Deterministically Polarized Fluorescence from Uniaxially Aligned Single-Dye Molecules

Introduction

In single-photon sources (SPS's) based on single-emitter fluorescence, a laser beam is focused into an area containing a low concentration of single emitters so that only one emitter becomes excited. The single emitter produces a single photon at a time.[1–4] There are various known methods for the production of single photons at definite time intervals, which are based on a single atom,[5,6] a single trapped ion,[7] a single molecule,[8–10] a single color center in diamond,[11] or the Coulomb-blockade effect in a micropin junction with quantum well as the active layer.[12–14] Tremendous progress has been made in the realization of SPS's based on excitonic emission from single heterostructured semiconductor quantum dots excited by pulsed laser light (see Refs. 1 and 3). In heterostructured quantum-dot SPS's,[15–28] microcavities have been used for spontaneous emission enhancement in the form of a whispering-gallery-mode resonator (turnstile device), 1-D photonic band gap, 3-D pillar microcavity, and 2-D photonic crystals. A weakness of heterostructured quantum-dot SPS's is that they operate *only at liquid-helium temperatures*. In addition, they are not readily tunable. To date, three approaches have been suggested for *room-temperature* SPS's: single molecules,[8–10,29–37] colloidal semiconductor quantum dots (nanocrystals),[38,39] and color centers in diamond.[11,40–43] The color-center source suffers from the challenge that it is not easy to couple out the photons and that the spectral bandwidth of the light is typically quite large (~120 nm).

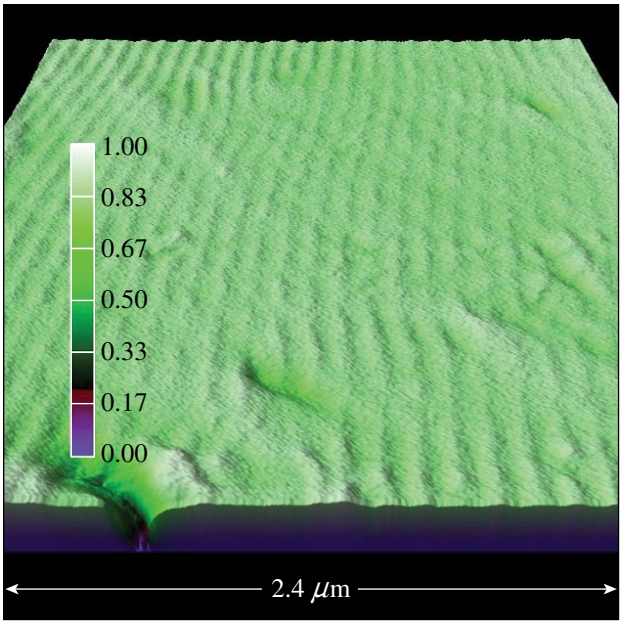
Both single molecules and colloidal semiconductor nanocrystals dissolved in a proper solvent can be embedded in photonic crystals to circumvent the deficiencies that plague the other systems. Colloidal semiconductor nanocrystals dissolved in PMMA were placed inside a 2-D photonic crystal cavity.[44] The nanocrystal emission at room temperature mapped out the cavity resonances and was enhanced relative to the bulk emission. A planar cavity was recently used to control the single-dye molecule fluorescence spectra and decay rate.[45] The primary problems with using fluorescent dyes and colloidal semiconductor nanocrystals in cavities are the emitters bleaching and blinking, nontunability of the source, and nondeterministic polarization of photons.

Our solution is based on a new material concept using single-emitter excitation in specially prepared *liquid crystal hosts*, which can exist both as monomers (fluid media) and oligomers or polymers. The advantages of using liquid crystal hosts are that they may be self-assembled in structures with photonic band-gap properties, and, at the same time, such a host can protect the emitters from bleaching. This source is a *room-temperature* alternative to cryogenic SPS's based on semiconductor heterostructures. In addition, the liquid crystal host provides both polarization purity and tunability of the source. Recent advances in liquid crystal technology, especially in the fabrication of electric-field/temperature-controlled 1-D, 2-D, and 3-D photonic crystal structures and the infiltration of photonic crystals with liquid crystals, can be used in SPS preparation with properties that other SPS methods failed to provide.

