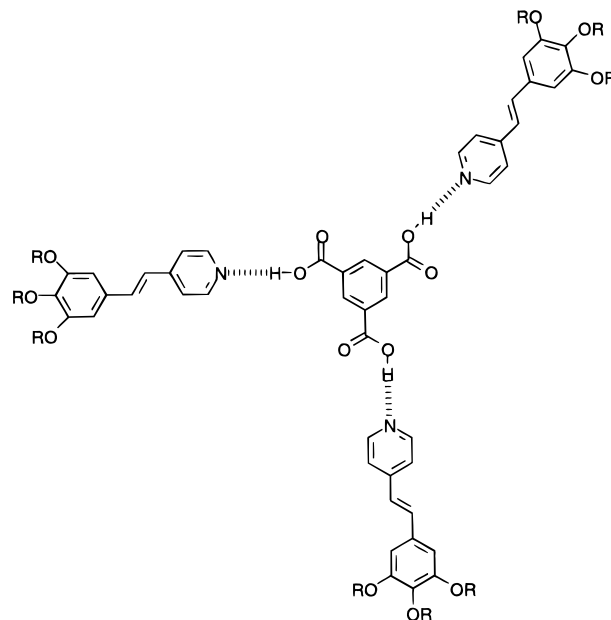

Figure 1. Potential hydrogen-bonded complex of trisalkoxystilbazoles with trimesic acid. R = *n*-octyl, *n*-decyl, and *n*-dodecyl.

hexacarboxylic acid), in 3:1 or 6:1 mole ratio, respectively, in THF or pyridine followed by evaporation, infrared and melting point criteria revealed formation of new compounds. The trimesic acid−stilbazole complexes chromatographed on silica gel TLC plates as single compounds of unique R_f which lacked the characteristic fluorescence of the pure stilbazoles. Optical microscopy, however, revealed that these solid state complexes decomposed at a temperature above the melting point of pure stilbazoles to give heterogeneous mixtures in which crystals floated on an isotropic melt.

In a second case, we attempted to prepare a 3:1 bis(*n*-decyloxy)phthalimide[19]−melamine complex (Figure 2). In this case no evidence of compound formation was observed. The bis(*n*-decyloxy)phthalimide melted at its characteristic melting point of 139 °C to give melamine crystals suspended in phthalimide melt.

Failure of these experiments is probably caused by the existence of very stable crystalline phases of the pure polycarboxylic acids and of melamine, rendering complex formation thermodynamically noncompetitive. Thus, we changed to the pyridone/phenanthridinone strategy obviating at once this problem and the requirement that two different compounds form a single phase. The thermodynamic driving force for dimer formation, $\Delta G° = -2.7$ kcal/mol and $\Delta H° = -5.9$ kcal/mol for pyridone itself in chloroform at 25°C,[20] led us to expect dimerization in the neat melt at temperatures below 200 °C.

Synthesis of 2,3,8,9-Tetrakis(*n*-alkoxy)-6(5*H*)-phenanthridinones. Originally, we synthesized tetraalkoxy-9-fluorenone

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(18) Synthetic details and spectral data for several alkoxystilbazoles are provided in the Supporting Information.

(19) Synthetic details and spectral data for 4,5-bis(*n*-decyloxy)phthalimide are provided in the Supporting Information.

