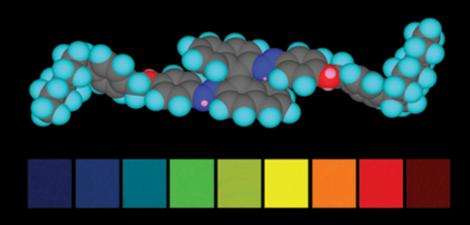
Liquid Crystals Beyond Displays

Chemistry, Physics, and Applications

Quan Li





LIQUID CRYSTALS BEYOND DISPLAYS

LIQUID CRYSTALS BEYOND DISPLAYS

CHEMISTRY, PHYSICS, AND APPLICATIONS

Edited by

Quan Li Liquid Crystal Institute Kent, OH



Copyright © 2012 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Liquid crystals beyond displays: chemistry, physics, and applications / edited by Quan Li, Liquid Crystal Institute, Kent, OH.

pages cm

Includes bibliographical references and index.

ISBN 978-1-118-07861-7

1. Liquid crystals-Research. 2. Optoelectronic devices-Research. I. Li, Quan, 1965- editor of compilation.

QC173.4.L55L55 2012

530.4'29-dc23

2011052325

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

CONTENTS

Preface	vi
Contributors	ix
1. Liquid Crystal Lasers Hideo Takezoe	1
2. Self-Organized Semiconducting Discotic Liquid Crystals for Optoelectronic Applications Chenming Xue and Quan Li	29
3. Magnetic Liquid Crystals Rui Tamura, Yoshiaki Uchida, and Katsuaki Suzuki	83
4. Ferroelectric Liquid Crystals for Nonlinear Optical Applications Yongqiang Zhang and Jesús Etxebarria	111
5. Photo-Stimulated Phase Transformations in Liquid Crystals and Their Non-Display Applications C. V. Yelamaggad, S. Krishna Prasad, and Quan Li	157
6. Light-Driven Chiral Molecular Switches or Motors in Liquid Crystal Media Yan Wang and Quan Li	213
7. Liquid Crystal-Functionalized Nano- and Microfibers Produced by Electrospinning Jan P. F. Lagerwall	251
8. Functional Liquid Crystalline Block Copolymers: Order Meets Self-Assembled Nanostructures Xia Tong and Yue Zhao	285
9. Semiconducting Applications of Polymerizable Liquid Crystals Mary O'Neill and Stephen M. Kelly	303

vi CONTENTS

10.	Liquid Crystals of Carbon Nanotubes and Carbon Nanotubes in Liquid Crystals Giusy Scalia	341
11.	Liquid Crystals in Metamaterials Augustine M. Urbas and Dean P. Brown	379
12.	Ferroelectric Colloids in Liquid Crystals Yuriy Reznikov	403
13.	Fact or Fiction: Cybotactic Groups in the Nematic Phase of Bent Core Mesogens Bharat R. Acharya and Satyendra Kumar	427
14.	Lyotropic Chromonic Liquid Crystals: Emerging Applications Heung-Shik Park and Oleg D. Lavrentovich	449
15.	Liquid Crystal-Based Chemical Sensors Jacob T. Hunter and Nicholas L. Abbott	485
16.	Polymer Stabilized Cholesteric Liquid Crystal for Switchable Windows Deng-Ke Yang	505
17.	Liquid Crystals for Nanophotonics Timothy D. Wilkinson and R. Rajesekharan	525
Ind	ex	569

Liquid crystals (LCs) were discovered more than 100 years ago, however the renaissance of research and development activities during the last quarter of 20th century led to the successful commercialization of LC devices for information displays. Currently the global market of LC displays (LCDs) stands more than \$100 billion annually. Though the LCDs ubiquitous in our daily life seem mature, there is still considerable interest in the development of 3D-displays using LCs. Nevertheless parallel to this development, nowadays there is an unprecedented growth of interest for non-display applications of LCs during the 1st decade of 21st century. Consequently the research and development of LCs are moving rapidly beyond displays and evolving into entirely new scientific frontiers, opening broad avenues for versatile applications such as lasers, photovoltaics, light-emitting diodes, field effect transistors, nonlinear optics, biosensors, switchable windows, and nanophotonics. These fields, which gain extensive attentions of physicists, chemists, engineers, and biologists, are of a most engaging and challenging area of contemporary research, covering organic chemistry, materials science, bioscience, polymer science, chemical engineering, material engineering, electrical engineering, photonics, optoelectronics, nanotechnology, and renewable energy.