Recently we reported a first demonstration of dye-fluorescence antibunching in liquid crystal hosts[35–37] that is evidence of the single-photon nature of the source. One-dimensional (Fig. 106.36) and two-dimensional (Fig. 106.37) photonic crystal structures were prepared.[35–37,46] One-dimensional photonic band-gap structures in cholesteric liquid crystals possess an additional advantage over conventional 1-D photonic crystals. Because the refractive index n varies gradually rather than abruptly in cholesterics, there are no losses into the waveguide modes, which, in the case of conventional 1-D photonic crystals, arise from total internal reflection at the border between two consecutive layers with a different n. These waveguide losses can reach ~20%.

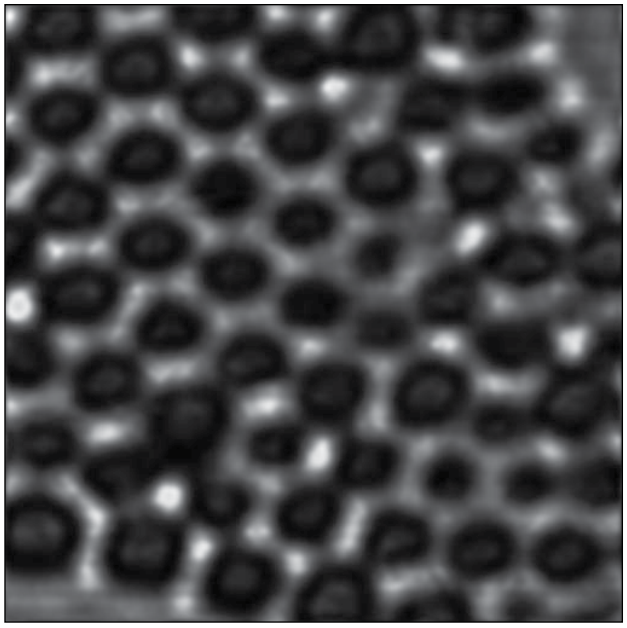
In addition, we observed a significant diminishing of dye bleaching by special preparation of liquid crystals; dye molecules did not bleach for periods of more than one hour under cw excitation.[35–37] (The first impressive experiments on avoiding dye bleaching in the hosts have been reported in Refs. 9 and 30. In Ref. 9, single terrylene-dye molecules in a *p*-terphenyl molecular crystal host did not bleach during several hours of pulsed, several-megahertz, pulse-repetition-rate excitation).

This article highlights another advantage of liquid-crystal hosts—*deterministically polarized* fluorescence from single-



G7148JRC

Figure 106.36
Perspective view of the AFM topographical image of a 1-D photonic band gap, planar-aligned, glassy, cholesteric liquid crystal.



G7149JR

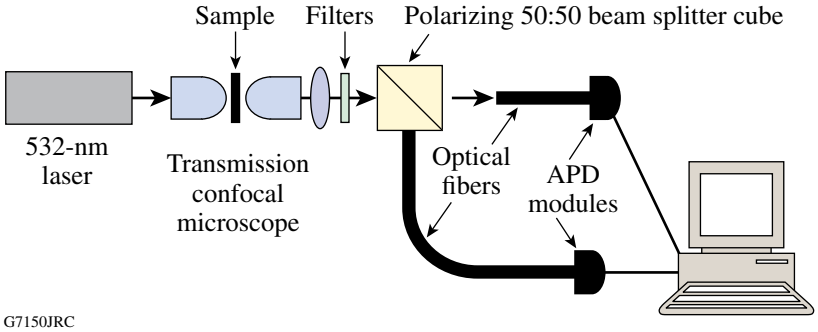
Figure 106.37
Near-field optical image of a 2-D photonic crystal self-assembly of a glassy cholesteric liquid crystal (5-μm × 5-μm scan).

dye molecules.[47–49] Single molecules of $DiIC_{18}(3)$ dye were embedded in a planar-aligned, glassy, *nematic* liquid crystal host and were aligned by liquid crystal molecules.

Experimental Setup

Single-molecule fluorescence microscopy was carried out on a Witec alpha-SNOM device in confocal transmission mode. Figure 106.38 shows the schematic of this experiment. The dye-doped liquid crystal sample was placed in the focal plane of a 1.4 numerical aperture, oil-immersion microscope objective. The sample was attached to a piezoelectric, XYZ translation stage. Light emitted by the sample was collected by a confocal setup using a 1.25 numerical aperture, oil-immersion objective with an aperture in the form of an optical fiber. The cw, spatially filtered (through a single-mode fiber), 532-nm, diode-pumped, Nd:YAG laser output excited single molecules. In focus, the intensities used were of the order of several kW/cm^2.

