



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 24 Sep 2006.

To cite this article: David M. Walba, Daniel J. Dyer, Xin Hua Chen, Uwe Müller, Peter Cobben, Renfan Shao & Noel A. Clark (1996): Design and Synthesis of Ferroelectric Liquid Crystals. 25. An Approach to New Materials for Ultra-Fast Electronic Electro-Optic Modulators, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 83-91

To link to this article: <http://dx.doi.org/10.1080/10587259608034586>

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DESIGN AND SYNTHESIS OF FERROELECTRIC LIQUID CRYSTALS. 25. AN APPROACH TO NEW MATERIALS FOR ULTRA-FAST ELECTRONIC ELECTRO-OPTIC MODULATORS¹

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Abstract Combining excellent processability on silicon integrated circuits with a thermodynamically stable polar structure, ferroelectric liquid crystals (FLCs) provide an attractive potential approach to synthesis of materials for second order nonlinear optics (NLO). In order for this potential to be realized, however, adequate magnitude of the second order susceptibility $\chi^{(2)}$ must be obtained. Recent results of experiments demonstrating orientation along the FLC polar axis of functional arrays with large molecular second order susceptibility, such as those found in the NLO dyes Disperse Red 1 and dimethylaminonitrostilbene, are described.

INTRODUCTION

Ferroelectric liquid crystals (FLCs) are LCs with polar symmetry and a switchable macroscopic electric dipole moment (the ferroelectric polarization). While several theoretical and experimental studies have been aimed at creation of smectic A² and discotic³ FLCs with polarization along the director, evidence for the existence of such a "longitudinal" polar structure in LCs is not yet absolutely compelling. Chiral tilted smectics, however, are clearly ferroelectric in the surface stabilized geometry, are helielectric in bulk, and can exhibit a high degree of polar stereocontrol in the thermodynamic global minimum configuration.⁴

This combination of LC processability and polar structure makes FLCs an attractive class of materials for electronic second order nonlinear optics (NLO) applications, since a polar structure assures the presence of a non-zero bulk second order susceptibility $\chi^{(2)}$. Herein are described recent results of a project aimed at design and synthesis of FLCs for NLO applications, the critical issue being creation of FLCs with $\chi^{(2)}$ values large enough for use in ultra-fast integrated electro-optic modulators.

AN APPROACH FOR OBTAINING FLCs WITH HIGH $\chi^{(2)}$

Rationale—FLC Integrated Optical Chips

FLC integrated optical chips—silicon very large scale integrated (VLSI) circuit write-only memories with optical read-out—are among the pioneers in a new family of devices poised to revolutionize information display and processing.⁵ The current generation of VLSI/FLC chips are electro-optic modulators with $256 \times 256 = 64$ K channels running in parallel at 10 kHz, providing about 0.5 Gbits/sec of data throughput. Next generation devices will drive $1280 \times 1024 = 1$ M channels at 10 kHz to afford 10 Gbits/sec of throughput. These modulators leverage the power of VLSI silicon with the processibility of FLCs, the latter enabling integration of optical quality organic electro-optic thin films on silicon in a highly efficient manner.

For many obvious applications, however, a single channel running at 10 Gbits/sec or faster is desirable. The response speeds required for such ultra-fast modulation precludes the use of conventional LC or FLC electro-optics, which involve collective molecular motions induced by applied electric fields. One promising approach for achieving such modulation frequencies involves exploitation of the linear electronic electro-optic (EEO) effect in organic films with electronic second order NLO susceptibility $\chi^{(2)}$.⁶ Since FLCs possess a thermodynamically stable polar supermolecular structure they indeed show non-zero $\chi^{(2)}$. This, combined with the above-mentioned processibility on silicon suggests VLSI/FLC integrated optics could also provide high bandwidth per channel modulators.