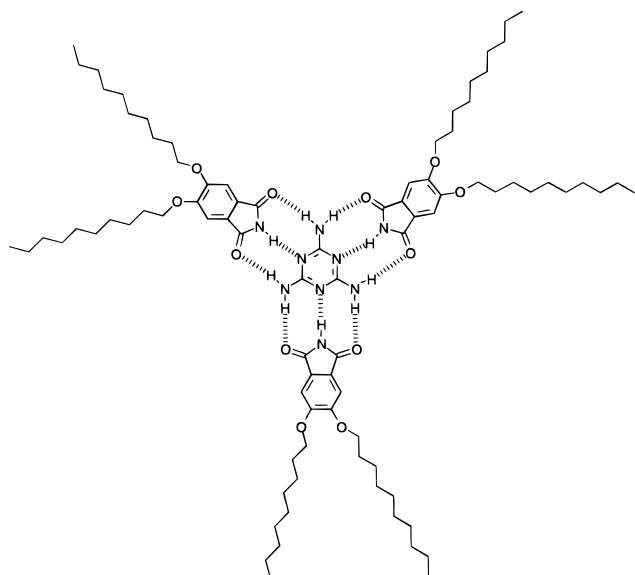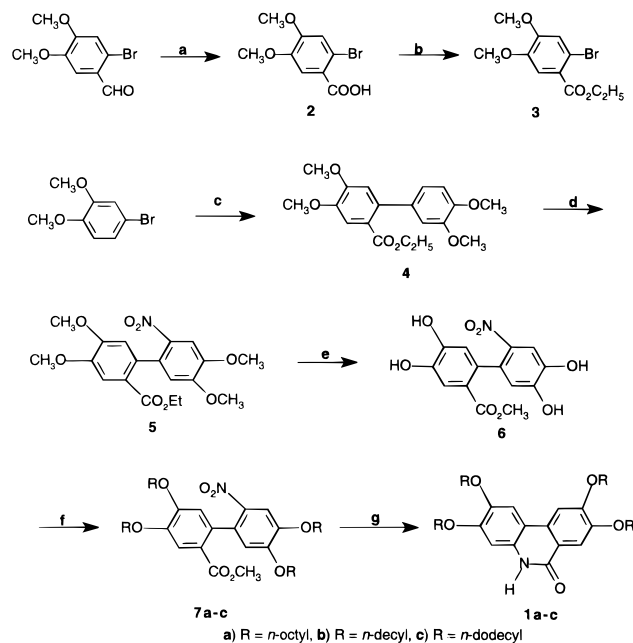(20) Hammes, G. G.; Park, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 956.

Figure 2. Potential hydrogen-bonded complex of bis(*n*-decyloxy)phthalimide with melamine.

Scheme 1. Synthesis of Phenanthridinone Derivatives*a*

a) R = *n*-octyl, **b**) R = *n*-decyl, **c**) R = *n*-dodecyl

a (a) KMnO$_4$, NaOH, 75 °C, 88%. (b) EtOH, H$_2$SO$_4$, reflux, 94%. (c) (i) *n*-butyllithium, ether, -78 to 0 °C; (ii) ZnCl$_2$, THF, 0 °C; (iii) **3**, Pd(PPh$_3$)$_2$Cl$_2$, DIBAL-H, THF, reflux, 54%. (d) HNO$_3$, HOAc, room temperature, 99%. (e) (i) BBr$_3$; (ii) MeOH. (f) RBr, K$_2$CO$_3$, KI, reflux, 4-methyl-2-pentanone. (g) Fe, HOAc, 100 °C; 20−24% for three steps.

derivatives and attempted to convert them into the desired phenanthridinone derivatives via a final Beckmann or Schmidt rearrangement. Although 9-fluorenone itself undergoes Beckmann or Schmidt rearrangement to give 6(5*H*)-phenanthridinone in reasonable yield,[21] our attempts were not successful under various conditions.[17]

Dow has reported synthesis of 2,3,8,9-tetrahydroxy-6(5*H*)-phenanthridinone via tetramethoxybiphenyl ester **4**.[22] Modification of this route as described in Scheme 1 led to the desired tetrakis(*n*-alkoxy)-6(5*H*)-phenanthridinones (**1a−c**).

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Table 1. DSC Results for Tetrakis(*n*-alkoxy)-6(5*H*)-phenanthridinones

	1a		1b		1c	
	K−M*a*	M−I*a*	K−M*a*	M−I*a*	K−M*a*	M−I*a*
heating (°C)	114.2*b*		98.8	118.4	88.3	108.0
ΔH (J/g)	68.0*b*		66.7	2.8	40.5	1.8
cooling (°C)	90.4	111.2	78.8	104.7	69.3	103.1
ΔH, (J/g)	66.0	2.3	69.0	2.7	57.9	2.0

a K: crystalline phase. M: mesophase. I: isotropic phase. *b* K−I transitions. Heating and cooling rates: 10 °C.

Following Dow's route, with the key step a modified Negishi−type coupling,[23] biphenyl ester **4** was obtained and quantitatively converted to nitrobiphenyl ester **5**, which was then demethylated (BBr$_3$) and quenched with methanol to give crude methyl ester **6**. Subsequent alkylation with alkyl bromide, potassium carbonate, and catalytic amounts of potassium iodide in refluxing methyl isobutyl ketone followed by chromatography yielded **7a−c** with minor impurities deduced to be the ethyl and octyl/decyl/dodecyl esters by ^{1}H NMR spectroscopy. Reduction of the crude **7a−c** followed by recrystallization or flash chromatography afforded the desired alkoxyphenanthridinones **1a−c** in 20−25% overall yield from nitroester **5**. The final products were chromatographically pure, and their IR, ^{1}H, and ^{13}C NMR spectra are in accord with the proposed structures. High-resolution mass spectrometry results were in agreement with calculated exact molecular masses.[24]

Thermal Phase Behavior. Thermal phase behavior of tetrakis(*n*-alkoxy)-6(5*H*)-phenanthridinones **1a−c** was studied using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction. Results of the DSC studies, which used heating and cooling rates of 10 °C/min, are presented in Table 1.