For polarized fluorescence measurements, we used a 50/50 polarizing beam splitter cube (as opposed to our antibunching correlation measurements,[35–37] in which a nonpolarizing beam splitter was used) with the confocal microscope apertures in the form of a 100-μm-core optical fiber placed in each arm of the beam splitter's output (Fig. 106.38). Residual transmitted excitation light was removed by two consecutive dielectric interference filters, yielding a combined rejection of better than 6 orders of magnitude at 532 nm.



G7150JRC

Figure 106.38
Experimental setup.

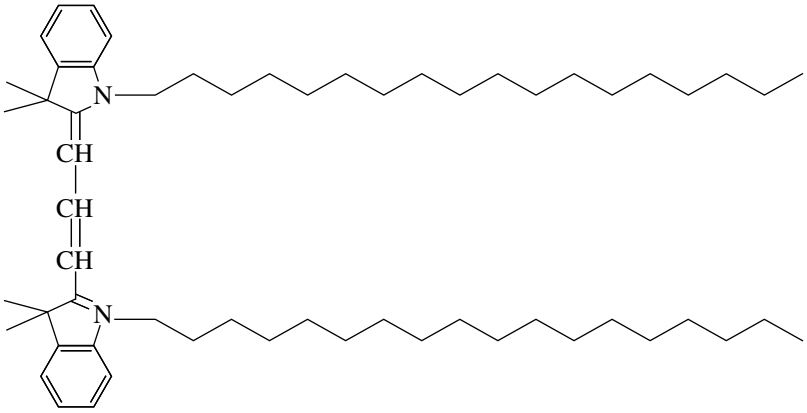
Photons in the two arms were detected by identical cooled avalanche photodiode modules (APD) in single-photon–counting Geiger mode (Perkin Elmer SPCM AQR-14).

Experimental Results: Deterministically Polarized Single-Molecule Fluorescence

For these experiments, we used $DiIC_{18}(3)$ dye (Fig. 106.39) in planar-aligned, glassy, nematic liquid crystal hosts[50] with a concentration of ~10^{-8} M. The nematic liquid crystal state of this material, which exists at elevated temperatures, is preserved at room temperature by slowly cooling the liquid crystal to the glassy state with frozen nematic order. We prepared ~100-nm-thick films of this glassy, nematic liquid crystal that was doped with dye molecules that were aligned deterministically through photoalignment using Staralign LPP coating and linearly polarized UV light. This new alignment technique prevents material contamination by particulates. We succeeded in the preparation of such an alignment over areas exceeding 10 mm × 10 mm (Refs. 47–49).

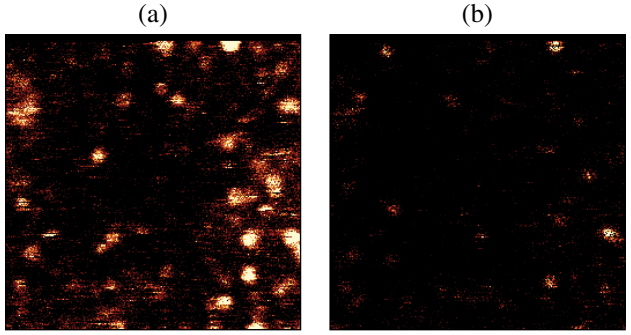
Figure 106.40 shows images of single-molecule fluorescence for polarization components (a) perpendicular and (b) parallel to the alignment direction under 532-nm cw excitation. These two components in the sample plane have been separated with a polarizing beam splitter cube (Fig. 106.38). Figure 106.40 clearly shows that for this sample, the polarization direction of the fluorescence of single molecules is predominantly in the direction perpendicular to the alignment of liquid crystal molecules. It is important that the background levels of Figs. 106.40(a) and 106.40(b) are the same (~10 counts/pixel or ~640 counts/s). The single-molecule fluorescence signal at maximum exceeds this background by up to 15 times.

The polarization anisotropy is defined here as $\rho = \left(I_{par} - I_{perp}\right)/\left(I_{par} + I_{perp}\right)$, where I_{par} and I_{perp} are fluorescence intensities for polarization components parallel and perpendicular to the alignment direction.[51] Processing the images in Fig. 106.40 shows that from a total of 38 molecules, 31 molecules have a negative ρ value (Fig. 106.41). The same



G7151JR

Figure 106.39
Molecular structure of $DiIC_{18}(3)$ dye.