Design of FLCs with High $\chi^{(2)}$

In order to create FLC-based ultra-fast EEO modulators, FLCs with improved $\chi^{(2)}$ are required, since known materials possess EEO coefficients too small to be useful in this application. For example **DOBAMBC** (Figure 1), the first demonstrated FLC,⁷ and the first FLC evaluated for $\chi^{(2)}$,⁸ has been shown to possess effective $\chi^{(2)}$ on the order of 0.002 pm/V by angle phase matched second harmonic generation (SHG) from 1064 nm light (type 1 eeo $d_{\text{eff}} = 0.001$ pm/V).⁹ Since values of $\chi^{(2)}$ on the order of 50 pm/V are required for fabrication of EEO modulators, **DOBAMBC** is clearly useless in this application. Even FLCs of the α -chloroester family with high ferroelectric polarization have been shown to possess small $\chi^{(2)}$ values on the order of 0.02 pm/V by SHG.¹⁰

Efforts directed at design of FLCs with increased $\chi^{(2)}$ have focused on two key issues: 1) Improving the molecular second order susceptibility β of the FLC mesogens; and 2) Achieving the correct supermolecular stereochemistry for $\chi^{(2)}$. Thus, mesogens wherein donor and acceptor groups coupled by an aryl ring conjugating spacer are oriented

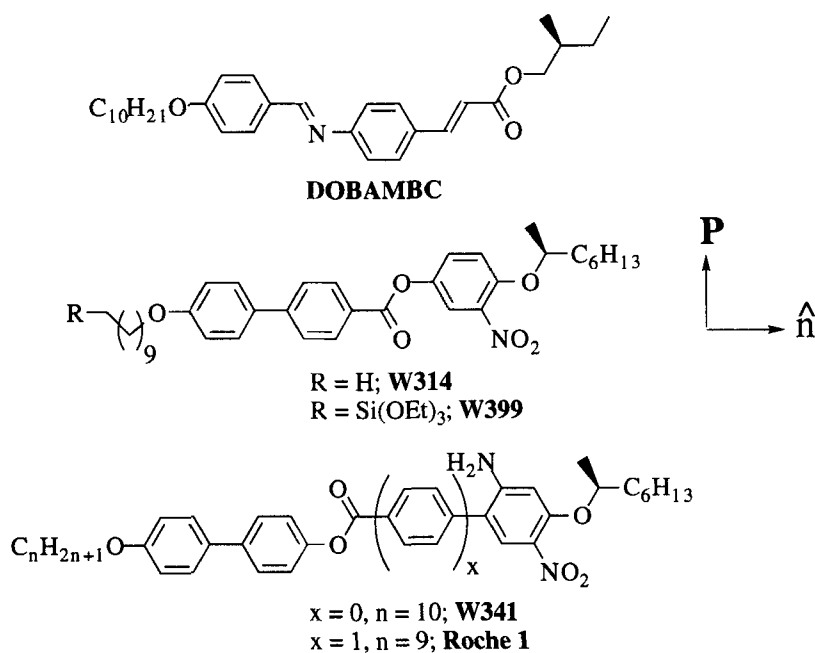


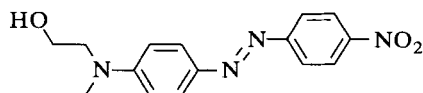
FIGURE 1 Some previously studied FLCs for NLO.

in the C* phase such that the charge transfer axis has a large component along the FLC polar axis (normal to \hat{n}) were designed. In the first application of this approach an alkoxy donor grouping was oriented ortho to a nitro acceptor.¹¹ The required polar orientation of these functional arrays was achieved by steric coupling of the 1-methylheptyloxy chiral tail¹² with the nitro grouping.¹³ This structural class provided materials with demonstrated electronic electro-optic (EEO) coefficients on the order of 1 pm/V for modulation of 633 nm light at 100 MHz (**W399**)¹⁴ and d coefficients on the order of 0.6 pm/V for SHG from 1064 nm light (**W314**).¹⁵