This book does not intend to exhaustively cover the field of LCs beyond displays, as it is extremely difficult to do so within a single book. Instead, the book focuses on the recent developments of most fascinating and rapidly evolving areas related to the theme. The chapters span the following topics: LC lasers (Chapter 1), self-organized semiconducting discotic LCs (Chapter 2), magnetic LCs (Chapter 3), ferroelectric LCs for nonlinear optical applications (Chapter 4), photo-stimulated phase transformations in LCs (Chapter 5), light-driven chiral molecular switches or motors in LC media (Chapter 6), LC functionalized nano- and microfibers produced by electrospinning (Chapter 7), functional LC block copolymers (Chapter 8), semiconducting applications of polymerizable LCs (Chapter 9), LCs of carbon nanotubes and carbon nanotubes in LCs (Chapter 10), LCs in metamaterials (Chapter 11), ferroelectric colloids in LCs (Chapter 12), cybotactic groups in the nematic phase of bent core mesogens (Chapter 13), lyotropic chromonic LCs: emerging applications (Chapter 14), LC-based chemical sensors (Chapter 15), LCs for switchable windows (Chapter 16), and LCs for nanophotonics (Chapter 17). In each chapter, the state-ofthe-art along with future potentials in the respective fields has been discussed and highlighted by the leading experts.

I hope this book is not only to introduce fundamental knowledge, illustrative examples, and successful applications beyond displays, but also to stimulate more

viii PREFACE

interest for further development in this realm of research, wishing the interdisciplinary actions of physicists, chemists, engineers, and biologists can bring grateful values to push the LCs research forward in the 21st century. For graduate students, researchers, and scientists from other fields who want to get involved in LCs, this book is anticipated to serve as a beginners' guide. For established researchers, this book is expected to provide insights into knowledge beyond their expertise. I sincerely hope this book can generate interest to readers and help researchers to spark creative ideas.

I would like to express my gratitude to Jonathan Rose at John Wiley & Sons, Inc. for inviting us to bring this exciting field of research to a wide audience, and to all our distinguished contributors for their dedicated efforts. Also I am indebted to my wife Changshu, my sons Daniel and Songqiao for their great support and encouragement.

QUAN LI KENT, OHIO

August 2011

CONTRIBUTORS

- **Nicholas L. Abbott**, Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI, USA
- Bharat R. Acharya, Platypus Technologies, Madison, WI, USA
- **Dean P. Brown**, Materials and Manufacturing Directorate, Air Force Research Laboratory WPAFB, OH, USA
- **Jesús Etxebarria**, Department of Condensed Matter Physics, University of the Basque Country, Bilbao, Spain
- **Jacob T. Hunter**, Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI, USA
- Stephen M. Kelly, Department of Physics and Chemistry, University of Hull, UK
- Satyendra Kumar, Department of Physics, Kent State University, Kent, OH, USA
- **Jan P. F. Lagerwall**, Graduate School of Convergence Science and Technology, Seoul National University, Gyeonggi-do, Korea
- **Oleg D. Lavrentovich**, Liquid Crystal Institute, Kent State University, Kent, OH, USA
- Quan Li, Liquid Crystal Institute, Kent State University, Kent, OH, USA
- Mary O'Neill, Department of Physics and Chemistry, University of Hull, UK
- Heung-Shik Park, Liquid Crystal Institute, Kent State University, Kent, OH, USA
- **S. Krishna Prasad**, Center for Soft Matter Research, Bangalore, India
- **R. Rajesekharan**, Electrical Engineering Division, University of Cambridge, Cambridge, UK
- **Yuriy Reznikov**, Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine
- **Giusy Scalia**, Department of Nanoscience and Technology, Seoul National University, Gyeonggi-do, Korea
- **Katsuaki Suzuki**, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan

X CONTRIBUTORS

Rui Tamura, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan

Hideo Takezoe, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan

Xia Tong, Department of Chemistry, University of Sherbrooke, Québec, Canada

Yoshiaki Uchida, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan

Augustine M. Urbas, Materials and Manufacturing Directorate, Air Force Research Laboratory WPAFB, OH, USA

Yan Wang, Liquid Crystal Institute, Kent State University, Kent, OH, USA

Timothy D. Wilkinson, Electrical Engineering Division, University of Cambridge, Cambridge, UK

Chenming Xue, Liquid Crystal Institute, Kent State University, Kent, OH, USA

Deng-Ke Yang, Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent, OH, USA

C. V. Yelamaggad, Center for Soft Matter Research, Bangalore, India

Yongqiang Zhang, Micron Technology, Inc., Longmont, CO, USA

Yue Zhao, Department of Chemistry, University of Sherbrooke, Québec, Canada

Liquid Crystal Lasers

HIDEO TAKEZOE

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan

1.1 INTRODUCTION

Liquid crystals (LCs) have fluidity and a long-range orientational order. These properties enable us to use LCs as display materials. Another important property is a positional order. The periodicity is in the range not only of the molecular length periodicity like in smectic LCs but also of visible light wavelength. The latter generally arises from chirality, and in many cases results in helical structures. The most well-known example is cholesteric LCs (CLCs), in which the local structure is nematic and the director rotates to form a helical structure with the helical axis perpendicular to the director. The media that have periodic structures in the optical wavelength are called photonic crystals. Hence, we can call CLC a one-dimensional (1D) photonic crystal. Like an energy gap for electrons propagating in periodic crystal structures, a stop band emerges at the edges of the first Brillouin zone in CLCs. Within the stop band, light dampens and cannot propagate. When the light propagation is limited along any direction, we call it the photonic bandgap (PBG) [1, 2]. In this chapter, the stop band is called PBG in a broad sense.