G7152JRC

Figure 106.40
Confocal fluorescence microscopy images of $DiIC_{18}(3)$ single-molecule fluorescence in a planar-aligned, glassy, nematic liquid crystal host (10-μm × 10-μm scan): (a) polarization perpendicular to the alignment direction and (b) parallel polarization.

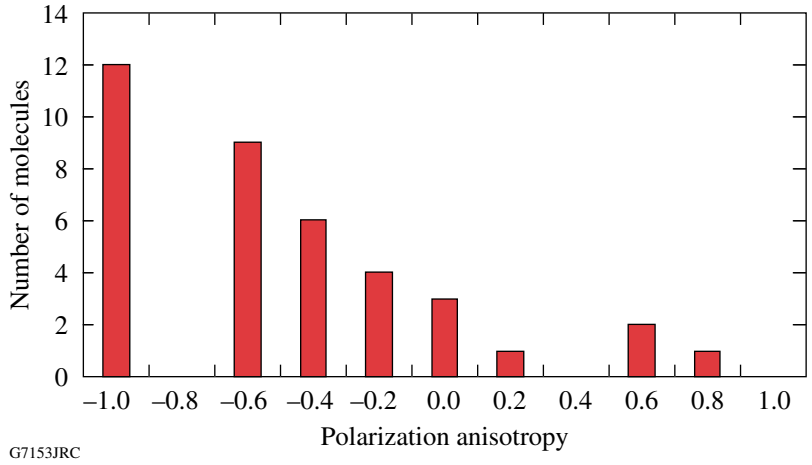


Figure 106.41
A histogram of the polarization anisotropy of 38 molecules of $DiIC_{18}(3)$ dye in a planar-aligned, glassy, nematic liquid crystal host.

sign of the polarization anisotropy was obtained in spectrofluorimeter measurements for a sample with a high (~0.5%) by weight concentration of the same dye in a planar-aligned, glassy, nematic liquid crystal layer that is ~4.1-μm thick [Fig. 106.42(a)]. Figure 106.42(b) shows *circular* polarized fluorescence from a planar-aligned, glassy, *chiral*-nematic (cholesteric) liquid crystal layer that is ~4.1-μm thick and has a 0.5% by weight concentration of $DiIC_{18}(3)$ dye.

This predominance of "perpendicular" polarization in Figs. 106.40, 106.41, and 106.42(a) can be explained by the $DiIC_{18}(3)$'s molecular structure (Fig. 106.39). The two alkyl chains likely orient themselves parallel to the rod-like liquid crystal molecules, but the emitting/absorbing dipoles that are nearly parallel to the bridge (perpendicular to alkyl chains) will be directed perpendicular to the liquid crystal alignment. $DiIC_{18}(3)$ molecules orient in the same manner in cell membranes.[52,53] It should be noted that in Ref. 54, single terrylene dye molecules were uniaxially oriented in rubbed polyethylene; however, this paper did not provide the results on deterministically polarized fluorescence of single molecules.

Note that the images in Fig. 106.40 were taken by raster scanning the sample relative to the stationary, focused laser beam. The scan direction was from left to right, line by line, from top to bottom. The size of the bright features is defined by the point-spread function of the focused laser beam. These images not only contain information about the spatial position of the fluorescent molecules, but also about the changes of their fluorescence in time. Dark horizontal stripes and bright semicircles instead of circles represent the blinking and bleaching of the molecules in time. Blinking and bleaching are a common single-molecule phenomenon and convincing evidence of the single-photon nature of the source. The explanation of the nature of the long-