Each of the compounds exhibited two, apparently first order, transitions. The lower temperature transitions exhibit large enthalpy changes, 40 to 70 J/g, and super-cooling, 19 to 24 °C, characteristic of melting or crystallization. The higher temperature transitions exhibit small enthalpy changes, 2−3 J/g, consistent with clearing (mesophase-isotropic) transitions. Super-cooling results are irregular: small for **1c**, and unexpectedly large but reproducible for **1b**. The mesophase for **1a** is observed only on cooling; thus this compound forms a monotropic mesophase. Two reproducible crystal−crystal endotherms were observed for **1c** below the melting transition.

Polarizing optical microscopy observations confirmed the existence of viscous fluid birefringent phases at temperatures between the DSC melting and clearing temperatures. Heating from the crystalline phase into the mesophase region gave focal conic textures consistent with columnar organization[25] for compounds **1b** and **1c**. Upon cooling from the isotropic phase, all three compounds exhibit dendritic mesophase growth,[26] which is a common feature of columnar mesophase formation, e.g., for triphenylene derivatives.[27] All the samples exhibited homeotropic regions.

X-ray diffraction from an unoriented sample of **1b** at room temperature produced numerous sharp reflections characteristic

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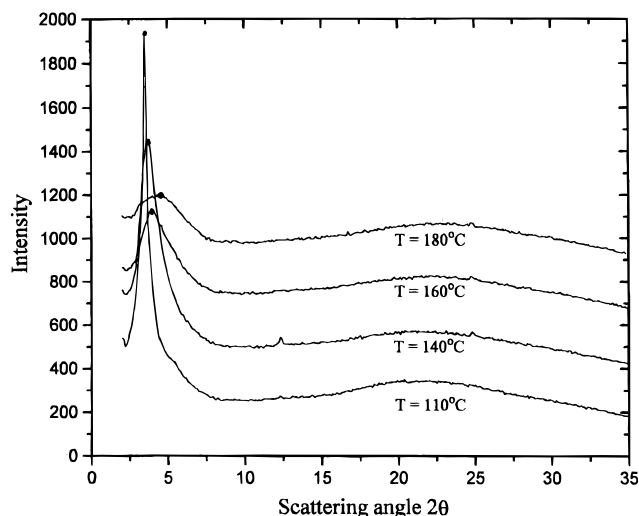
Figure 3. X-ray scattering diagrams of the unoriented mesophase and isotropic phase of 2,3,8,9-tetrakis(*n*-decyloxy)-6(5*H*)-phenanthridinone (**1b**) from 110 to 180 °C.

of a well-ordered crystalline phase; however, elevation of the temperature to the mesophase region left only two prominent reflections. The sharp, intense small angle reflection, which corresponds to intercolumnar spacing, and the broad halo at 4.5 Å, which corresponds to disordered, liquid-like side chains are presented as a function of temperature in Figure 3. The sharp reflection at small angle does not disappear suddenly at the clearing temperature, 120 °C. Rather it broadens in a roughly continuous fashion as the temperature increases, persisting even at 180 °C, more than 60 °C above the thermodynamic and optical clearing temperature. This behavior, which suggests that local stacking of disks persists above T_c, has been reported previously for Lattermann's cyclohexane-1,3,5-triol monoesters.[28]

At longer exposure, an unoriented sample of **1b** mesophase revealed sharp reflections corresponding to Bragg spacings of 26, 15, and 13 Å (Figure 4), consistent with hexagonal ordering of columns. The low intensity of higher order reflections observed here is in accord with expectation for a columnar hexagonal organization as pointed out by Levelut[29] but not with a simple lamellar organization. In addition, a broad shoulder, which we assigned to the 3.6 Å average spacing between disks in a column, appeared on the wide angle side of the 4.5 Å halo. To verify the columnar structure, we oriented a sample of **1b** in the mesophase by allowing it to flow down the wall of a quartz X-ray capillary. The insert in Figure 4 presents the azimuthal intensity distribution of this broad reflection, which demonstrated that it is orthogonal to the column axes, which aligned in the flow direction. Final confirmation of hexagonal ordering of columns was obtained by orienting the flow direction parallel to the X-ray beam. In this case, the diffraction pattern revealed six hexagonally arranged reflections, (Figure 5).

