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Three types of liquid crystalline materials were prepared and characterized: discotic aza-macrocycles, discotic phthalocyanines, and donor-acceptor substituted side chain stilbene polyacrylates. The stilbene polymers have both second-order and third-order nonlinear optical responses, have liquid crystal phases at elevated temperature and can be cooled to anisotropic glasses at room temperature, and form stable monolayers on a water surface. Certain of the phthalocyanines form clear thin films.			
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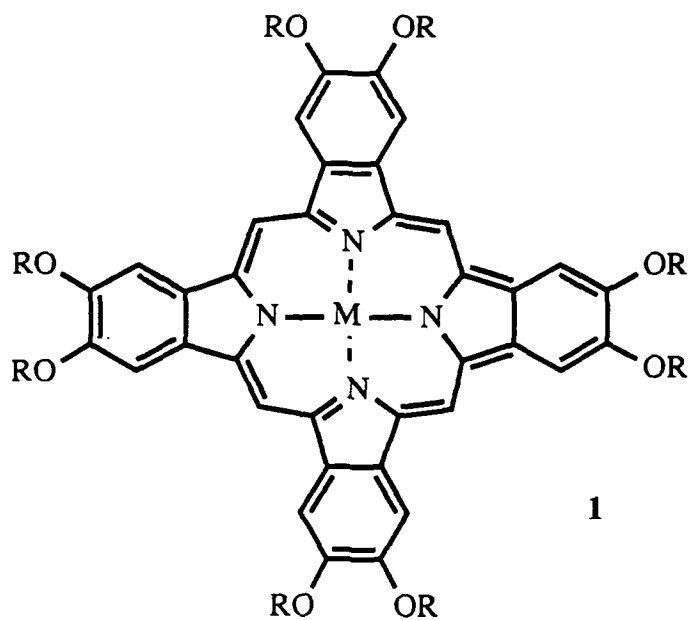
Final Report
Polymer Liquid Crystals with Side Chain Discogens
Warren T. Ford
Oklahoma State University

With the long term goal of creating new polymers that have novel optical and electronic properties and can be fabricated as thin films, we have investigated three classes of liquid crystalline materials: discotic aza-macrocycles that may form complexes with metal ions with high selectivity, discotic phthalocyanines that may have strong nonlinear optical properties and are semiconductors, and polarized stilbenes that have strong second and third order nonlinear optical responses. Except for the research on the discotic phthalocyanines, the results have been described in technical reports based on manuscripts submitted for publication. The unpublished work is described here in some detail, and expanded abstracts of the manuscripts are provided. → (110) R

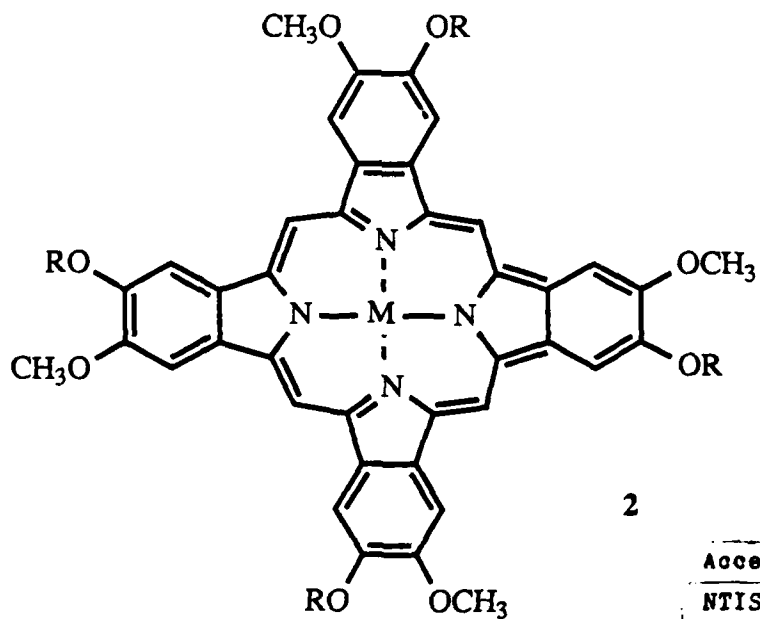
Discotic Phthalocyanines

The combination of semiconductor properties, strong absorption of visible light, and thermal and chemical stability make phthalocyanines (Pc's) candidates for molecular electronic materials. Many monomeric Pc's with flexible side chains have discotic mesophases. Unsubstituted metalloPc's coated as thin films onto electrodes are photovoltaic and photoelectrolytic devices in which the active potentials depend upon the metal. Langmuir Blodgett films of substituted metalloPc's are sensitive to low concentrations of solvents, which can be detected by surface acoustic wave spectroscopy. Several NLO experiments on phthalocyanines have been reported.

