Liquid Crystal Gel-Dispersed Quantum Dots: Reversible Modulation of Photoluminescence Intensity Using An Electric Field

Xia Tong and Yue Zhao[*]

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

1) Experimental Details

The synthesis of the gelator G1 was previously reported.[1] The nematic E7, the chiral dopant R811 and the LC diacrylate monomer RM257 were purchased from Merck, the photoinitiator BME from Aldrich and the core-shell CdSe/ZnS quantum dots from Evident Technologies. To prepare a homogeneous mixture of cholesteric liquid crystal (CLC, E7 doped with 5% of R811) with QD and G1, G1 and CLC were first dissolved in the toluene solution of CdSe/ZnS (the QD came in toluene). After evaporation of toluene under reduced pressure, the mixture was redissolved in THF with stirring at a total concentration of about 1%. The solution was solicited for ~ 10 s before THF was removed by evaporation under reduced pressure. We found that the additional step of re-dissolving the mixture in THF resulted in a more homogeneous dispersion of QD. To enter the mixture in an ITO-coated cell (50 μm gap), it was warmed to 60 ^{o}C and flow-filled into the cell through capillary effect. To obtain the physical network formed by fibrous aggregates of G1 in the CLC-dispersed QD within the homeotropic LC orientation, the cell was heated to 65 ^{o}C for 5 min, and then cooled to 50 ^{o}C, at which CLC was in its chiral nematic phase while the gelator G1 remained dissolved in the CLC host (no aggregation). An electric field (a.c., 1000 Hz, 100 V, rms) was applied to align LC molecules before the mixture was cooled slowly to room temperature under voltage. Here we mention that there are no special reasons for the choice of G1 (an azo-gelator). In principle, any LC gelators could work. The only condition of obtaining a physical network formed in the homeotropic LC texture is that the aggregation temperature of the gelator at a given concentration should be lower than the isotropic-to-nematic phase transition temperature of the LC host on cooling. In the case of the mixture of CLC (E7 doped with 3% of R811) with QD, LC diacrylate monomer and BME, a similar preparation procedure was employed. To obtain a crosslinked polymer that stabilizes the planar texture of CLC, the mixture in an ITO-coated cell (25 μm gap) was placed inside a microscope hotstage (Instec) and held at 30 ^{o}C to allow the planar texture to develop. After the planar texture was observed on a polarizing optical microscope, the mixture was exposed to low-intensity UV light (~ 340 nm, 0.07 mW cm^{-2}) for 8 h for the photopolymerization of the monomer. The whole process was performed under nitrogen atmosphere. The reason of using a CLC in this study is as follows. On one hand, the formation of a self-assembled physical network in a CLC under the homeotropic LC texture was found to generate a larger contrast of optical transmittance between the field-off and field-on states than using simple nematic LCs.[2] This is important in order to obtain a large contrast of photoluminescence intensity of QD due to the scattering-based mechanism. On the other hand, for the reverse mode of modulation, we need a transparent state at field-off and a scattering state at field-on. We were aware of the possibility of using a polymer-stabilized homogeneous planar texture, formed by CLC, for the transparent state at field-off and its destabilization-induced scattering state at field-on.[3]

Steady-state fluorescence emission spectra (excitation at 490 nm) were recorded on a SPEX 1680 double-monochromator spectrophotometer, slit widths being set to 10-nm band-pass for both excitation

and emission. For these measurements, the cell containing the LCGDQD was positioned with its normal making an angle of 45° to the excitation beam and 135° to the emission path to the detector.[2] Optical transmittance of the LC gels was measured using a probe light from a low-power He-Ne laser (633 nm, 4 mW), with a high-speed photodetector (Displaytech) connected to a digital oscilloscope (Tektronix, TDS 420A). For the measurements of electrical switching of photoluminescence, a high-voltage waveform generator (WFG500, FLC Electronics) was used to apply an a.c. field (1000 Hz, sinusoidal) through the cell. For the measurements of the switching times, a square-wave field (200 ms duration) was utilized. The LCGDQD samples were observed on a polarizing optical microscope (Leica-MP) and a fluorescence microscope (Leica DMRX) equipped with an excitation filter of 450-490 nm and detection >510 nm. For all fluorescence measurements in this study, unpolarized excitation beam was utilized. The polarization of the excitation light may be an interesting variable to be used to affect the scattering efficiency if incident light of different polarizations feels different refractive index variations in the material. This is not the case here with spherical QDs and the LC textures whose changes in refractive index at the field-off and field-on states are not sensitive to the polarization of the excitation beam.