The dispersion relation between angular frequency ω and wavenumber k in vacuo is given by $\omega=ck$, where c is the velocity of light (Figure 1.1a). In CLCs, the refractive index changes periodically, so the incoming light to the helix undergoes reflection if the light wavelength coincides with the optical pitch (structural pitch multiplied by an average refractive index), that is, Bragg reflection. Helical periodic structure makes the reflection very unique; that is, only a circularly polarized light (CPL) with the same handedness as the helix is reflected and another CPL with opposite handedness just passes through. This is called selective reflection. Such light propagation characteristics along the helical axis are rigorously solved, giving an analytical solution [3]. The dispersion relation thus obtained is shown in Figure 1.1b. Another unique feature compared with the other periodic structure is the sinusoidal

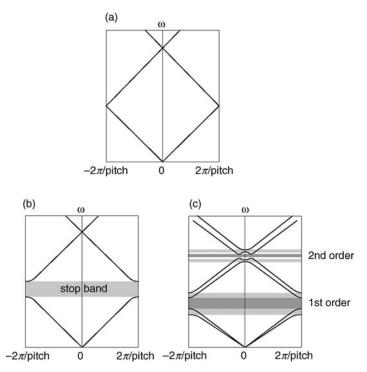


FIGURE 1.1 Dispersion relation (a) *in vacuo*, (b) in CLC at normal incidence, and (c) in CLC at oblique incidence. At oblique incidence, higher order reflection and total reflection regions are recognized.

change of the refractive index. Because of this, only the first-order Bragg reflection takes place (Figure 1.1b). For oblique incidence of light with respect to the helical axis, the periodic structure is no more than sinusoidal, so higher order reflections occur [4]. In addition, total reflection band(s) emerges, where light with any polarization states is reflected [5]. The dispersion relation (Figure 1.1c) calculated by the 4×4 matrix method [6] clearly reveals such behaviors. The emergence of higher order reflections and total reflection can be brought about by deforming the sinusoidal helical structure, for example, by applying an electric field. Such optical properties are similarly observable in other helical LC phases such as chiral smectic C^* (SmC*) and twist grain boundary (TGB) phases.

Because of the selective reflection in visible wavelength regions, it is a natural question how the emission from dye molecules existing inside the helical structure is affected by the Bragg condition. Actually, Kogelnik and Shank [7] studied possible distributed feedback (DFB) lasers. Namely, lasing may occur if emitted light is confined in a DFB cavity made of CLC. The lifetime of the luminescence from dyes embedded in CLCs was also examined [8, 9]. The first observation of lasing from CLC was reported by Il'chishin et al. in 1980 [10]. They even showed the lasing wavelength tuning by temperature. However, it took almost two decades to be paid

much attention from other groups until Kopp et al. [11] reported a CLC microlaser. For historical details, please refer to an article by Bartolino and Blinov [12].

Let us consider efficient lasing conditions. In an isotropic medium, the rate *R* of photon emitted from an excited molecule is described by Fermi's golden rule:

$$R_{\rm iso} \sim M_{\rm iso} |E \cdot \mu|^2 \tag{1.1}$$

where $M_{\rm iso}$ is the density of state (DOS), μ is the transition dipole moment, and E is the electric field. In isotropic media, M is independent of the polarization and the radiation direction. In anisotropic media, the emission depends on the orientation of transition dipole moment μ with respect to the polarization of light, that is, E. When emission occurs from the excited CLC molecules, light propagates as one of the two eigenmodes E_1 and E_2 . Then, emission rate for eigenmode E_i (R_i) is described as

$$R_i \sim M_i |E_i \cdot \mu|^2 \tag{1.2}$$

where M_i is the DOS associated with the eigenmode E_i . The fluorescent molecules embedded in CLCs have a certain degree of the nematic order, resulting in an anisotropic orientation distribution of the transition dipole moment. Hence to have large R_i , it is profitable that μ is parallel to the polarization of the eigenmode E_i . Now the other factor to have large R_i is DOS M, which is defined as

$$M = \left| \frac{\mathrm{d}}{\mathrm{d}\omega} \mathrm{Re}(k) \right| \tag{1.3}$$

Figure 1.2 shows a simulated transmittance spectrum and DOS (*M*). DOS shows maxima at the PBG edges where group velocity approaches to zero.

1.2 TYPES OF LASERS

There are several types of CLC microlasers. DFB lasers and defect mode lasers are the most popular ones, which will be described later. For more detail on these modes, please refer to a review by Kopp et al. [13]. In this chapter, we do not include random lasing and lasing from artificial structures such as grating.

1.2.1 DFB CLC Lasers

When light propagates in periodic media with the same periodicity as the light wavelength, the light suffers reflection due to the PBG. Hence, if CLC is doped with dyes, emitted light within the PBG is confined and amplified in CLC, and finally lasing results. This type of cavity without using mirrors is called DFB cavity. Lasers using DFB cavities are called DFB lasers. The DFB cavity is widely