We have synthesized a series of symmetrical octaalkoxy H_2Pc and $CuPc$ compounds (1), and isomeric mixtures of the tetramethoxytetraalkoxy H_2Pc and $CuPc$ compounds (2), and characterized them by 1H NMR, IR, and UV-visible spectroscopy, and by DSC and polarizing microscopy. Unknown to us simultaneously several of the same materials were investigated in the laboratories of Prof. Wiendelt Drenth at the University of Utrecht (*Rec. Trav. Chim. Pays-Bas* 1988, 107, 615; *Liq. Cryst.*, 1989, 6, 577) and Prof. J. Simon in Paris (*Liq. Cryst.* 1989, 4, 707). Their work is now mostly published. Ours is not. The following description of materials mentions only compounds that we have made, but phases and properties that are the results of X-ray, electronic conduction, and luminescence experiments are due to Drenth or to Simon. The phase transitions of our materials are listed in Table I. Drenth and Simon assigned the D_{ho} (discotic hexagonal ordered) phases from X-ray analyses. We observe no change in the polarizing microscopic texture at the crystal to D_{ho} transition. Some of our compounds show transitions by DSC that are not detected by polarizing microscopy. These have arbitrarily been called crystalline at room temperature and liquid crystalline in all higher temperature phases, but some of those higher temperature phases may be crystals with disorder only in the side chains. The D_{ho} phases are liquid crystalline, for they lack 3-dimensional crystallographic order, but they do not flow at temperatures up to 250 °C during our microscopic observations. Exciton migration lengths of >4000 molecules per stack at 300 K have been calculated from quenching of the fluorescence of



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Table I. Thermal transitions of octaalkoxy Pc's.^a

structure	transitions in °C (ΔH , cal/g) ^b	ref
1a: R = <i>n</i> -octyl, M = H,H	C 106(10.6) D _{ho} C 94 D _{ho}	Drenth
1b: R = <i>n</i> -octyl, M = Cu	C 119(11.8) D _{ho} C 112 D _{ho}	Drenth
1c: R = 2-ethylhexyl, M = H,H	C 158 M ₁ 224 N _d 255 I C 170 M ₁ 223 N _d 270 I	Simon
1d: R = 2-ethylhexyl, M = Cu	C 200 M ₁ 240 M ₂ 288 U	
1e: R = <i>n</i> -dodecyl, M = H,H	C 91(13.2) D _{ho} 310(1.0) U C 91(15.6) D _{ho} >300	Simon
	C 75 D _{ho} 265 U	Cho ^c
	C 83 D _{ho} 309 I	Drenth
1f: R = <i>n</i> -dodecyl, M = Cu	C 99(10.8) D _{ho} C 78 D _{ho} 307 U C 95 D _{ho} >300	Cho ^c Drenth
1g: R = <i>n</i> -octadecyl, M = H,H	C 53(1.1) M ₁ 60(3.0) M ₂ 197	
1h: R = <i>n</i> -octadecyl, M = Cu	C 34 M ₁ 45 M ₂	
2a: R = <i>n</i> -dodecyl, M = H,H	C 79(0.5) M	
2b: R = <i>n</i> -dodecyl, M = Cu	C 66(1.1) M ₁ 249(0.05) M ₂	
2c: R = <i>n</i> -octadecyl, M = H,H	C 53(3.4) M ₁ 57 M ₂ 87(0.5) M ₃ 158(0.4) M ₄	
2d: R = <i>n</i> -octadecyl, M = Cu	C 52(6.7) M ₁ 80(1.2) M ₂	

^aAll transition temperatures are from the first heating scan by DSC. All samples were examined up to 310 °C by DSC. ^bC = crystal; M = unidentified mesophase; I = isotropic; U = unknown, either mesophase or isotropic.

^cCho and Lim, *Mol. Cryst. Liq. Cryst.* **1988**, 154, 9.

octa(dodecyloxy)PcH₂ by traces of the PcCu. (Drenth, *Chem. Phys. Lett.* **1989**, 154, 420). A stack of 4000 molecules separated by the graphite interplanar distance of 3.4 Å is 1.4 μm high, greater than the thickness of many spin-coated films. The luminescence intensity decreases markedly upon heating into the D_{ho} phase, but transient current measurements on the D_{ho} phase show irregular periods of as long as ten seconds with high conductivity through a thin film, which has been attributed to dynamic formation and breakup of stacks that persist through the thickness of the film. (Drenth, *Electroanal. Chem.* **1989**, 271, 41). Thus the fluorescence and conduction results indicate that films of our Pc's may be ordered with some of the discotic stacks extending through the complete thickness of the film.