In order to increase $\chi^{(2)}$, introduction of an improved donor (an amino grouping) para to the acceptor was accomplished, as indicated for the FLC dopant **W341**.¹⁶ The desired orientation of the p-nitroaniline grouping along the polar axis with excellent supermolecular stereocontrol in this system was demonstrated by measurement of large ferroelectric polarization in C* mixtures containing **W341**.^{1b} This interpretation was confirmed experimentally with the characterization of the **W341** analog **Roche 1**,¹⁷ which exhibited $d_{\text{eff}} = 5$ pm/V by SHG in an electric-field induced tilted smectic phase. Thus, an improvement of about a factor of 5,000 in the $\chi^{(2)}$ of FLCs has been achieved since the

initial work with **DOBAMBC**. Further improvements are required, however, if the required EEO coefficients on the order of 50 pm/V are to be realized.

The most promising approach for achieving larger $\chi^{(2)}$ in FLCs involves orientation of “large β ” functional arrays along the polar axis.¹⁸ Conventional large β structures include a donor-substituted aromatic ring and an acceptor substituted aromatic ring joined by a conjugating spacer unit such as a double bond. The prototype of this class of molecules is the classic NLO dye Disperse Red 1 (DR1)—in this case the donor is a dialkylamino group, the acceptor is a nitro group, and the conjugating spacer is the azo linkage.



Disperse Red 1

Excellent supermolecular stereocontrol is achievable in FLCs (on the order of 60% polar excess has been demonstrated as evidenced by ferroelectric polarization measurements),¹⁹ and “large β ” functional arrays are easily incorporated into LC structures.²⁰ Even **DOBAMBC** is expected to possess reasonable β (between that of DR1 and p-nitroaniline). However, in all previously known cases such functional arrays orient along the liquid crystal director \hat{n} , while the FLC polar axis is normal to the director.²¹ This incorrect supermolecular structure leads to small $\chi^{(2)}$.

Side-by-Side Dimer Mesogens for NLO

In order to obtain mesogens possessing large β units and the correct supermolecular structure for large $\chi^{(2)}$, a molecular structural motif was explored wherein two chiral smectic mesogenic units, one substituted with a donor and the other with an acceptor, are joined by a conjugating spacer. Initial synthetic work in this area produced the azo dye **1**, with a phenyl biphenylcarboxylate donor unit, a phenyl tolancarboxylate acceptor, and the azo linkage as conjugating spacer, as shown in Figure 2.

While dimer **1** is not itself mesogenic (mp 139-140°C), smectic C* mixtures up to 30% by weight of **1** in the C phase host racemic **W314**²² were characterized as indicated in Figure 2. The data show that indeed the azo unit is oriented at a large angle from the director (negative visible light dichroism). Furthermore, the sign and magnitude of the ferroelectric polarization of the mixtures are consistent with the desired supermolecular structure, suggesting a polar excess for orientation of the DR1 chromophore of about 10% assuming an average dipole moment normal to the director of about 5 D.²³



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calculated dipole moment normal to the director of ~ 4 D (MOPAC with the AM1 Hamiltonian).

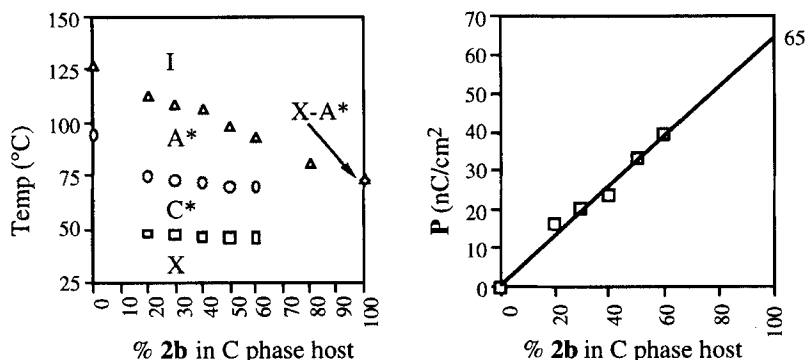


FIGURE 4 Phase diagram and measured "saturation" ferroelectric polarization for mixtures of **2b** in racemic **W314**.