Monomers or Dimers? We next consider whether the discotic entity is a monomeric tetrakis(*n*-alkoxy)-6-(5*H*)-phenanthridinone, a dimeric, or a higher aggregate. The small-angle reflections we have observed correspond to a interco-lumnar spacing of 31 ± 1 Å. This does not fit monomeric tetrakis(*n*-decyloxy)phenanthridinone, a molecule of the size of 21 × 33 Å². It would require the side chains to be fully extended in the mesophase, and without interpenetration in neighboring columns. An additional diffraction experiment with the tetrakisdodecyl derivative **1c** yielded an identical column
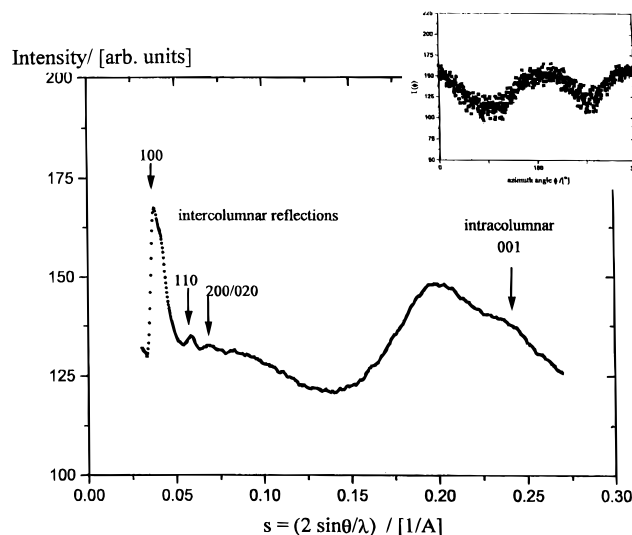
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Figure 4. X-ray scattering diagram for the mesophase of 2,3,8,9-tetrakis(*n*-decyloxy)-6(5*H*)-phenanthridinone (**1b**). The radial intensity distribution $I_{(s)}$ display reflections from inter- and intracolumnar order. The insert shows the azimuthal intensity distribution $I(f, s = 0.25\ \text{Å}^{-1})$ of the intracolumnar reflections, derived from a densitometer-scan, performed on a flat-chamber X-ray diagram. The original X-ray pattern was taken from an oriented sample at 110 °C in the mesophase region.
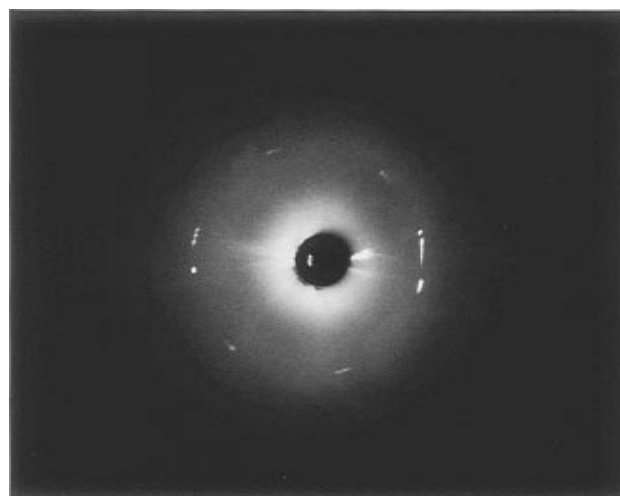

Figure 5. Diffraction pattern from the oriented mesophase of **1b**. The flow direction is approximately parallel to the X-ray beam.

diameter within the limit of experimental uncertainty. Combination of this value with the 3.6-Å intracolumnar disk spacing yields a value of 3.0×10^{-21} cm^{-1} for the volume of the unit cell that comprises one discotic entity. If this is a single phenanthridinone molecule, it leads to the unreasonably low calculated mesophase density of 0.45 g cm^{-3}, while if it is a dimer a reasonable density of 0.90 g cm^{-3} at 110 °C is calculated. The same analysis eliminates higher aggregates. Thus, the discotic entity must be the expected phenanthridinone dimer.