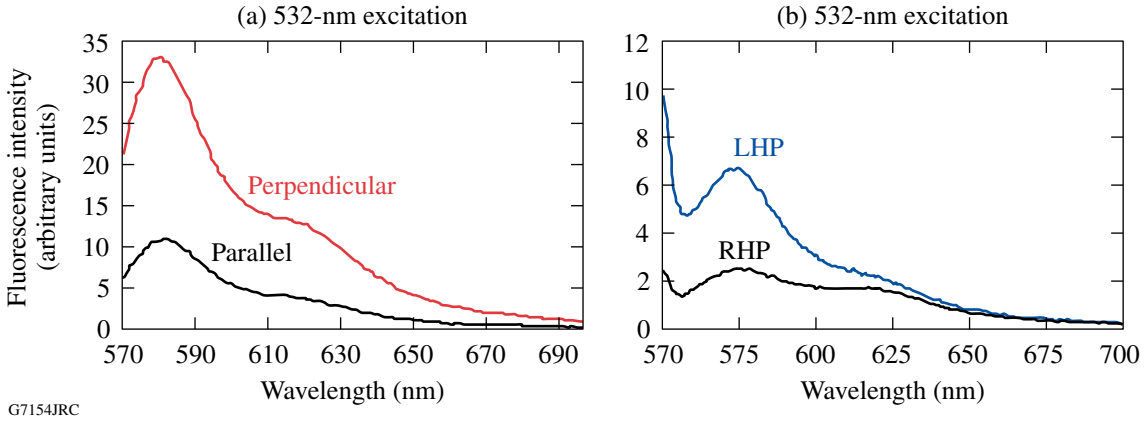


Figure 106.42
Spectrofluorimeter measurements of a polarized fluorescence of $DiIC_{18}(3)$ dye doped in planar-aligned, glassy, liquid crystal hosts under excitation with a nonpolarized, 532-nm light. (a) Fluorescence spectra in a nematic host for different linear polarizations. (b) Fluorescence spectra in a cholesteric host for circular polarization of different handedness.

time blinking from milliseconds to several seconds remains a subject of debate in the literature (see, e.g., Ref. 55).

The maximum count rate of single-molecule images was approximately 10 kcounts/s (~160 counts/pixel with ~4 s per line scan, 256 pixels per line) with a fluorescence molecule lifetime of approximately several nanoseconds. Note that the detector dark counts were fewer than 100 counts/s.

Seven molecules in Figs. 106.40 and 106.41 have either positive or zero anisotropy. These molecules can be either a small amount of impurities in the Staralign photoalignment agent, which have not been bleached even after the UV irradiation of Staralign-coated slips, or impurities of the glassy oligomer host.[56] Figure 106.43(a) shows single-molecule fluorescence images of the Staralign photoalignment agent before UV irradiation. The single-molecule fluorescence microscopy method is very sensitive to material impurities. We sometimes observed single-molecule fluorescence from the impurities in glassy LC oligomers [Fig. 106.43(b)] even when a chromatographic analysis did not detect them. For this reason, the Polyimide and Nylon 6/6 thin films usually used for buffing alignment were not utilized in our experiments because of the finding that they possess a higher fluorescence count rate than single molecules of fluorescence dyes.

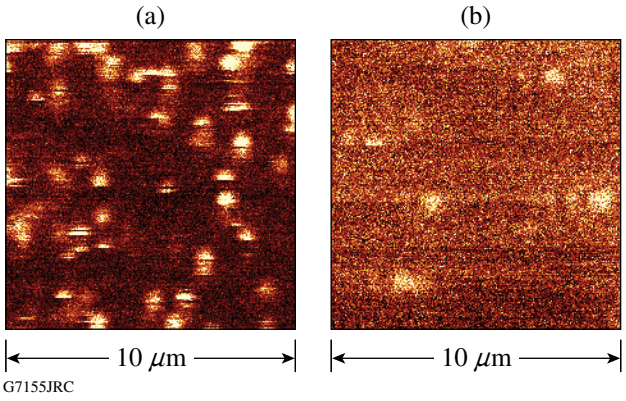


Figure 106.43
Parasitic fluorescence from single-molecule impurities in the Staralign photoalignment agent without (a) UV treatment and (b) undoped oligomer material.

Conclusions

This article shows the advantages of using liquid crystals as the hosts for single-photon sources; deterministically polarized fluorescence from single emitters embedded in liquid crystal hosts was demonstrated for the first time at room temperature. Single-dye molecules were deterministically aligned by liquid crystal molecules in one direction and produced deterministically linearly polarized single photons.