The data shown in Figure 4 for compound **2b** are consistent with the desired structure in the C* phase; specifically that the dimer orients with the phenyl biphenylcarboxylates along the director and the azo dye at about 60° from the director. Proof of this structure was readily obtained by measuring the visible light dichroism of **2b** in the smectic A* phase. While the neat sample was too strongly absorbing to afford good data, in a 10% mixture of **2b** in a room temperature A* host,²⁴ the absorbance as a function of incident angle is well behaved, and a dichroic ratio (absorbance parallel to \hat{n} /absorbance normal to \hat{n}) of 0.52 is observed. This leads to a calculated angle of 63° between the director and the azo dye transition moment—in good agreement with expectation. In addition, compound **2b** exhibits negative birefringence in the neat A* phase; also consistent with the proposed supermolecular structure. To our knowledge this material is the only known smectic mesogen with negative birefringence.

Since dimethylaminonitrostilbene (DANS) is known to possess a larger β value than DR1, the carbon analogs **3** and **4** of the azo dyes were synthesized. As indicated in Figure 5, the tolan bis-phenylbiphenylcarboxylate **3** shows excellent mesogenicity, with enantiotropic N* and A* phases. Unfortunately, the DANS dimer **4** is not mesogenic. Not surprisingly, characterization of **4** in a mixture with racemic **W314** suggests that the supermolecular structure obtained with the DANS dimer is similar to that obtained in the DR1 case, with a 10% polar excess for orientation of the chromophore indicated by the observed ferroelectric polarization.

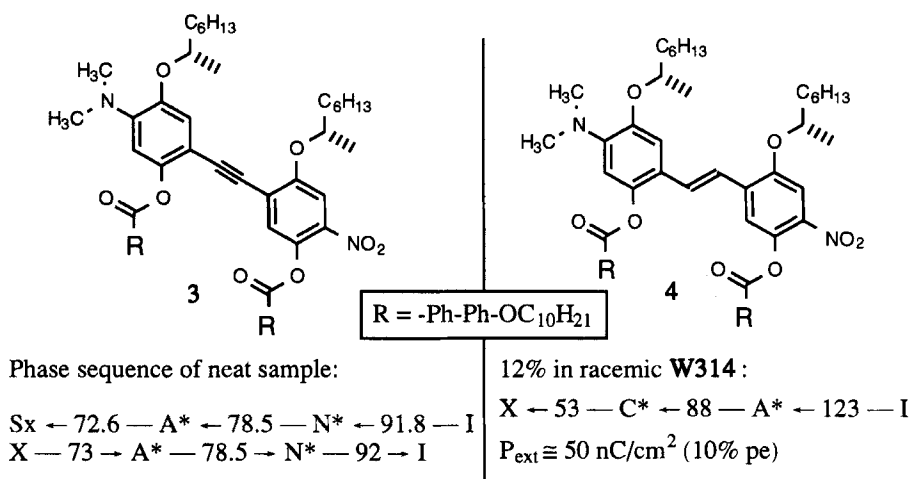


FIGURE 5 Structure and some properties of compounds **3** and **4**, containing the dimethylaminonitrotolan and dimethylaminonitrostilbene (DANS) NLO chromophores, respectively.

CONCLUSIONS

In the context of electronic second order NLO in FLCs, initial results with side-by-side dimer structures are highly encouraging, suggesting that it will prove possible to obtain C^* materials with large β NLO chromophores oriented along the polar axis. Critical issues to be dealt with include most importantly improvement of the degree of polar stereocontrol achievable in the dimer mesogens, with a very realistic target being realization of 30% polar excess in orientation of the DR1 or DANS chromophores in the C^* phase.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research, and by the National Science Foundation (DMR-9224168).

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24. The room temperature A* material (S)-4''-(1-Methylheptyloxy)-3''-nitro-4'-biphenyl-4-(4-E-decyloxy)benzoate (**5**) was used as host in this experiment. Details of the properties of this material will be reported elsewhere.