In collaboration with the group of Prof. Richard C. Powell of the Physics Department at Oklahoma State University we attempted to measure third order nonlinear optical susceptibility by the degenerate four wave mixing (DFWM) method at 532 nm with an amorphous dispersion of 1c in polystyrene. However, the green Pc bleached too quickly in the laser to record an output signal. Although the absorption spectra of Pc's in solution have a local minimum at 532 nm, the molar extinction coefficients at that minimum still exceed 10³ L mol⁻¹ cm⁻¹. With equipment available in the Powell laboratory we plan to shift our attention to nonresonant DFWM experiments at 1064 nm. Dr. James S. Shirk and coworkers at the Naval Research Laboratory observed DFWM at 1064 nm with

metalloPc solutions but not with thin films, which are needed for practical devices. (*Appl. Phys. Lett.* 1989, 55, 1287). According to Shirk (personal communication) preliminary attempts to observe DFWM of their films failed because of excessive scattering. The key to success is the preparation of optically clear films. *We have prepared intensely green films of 1c so clear that through them we can see the mortar between the bricks of a building 50 meters away.* CuPc's will be used for initial experiments because Shirk observed ten times greater $\chi^{(3)}$ with a CuPc than with a H₂Pc. It may be possible to prepare by spin coating films of 1d in polystyrene and of 1d alone with high optical clarity for 1064 DFWM measurements.

Discotic Aza-macrocycles

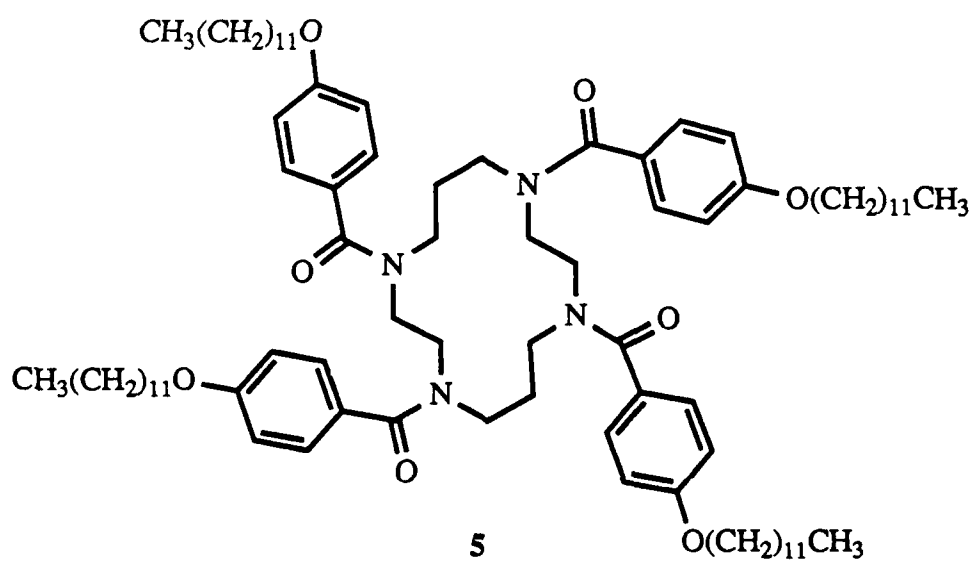
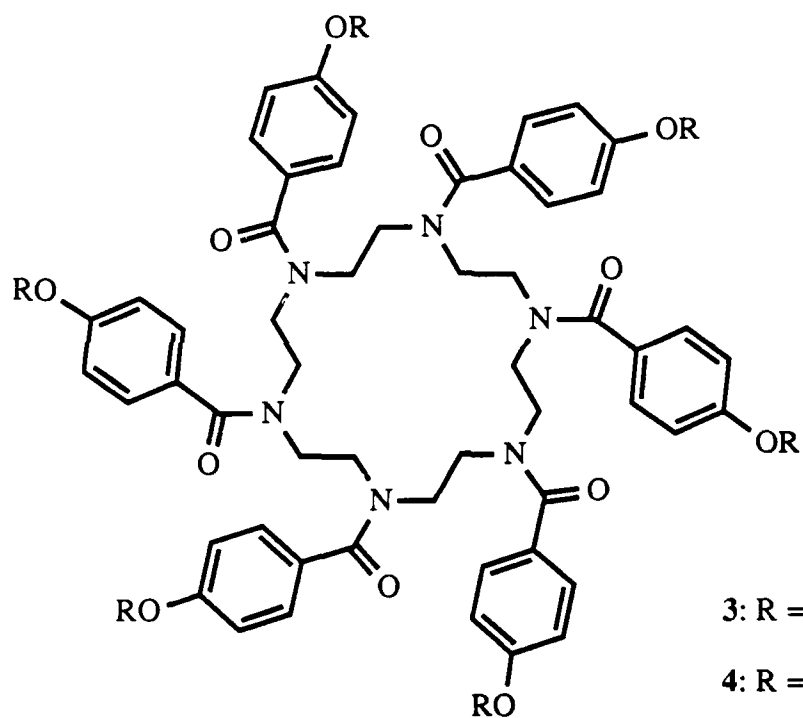
The hexa-(4-dodecyloxy)benzamide and hexa-(4-hexyloxy)benzamide derivatives of [18]-N₆ (3 and 4) and the tetra-(4-dodecyloxy)benzamide derivative of [14]-N₄ (5) were prepared, and their phase transition temperatures were determined by DSC and polarizing microscopy. The melting and isotropic transition temperatures (101 and 135 °C) of the mesophase of 3 differed substantially from those reported earlier (121.5 and 141.5 °C, and 105 and 140 °C in two other laboratories), apparently due to the presence of 4 molecules of water per macrocycle in our material. No liquid crystal phase was detected for compounds 4 and 5. (Technical Report No. 1)