Several related observations are consistent with this conclusion. First, tetrakis(*n*-decyloxy)-9-fluorenone synthesized in our laboratory,[17] which approximates the shape of monomeric **1a**−**c** but lacks hydrogen-bonding sites, exhibits no mesophase. More persuasive, however, are the results of a variable-temperature infrared study of **1c** from 70 to 170 °C, a range which spans crystalline, mesotropic, and isotropic phases. The amide I band at *ca.* 1670 cm^{-1} underwent only minor shifts in frequency over this temperature range. No high-frequency band indicative of non-hydrogen bonded amide carbonyl was detected.[30]   N−H

absorption appeared as a broad featureless band near 3200−3300 cm^{-1} throughout the entire temperature range. Had a few percent of monomer been present, this should have been observed as a small sharp N−H band near 3440 cm^{-1}.[30]

Conclusion

In several attempts to produce self-assembling discotics in which four to seven molecules comprising two chemical components were required to associate, we were unable to observe mesophase formation. Causes for failure may be manifold, but prominent among them is the existence of a very stable crystalline phase for one of the components. This problem was obviated by use of tetrakis(*n*-alkoxy)-6-(5*H*)-phenanthridinones. The octyloxy, decyloxy, and dodecyloxy derivatives all dimerize as predicted to give discotic entities which form hexagonal columnar mesophases.

Experimental Section

General Data. All chemical reagents and solvents were purchased from Aldrich Chemical Company or Fisher Scientific unless specified and were used without prior purification, unless otherwise stated. Dry tetrahydrofuran and dry diethyl ether were distilled from sodium benzophenone. Dry methylene chloride was distilled from calcium hydride.

Thin layer chromatography was performed on Whatman flexible plates (PE SIL G/UV) or Baker-Flex plates (Silica Gel IB2-F). Flash chromatography was performed using 60 Å, 200−400 mesh silica gel, purchased from Aldrich, under dry nitrogen pressure. ^{1}H NMR and ^{13}C NMR spectra were obtained from Brucker AC200 and MSL300 instruments at 200 and 75 MHz, respectively, with tetramethylsilane as internal standard. Routine IR spectra were obtained on a Perkin-Elmer 1420 ratio recording infrared spectrometer. Mass spectrometry was performed by the Midwest Center for Mass Spectrometry, University of Nebraska−Lincoln following the FAB method with a 3-NBA matrix.

Differential scanning calorimetry was performed with a Perkin-Elmer DSC 7 Series instrument at heating and cooling rates of 10 °C/min. A nitrogen atmosphere was maintained over *ca.* 5-mg samples. Daily calibration of temperature and enthalpy was performed with an indium standard. Polarizing optical microscopy was performed with a Leitz microscope equipped with a LINKAM heating stage. Samples were placed between clean glass slides and observed under crossed polarizers as they were heated at the rate of 5 °C/min.

Wide angle X-ray scattering was performed on a Siemans D-500 goniometer, using Cu Kα radiation (λ = 1.54 Å) operating in the reflection mode. Heating was maintained with a home-made heating stage. Flat chamber exposures on samples, annealed just below the clearing temperature, were performed with a Statton camera, using an X-ray beam collimated with a 200-mm pinhole.

2-Bromo-4,5-dimethoxybenzoic Acid (2). A solution of KMnO$_4$ (1.11 g, 7.0 mmol) in water was added to a mixture of 6-bromoveratraldehyde (1.22 g, 5.0 mmol) and water (20 mL) at 75 °C over a period of 20 min. The reaction mixture was heated at this temperature for 2 h with vigorous stirring. Aqueous KOH (20%) was then added until the reaction mixture was strongly alkaline. The mixture was filtered hot, and the residue was washed thoroughly with hot water. The combined filtrate and washings were cooled to room temperature, and unreacted aldehyde (121 mg) was removed by gravity filtration. The clear colorless filtrate was then acidified using concentrated HCl to pH 2. The white precipitate was collected by filtration and washed with cold water to afford 2-bromo-4,5-dimethoxybenzoic acid as a white powder (1.03 g, 88% adjusted for recovered aldehyde), mp 190.5−191.5 °C. This chromatographically and spectrally pure sample was not further purified. IR (KBr): 1710 cm^{-1} (C=O str). ^{1}H NMR (CDCl$_3$): δ 7.60 (s, 1H, H_6), 7.14 (s, 1H, H_3), 3.95 (s, 3H, −OCH_3), 3.93 (s, 3H, −OCH_3).

Ethyl 2-Bromo-4,5-dimethoxybenzoate (3). A mixture of 2-bromo-4,5-dimethoxybenzoic acid (2.6 g, 10 mmol), absolute ethanol (50 mL), and concentrated H$_2$SO$_4$ (5 mL) was heated at reflux with stirring under dry argon overnight. Excess ethanol was removed on a rotary evaporator, and the residue was dissolved in ethyl acetate. The solution was washed with water (3×), saturated NaHCO$_3$, water, and brine and dried (Na$_2$SO$_4$). Solvent was evaporated to afford ethyl 2-bromo-4,5-dimethoxybenzoate as white powder (2.7 g, 94%), mp 88.5−89 °C. IR (KBr): 1720 cm^{-1} (C=O str). ^{1}H NMR (CDCl$_3$): δ 7.40 (s, 1H, H_6), 7.10 (s, 1H, H_3), 4.39 (q, ^3J = 7 Hz, 2H, −OCH_2), 3.92 (s, 3H, −OCH_3), 3.91 (s, 3H, −OCH_3), 1.41 (t, ^3J = 7 Hz, 3H, −OCH$_2$CH_3).