Circularly polarized single photons with deterministic handedness [see, e.g., Fig. 160.42(b) for a high dye concentration] can be produced efficiently using 1-D photonic band gaps in cholesteric liquid crystals matching the dye-fluorescence band. We hope to increase SPS efficiency in cholesteric liquid crystal, 1-D photonic-band-gap structures from the current 4% to at least 40% (see Ref. 35) to narrow the fluorescence bandwidth (to ~1 to 10 nm) and decrease the fluorescent lifetime from a few nanoseconds to the hundreds of picoseconds necessary for high-speed communications. One-dimensional photonic band-gap structures in cholesteric liquid crystals, 2-D/3-D photonic crystals in holographic polymer-dispersed liquid crystals,[57] a 3-D photonic crystal structure of a liquid crystal blue phase,[58] and photonic crystals/microstructured fibers infiltrated with liquid crystals[59,60] may be prepared for this purpose. By using various fluorescence emitters [dye molecules, colloidal semiconductor nanocrystals (dots and rods), carbon nanotubes, and rare-earth ions], it will be possible to extend the working region of the source from the visible to communication wavelengths (1.3 and 1.55 μm).

ACKNOWLEDGEMENT

The authors acknowledge the support by the U.S. ARO under Award No. DAAD19-02-1-0285, NSF Awards ECS-0420888, EEC-0243779, PHY-0242483, and the U.S. Department of Energy Office of Inertial Confinement Fusion Award under Cooperative Agreement No. DE-FC52-92SF19460. The receipt of liquid crystals from Prof. S.-H. Chen is gratefully acknowledged. The authors thank L. Novotny, A. Lieb, A. Trajkovska, and S. Culligan for advice and help; S. Papernov for help in AFM imaging; and J. Dowling for the discussion that provided a better understanding of the fluorescence in chiral-nematic structures.

REFERENCES

1. Y. Yamamoto *et al.*, Prog. Informatics, No. 1, 5 (2005).
2. B. Lounis and M. Orrit, Rep. Prog. Phys. **68**, 1129 (2005).
3. P. Kumar *et al.*, Quantum Information Processing **3**, 215 (2004).
4. P. Grangier, B. Sanders, and J. Vućković, eds., New J. Phys. **6** (2004).
5. A. Kuhn, M. Hennrich, and G. Rempe, Phys. Rev. Lett. **89**, 067901 (2002).
6. J. McKeever *et al.*, Science **303**, 1992 (2004).
7. Ch. Schwedes *et al.*, Phys. Rev. A **69**, 053412 (2004).
8. C. Brunel *et al.*, Phys. Rev. Lett. **83**, 2722 (1999).
9. B. Lounis and W. E. Moerner, Nature **407**, 491 (2000).
10. F. Treussart *et al.*, Phys. Rev. Lett. **89**, 093601 (2002).
11. A. Beveratos *et al.*, Eur. Phys. J. D **18**, 191 (2002).