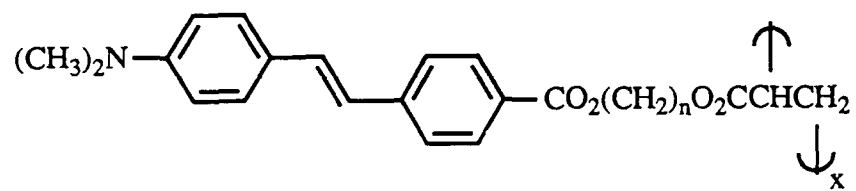
Polarized Stilbenes

ω -Acryloxyalkyl 4-dimethylamino-*trans*-stilbene-4'-carboxylates with (CH₂)_n spacer chains having n = 2, 4, 6, 8, and 10 (P-n) have been synthesized and polymerized to give side chain liquid crystal polymers. DSC and polarizing microscopy show that the polymers have glass and isotropization transition temperatures that decrease with increasing length of the spacer chain to T_g = 83 °C and T_i = 125 °C for the polymer P-10. Low isotropization enthalpies of ≤ 1.2 cal/g and polarizing microscopic textures indicate a low degree of order in the liquid crystal phases. The polymers are soluble, which indicates no significant cross-linking through the stilbene double bond, and the *trans* configuration of the stilbene was maintained throughout the syntheses. (Technical Report No. 2)

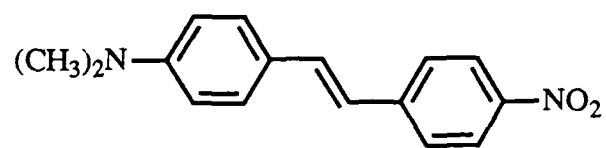
The polymers P-n with 2, 6, and 10-carbon spacer chains spread on water, and can be compressed to form stable monolayers and transferred to substrates to form Langmuir-Blodgett films. (Preliminary experiments by Dr. R. S. Duran at the University of Florida).

Thin films of the side chain liquid crystal polymer (P-10) with a 4-dimethylaminostilbene-4'-carboxylic ester mesogen were measured to have degenerate four wave mixing efficiencies at 532 nm 90 times that of carbon disulfide and 0.5 times that of a film of 4-dimethylamino-4'-nitrostilbene (DANS) in poly(methyl methacrylate) [PMMA] and second harmonic generation efficiencies at 1064 nm 0.17 times that of a film of DANS in PMMA. Single shot and cumulative laser induced damage thresholds were measured at both wavelengths. (Technical Report No. 3)





P-n



DANS

Technical Reports and Journal Articles

Technical Report No. 1. Liquid Crystalline Macrocycles and Polyacrylates Containing 4-Alkoxybenzoic Acid and 4-Alkoxybenzamide Structural Units, D. Tatarsky, K. Banerjee, and W. T. Ford.

Technical Report No. 2. Side-Chain Polyacrylates with 4-Dimethylamino-4'-stilbenecarboxylic Ester Mesogens, M. Zhao and W. T. Ford.

Technical Report No. 3. Second-order and third-order nonlinear optical responses and laser damage thresholds of a polarized stilbene side chain liquid crystal polymer. R. J. Reeves, R. C. Powell, M. Bautista, M. Zhao, and W. T. Ford.

D. Tatarsky, K. Banerjee, and W. T. Ford, Synthesis and Phase Transitions of 4-(Dodecyloxy)benzamide Derivatives of Azacrowns [14]-N₄ and [18]-N₆, *Chem. Mater.* **1990**, in press.

M. Zhao and W. T. Ford, Side-Chain Polyacrylates with 4-Dimethylamino-4'-stilbenecarboxylic Ester Mesogens, *Macromolecules*, submitted.

R. J. Reeves, R. C. Powell, M. Bautista, M. Zhao, and W. T. Ford, Second-order and third-order nonlinear optical responses and laser damage thresholds of a polarized stilbene side chain liquid crystal polymer, *J. Opt. Sci. Am., B*, submitted.

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