Ethyl 3′,4,4′,5-Tetramethoxybiphenyl-2-carboxylate (4).[31] To a −78 °C solution of 4-bromoveratrole (1.50 g, 6.92 mmol) in 10 mL of anhydrous ethyl ether was added *n*-butyllithium (3.00 mL, 2.5 M in hexane, 7.5 mmol) to produce a thick white slurry under dry argon. This slurry was allowed to warm to 0 °C and stirred under argon at this temperature for 30 min. Anhydrous THF (5 mL) was then added to the mixture, and the white slurry was transferred slowly with a dry syringe to a cold (0 °C) stirred solution of ZnCl$_2$ (1.10 g, 8.07 mmol, fused immediately prior to use) in THF (10 mL). The resulting turbid solution was stirred at 0 °C for 30 min.

In another flask, diisobutylaluminum hydride (0.25 mL × 1.0 M in CH$_2$Cl$_2$) was added to a solution of Pd(PPh$_3$)$_2$Cl$_2$ (121 mg, 0.25 mmol) in anhydrous THF (5 mL) via a dry syringe to give a deep black solution. After all yellow Pd(II) crystals disappeared, ethyl 2-bromo-4,5-dimethoxybenzoate (1.00 g, 3.46 mmol) was added, and the resulting solution was transferred with a dry syringe to the arylzinc chloride solution at 0 °C. After the mixture was brought to room temperature, a condenser was attached, and the mixture was heated at reflux for 40 h. After cooling to room temperature, the mixture was poured into ice-cold 1 M HCl solution. The organic materials were extracted with ethyl acetate, washed with water (3×), saturated NaHCO$_3$, and brine, and dried (Na$_2$SO$_4$). The solvent was evaporated, and the residue was purified by flash chromatography (30% ethyl acetate in hexane, 250 g of silica gel) to afford ethyl 3′,4,4′,5-tetramethoxy-biphenyl-2-carboxylate as a yellowish-white solid (645.1 mg, 54%). IR (KBr): 1706, 1730 cm^{-1} (C=O str) ^{1}H NMR (CDCl$_3$): δ 7.39 (s, 1H, H_3), 6.89 (d, ^3J = 10 Hz, 1H, $H_{5'}$), 6.88 (bs, 1H, $H_{2'}$), 6.83 (d, ^3J = 10 Hz, 1H, $H_{6'}$), 6.82 (s, 1H, H_6), 4.08 (q, ^3J = 7 Hz, 2H, −OCH_2), 3.96 (s, 3H, −OCH_3), 3.94 (s, 3H, −OCH_3), 3.93 (s, 3H, −OCH_3), 3.88 (s, 3H, −OCH_3), 1.02 (t, ^3J = 7 Hz, 3H, −OCH$_2$CH_3).

Ethyl 2′-Nitro-4,4′,5,5′-tetramethoxybiphenyl-2-carboxylate (5). To a stirred solution of ethyl 3′,4,4′,5-tetramethoxybiphenyl-2-carboxylate (600 mg, 1.73 mmol) in glacial acetic acid (10 mL) was added concentrated nitric acid (25 drops, about 0.4 mL). After being stirred for about 10 min, the reaction mixture was poured onto ice, and the bright yellow solid was extracted with ethyl acetate. The organic phase was washed with H$_2$O, 20% NaOH, and brine and dried (Na$_2$SO$_4$). Removal of solvent afforded ethyl 2′-nitro-4,4′,5,5′-tetramethoxybi-phenyl-2-carboxylate as a bright yellow powder (668 mg, 98.5%), mp 125−127 °C (lit.[22] mp 126−128 °C). IR (KBr): 1710 (C=O str), 1515 and 1340 cm^{-1} (N−O str). ^{1}H NMR (CDCl$_3$): δ 7.73 (s, 1H, H_3), 7.61 (s, 1H, $H_{3'}$ or $H_{6'}$), 6.66 (s, 1H, H_6), 6.65 (s, 1H, $H_{6'}$ or $H_{3'}$), 4.08 (q, ^3J = 7 Hz, 2H, −CO$_2$CH_2−), 4.01 (s, 3H, −OCH_3), 3.99 (s, 3H, −OCH_3), 3.93 (s, 3H, −OCH_3), 3.91 (s, 3H, −OCH_3), 1.09 (t, ^3J = 7 Hz, 3H, −CO$_2$CH$_2$CH_3).