12. A. Imamoglu and Y. Yamamoto, Phys. Rev. Lett. **72**, 210 (1994).
13. J. Kim *et al*., Nature **397**, 500 (1999).
14. E. Moreau *et al*., Appl. Phys. Lett. **79**, 2865 (2001).
15. P. Michler *et al*., Science **290**, 2282 (2000).
16. C. Santori *et al*., Phys. Rev. Lett. **86**, 1502 (2001).
17. J. Vućković *et al*., Appl. Phys. Lett. **82**, 3596 (2003).
18. C. Santori, D. Fattal, and J. Vućković, Nature **419**, 594 (2002).
19. W.-H. Chang *et al*., Phys. Rev. Lett. **96**, 117401 (2006).
20. V. Zwiller *et al*., Appl. Phys. Lett. **78**, 2476 (2001).
21. Z. Yuan *et al*., Science **295**, 102 (2001).
22. G. S. Solomon, M. Pelton, and Y. Yamamoto, Phys. Rev. Lett. **86**, 3903 (2001).
23. B. Gayral *et al*., Appl. Phys. Lett. **72**, 1421 (1998).
24. D. Englund *et al*., Phys. Rev. Lett. **95**, 013904 (2005).
25. A. Daraei *et al*., Appl. Phys. Lett. **88**, 051113 (2006).
26. D. C. Unitt *et al*., Phys. Rev. B **72**, 033318 (2005).
27. C. Santori *et al*., New J. Phys. **6**, 89 (2004).
28. M. Benyoucef *et al*., New J. Phys. **6**, 91 (2004).
29. W. P. Ambrose *et al*., Chem. Phys. Lett. **269**, 365 (1997).
30. L. Fleury *et al*., Phys. Rev. Lett. **84**, 1148 (2000).
31. F. Treussart *et al*., Opt. Lett. **26**, 1504 (2001).
32. P. Kumar *et al*., J. Am. Chem. Soc. **126**, 3376 (2004).
33. C. W. Hollars, S. M. Lane, and T. Huser, Chem. Phys. Lett. **370**, 393 (2003).
34. D. A. Bussian *et al*., Chem. Phys. Lett. **388**, 181 (2004).
35. S. G. Lukishova, A. W. Schmid, A. J. McNamara, R. W. Boyd, and C. R. Stroud, Jr., IEEE J. Sel. Top. Quantum Electron. **9**, 1512 (2003).
36. S. G. Lukishova, A. W. Schmid, C. M. Supranowitz, N. Lippa, A. J. McNamara, R. W. Boyd, and C. R. Stroud, Jr., J. Mod. Opt. **51**, 1535 (2004).
37. *LLE Review Quarterly Report* **94**, 97, Laboratory for Laser Energetics, University of Rochester, Rochester, NY, LLE Document No. DOE/SF/19460/485, NTIS Order No. PB2006-106666 (2003). Copies may be obtained from the National Technical Information Service, Springfield, VA 22161.
38. B. Lounis *et al*., Chem. Phys. Lett. **329**, 399 (2000).
39. G. Messin, Opt. Lett. **26**, 1891 (2001).
40. A. Beveratos *et al*. Phys. Rev. Lett. **89**, 187901 (2002).
41. C. Kurtsiefer *et al*., Phys. Rev. Lett. **85**, 290 (2000).
42. R. Brouri *et al*., Opt. Lett. **25**, 1294 (2000).
43. A. Beveratos *et al*., Phys. Rev. A **64**, 061802(R) (2001).
44. I. Fushman, D. Englund, and J. Vućković, Appl. Phys. Lett. **87**, 241102 (2005).
45. M. Steiner *et al*., ChemPhysChem **6**, 2190 (2005).
46. S. G. Lukishova and A. W. Schmid, "Near-Field Optical Microscopy of Cholesteric Oligomeric Liquid Crystal Layers," to be published in Molecular Crystals and Liquid Crystals.
47. S. G. Lukishova, A. W. Schmid, R. Knox, P. Freivald, R. W. Boyd, and C. R. Stroud, Jr., presented at Quantum Optics II, Cozumel, Mexico, 6–9 December 2004. For presentation see http://speckle.inaoep.mx/QOII/ppts/Lukishova.pdf.
48. S. G. Lukishova, A. W. Schmid, R. Knox, P. Freivald, R. W. Boyd, C. R. Stroud, Jr., and K. L. Marshall, in *Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science and Photonic Applications, Systems and Technologies 2005* (Optical Society of America, Washington, DC, 2005), Paper QTuE6.
49. S. G. Lukishova, A. W. Schmid, R. Knox, P. Freivald, R. W. Boyd, C. R. Stroud, Jr., and K. L. Marshall, presented at IQEC/CLEO 2005, Tokyo, Japan, 11–15 July 2005 (Paper JWH1-2).
50. H. M. P. Chen, D. Katsis, and S. H. Chen, Chem. Mater. **15**, 2534 (2003).
51. I. Chung, K. T. Shimizu, and M. G. Bawendi, Proc. Natl. Acad. Sci. USA **100**, 405 (2003).
52. B. C. Stevens and T. Ha, J. Chem. Phys. **120**, 3030 (2004).
53. D. Axelrod, Biophys. J. **26**, 557 (1979).
54. J. Y. Butter *et al*., ChemPhysChem **7**, 261 (2006).
55. F. Vargas *et al*., J. Chem. Phys. **117**, 866 (2002).
56. S. G. Lukishova, A. W. Schmid, R. P. Knox, P. Freivald, A. McNamara, R. W. Boyd, C. R. Stroud, Jr., and K. L. Marshall, "Single-Photon Source for Quantum Information Based on Single Dye Molecule Fluorescence in Liquid Crystal Host," to be published in Molecular Crystals and Liquid Crystals.
57. M. J. Escuti, J. Qi, and G. P. Crawford, Opt. Lett. **28**, 522 (2003).
58. W. Cao *et al*., Nature Materials **1**, 111 (2002).
59. E. Yablonovitch, Nature **401**, 539 (1999).
60. T. Larsen *et al*., Opt. Express **11**, 2589 (2003).