Methyl 2′-Nitro-4,4′,5,5′-tetrahydroxybiphenyl-2-carboxylate (6). To a solution of ethyl 2′-nitro-4,4′,5,5′-tetramethoxybiphenyl-2-carboxylate (100 mg, 0.256 mmol) in anhydrous CH$_2$Cl$_2$ was added boron tribromide (0.12 mL, 0.32 g, 1.3 mmol) at −78 °C via a syringe. The resulting dark red solution was brought to room temperature and stirred at room temperature for 2 h. Ten milliliters of anhydrous methanol was injected with caution through another dry syringe. The solution was heated at reflux with stirring overnight; then most of the solvent along with the trimethyl borate generated was distilled. Dry methanol was added to the residue. The mixture was heated at reflux for 2 h and methanol and methylborate were removed by distillation. This was repeated one more time, and the residue was further concentrated *in vacuo* to afford a deep brown colored solid. ^{1}H NMR (acetone-d_6)

(30) Conley, R. T. *Infrared Spectroscopy*; Allyn and Bacon: Boston, MA, 1966; pp 150 and 164.

(31) Adopted from the method of Dow, see ref 22.

revealed no aryl methyl ether signals. This crude methyl 2′-nitro-4,4′,5,5′-tetrahydroxybiphenyl-2-carboxylate was used in the subsequent alkylation.

2,3,8,9-Tetrakis(*n*-decyloxy)-6(5*H*)-phenanthridinone (1b). A mixture of crude methyl 2′-nitro-4,4′,5,5′-tetrahydroxybiphenyl-2-carboxylate, K_2CO_3 (5 g), KI (0.1 g), 1-bromodecane (0.50 mL, 0.53 g, 2.4 mmol), and 25 mL of methyl isobutyl ketone was heated at reflux under dry argon with vigorous stirring for 4 days. At the end of the 4 day period, the mixture was filtered hot, and the residue was washed with hot Skelly C (bp 88−99 °C). The combined filtrate was concentrated *in vacuo*, the concentrate was dissolved in ethyl acetate, washed with 10% K_2CO_3, water, and brine, and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography (ethyl acetate−hexane (1:10) as eluent) afforded methyl 2′-nitro-4,4′,5,5′-tetrakis(*n*-decyloxy)biphenyl-2-carboxylate (**7b**) as a light yellow solid (117.9 mg) with minor impurities. IR (KBr): 1720 cm^{-1} (C=O str). ^{1}H NMR (CDCl$_3$): δ 7.69 (s), 7.58 (s), 6.62 (s), 4.0 (m), 3.63 (s), 1.8 (m), 1.3 (m), 0.8 (m).

To this ester (**7b**) was added glacial acetic acid (10 mL). About 1 mL of dry THF was added to make sure the ester **7b** was totally dissolved. Fine iron powder (250 mg, 4.5 mmol) was added to the solution, and the mixture was heated under argon with vigorous stirring at 100 °C overnight. When the reaction mixture was cooled to room temperature, excess iron was removed with the magnetic stir bar and the white suspension was poured onto ice to produce a white precipitate. The white precipitate was collected by filtration and washed with cold water. The crude product was subjected to flash chromatography on a silica gel column (ethyl acetate−hexane 5:95) to afford 2,3,8,9-tetrakis(*n*-decyloxy)-6(5*H*)-phenanthridinone (**1b**) as a white powder (50 mg, 24% from **5** in three steps), K 99 °C M 118 °C I. IR (KBr): 3400 (br, N−H str), 1670 cm^{-1} (C=O str). ^{1}H NMR (CDCl$_3$): δ 9.53 (s, 1H, −N*H*), 7.86 (s, 1H, H_7), 7.49 (s, 1H, H_{10}), 7.41 (s, 1H, H_1), 6.69 (s, 1H, H_4), 4.2−4.0 (m, 8H, −OC*H$_2$*), 1.9 (m, 8H, −OCH$_2$C*H$_2$*), 1.5−1.2 (m, 56H, −(C*H$_2$*)$_7$−), 0.88 (t, ^3J = 7 Hz, 12H, −C*H$_3$*). ^{13}C NMR (CDCl$_3$): δ 162.0 (C_6); 153.7, 151.3, 149.1, and 145.4 ($C_{2,3,8,9}$); 130.8 (C_{4a}); 129.7, 118.4, and 111.4 ($C_{6a,10a,10b}$); 110.0, 108.9, 104.3, and 100.6 ($C_{1,4,7,10}$); 71.0, 69.3, and 69.2 (−OC*H$_2$*−); 31.9, 29.6, 29.5, 29.2, 26.1, and 22.7 (−C*H$_2$*−); 14.1 (−C*H$_3$*). MS: Calcd for $C_{53}H_{89}NO_5$: 819.6741. Found: [M$^+$] 819.6741, [M$^+$ + 1] 820.6797. Anal. Calcd for $C_{53}H_{89}NO_5$: C, 77.60; H, 10.96; N, 1.71. Found: C, 77.35; H, 11.27; N, 2.02.

The following compounds were obtained by using the same procedure:

2,3,8,9-Tetrakis(*n*-octyloxy)-6(5*H*)-phenanthridinone (1a): 20% from **5**, mp 114 °C; purified by recrystallization from ethyl acetate. IR (KBr): 3400 (br, N−H str), 1670 cm^{-1} (C=O str). ^{1}H NMR (CDCl$_3$): δ 10.23 (bs, 1H, N*H*), 7.89 (s, 1H, H_7), 7.50 (s, 1H, H_{10}), 7.42 (s, 1H, H_1), 6.77 (s, 1H, H_4), 4.24−4.07 (m, 8H, −OC*H$_2$*−), 1.90 (quin, ^3J = 7 Hz, 8H, −OCH$_2$C*H$_2$*), 1.3 (m, 40H, −C*H$_2$*−), 0.89 (t, ^3J = 6 Hz, 12H, −C*H$_3$*). ^{13}C NMR (CDCl$_3$): δ 162.2 (C_6); 153.7, 151.3, 149.0, and 145.4 ($C_{2,3,8,9}$); 130.9 (C_{4a}); 129.8, 118.3, and 111.4 ($C_{6a,10a,10b}$); 109.9, 108.8, 104.3, and 100.7 ($C_{1,4,7,10}$); 71.0, 69.3, and 69.2 (−OC*H$_2$*−); 31.8, 29.6, 29.4, 29.3, 29.2, 26.1, and 22.7 (−C*H$_2$*−); 14.1 (−C*H$_3$*). MS: Calcd for $C_{45}H_{73}NO_5$: 707.5489. Found: [M$^+$] 707.5487, [M$^+$ + 1] 708.5548.

2,3,8,9-Tetrakis(dodecyloxy)-6(5*H*)-phenanthridinone (1c): 24% from **5**, K 88 °C M 108 °C I. IR (KBr): 3400 (br, N−H str), 1670 cm^{-1} (C=O str). ^{1}H NMR (CDCl$_3$): δ 9.89 (bs, 1H, N*H*), 7.88 (s, 1H, H_7), 7.49 (s, 1H, H_{10}), 7.41 (s, 1H, H_1), 6.73 (s, 1H, H_4), 4.24−4.06 (m, 8H, −OC*H$_2$*), 1.90 (quin, ^3J = 7 Hz, 8H, −OCH$_2$C*H$_2$*−), 1.5−1.3 (m, 72H, −C*H$_2$*−), 0.88 (t, ^3J = 6 Hz, 12H, −C*H$_3$*). ^{13}C NMR (CDCl$_3$): δ 162.2 (C_8); 153.7, 151.3, 149.0, and 145.4 ($C_{2,3,8,9}$); 130.8 (C_{4a}); 129.7, 118.4, and 111.4 ($C_{6a,10a,10b}$); 110.0, 108.9, 104.3, and 100.7 ($C_{1,4,7,10}$); 71.0, 69.3, and 69.2 (−OC*H$_2$*−); 31.9, 29.72, 29.68, 29.53, 29.46, 29.39, 29.2, 26.1, and 22.7 (−C*H$_2$*−); 14.1 (−C*H$_3$*). MS: Calcd for $C_{61}H_{105}NO_5$: 931.7993. Found: [M$^+$] 931.8028, [M$^+$ + 1] 932.8101.

Supporting Information Available: Synthetic details for 4-(3′,4′,5′-tris(*n*-alkoxy)styryl)pyridines and 4,5-bis(*n*-decyloxy)phthalimide; IR, ^{1}H, ^{13}C, and high-resolution mass spectra for **1a**−**c**; DSC traces for **1a**−**c** and partial variable temperature FT-IR spectra for **1c** (20 pages). See any current masthead page for ordering and Internet access instructions.

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