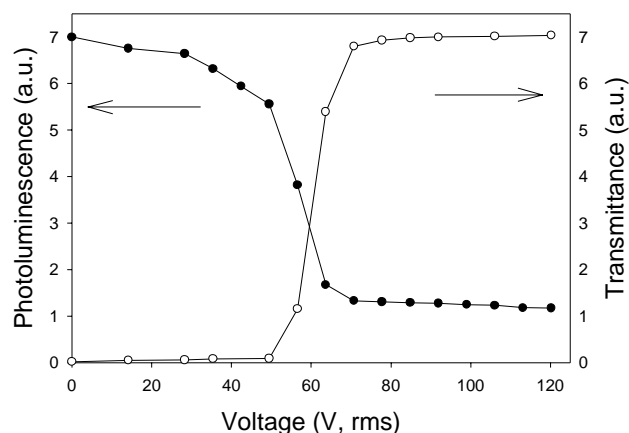## 2) Additional Results for LCGDQD with A Self-Assembled Physical Network

Figure S1

Figure S1 shows the plots of photoluminescence (measured at 610 nm with λ_{ex}=490 nm) and optical transmittance (measured using a probe light at λ=633 nm) vs. applied voltage (rms) for a sample containing 0.2% of CdSe/ZnS QD and 1% of gelator (in a 50-μm gap cell). The data clearly show that as the transmittance goes up, as a result of the electric field-induced LC orientation, the fluorescence intensity of QD goes down.
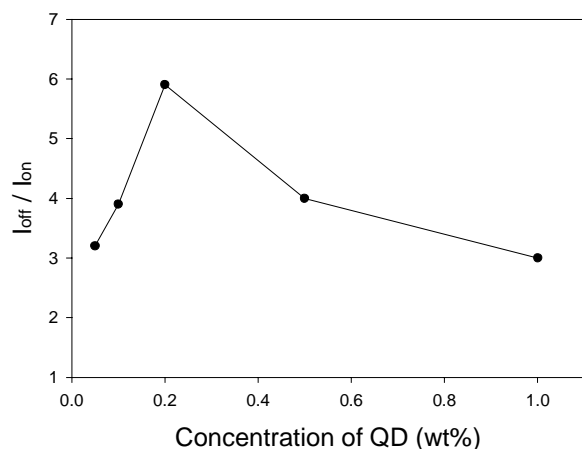
Figure S2

Figure S2 is the plot of the fluorescence emission contrast ratio, defined as the high intensity at field-off over the low intensity at field-on (2.4 V μm^{-1}, rms), as a function of the concentration of CdSe/ZnS with the same amount of gelator at 1%. The results show that the contrast decreases when the concentration of QD is above or below 0.2%. An increased agglomeration of QD at higher concentrations is likely to be the cause, while at lower concentrations the different internal scattering seems to be unable to generate a high contrast despite the good dispersion. The optimal amount of QD for high contrast ratio should be related to the concentration and morphology of the physical network as well as the dispersion state of QD.
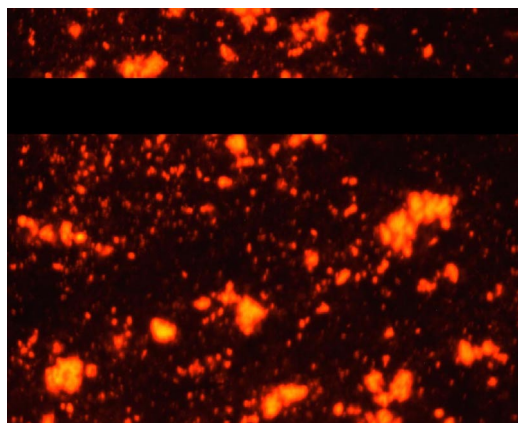

Figure S3

Figure S3 is a fluorescence microscope image (340×412 μm) of the LCGDQD containing 0.2% of CdSe/ZnS. Aggregates of the fluorescent QD of variable sizes can be noticed.
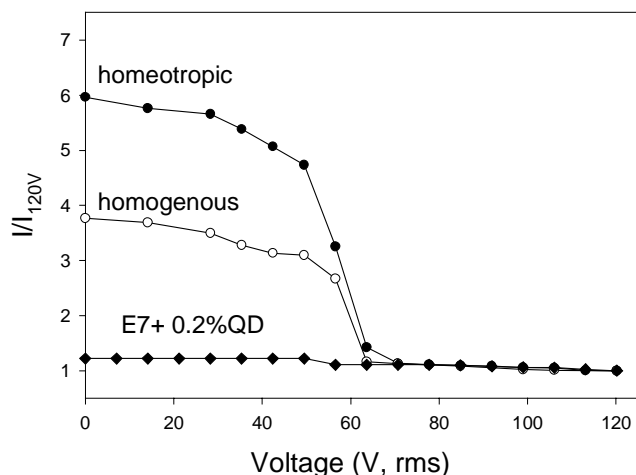
Figure S4

Figure S4 compares the change in fluorescence intensity normalized to that at 120 V vs. voltage for LCGDQD (0.2% of QD) prepared with the gelation occurred under the homeotropic and homogeneous (in plane) LC orientational states, and for E7 with 0.2% of QD without the gelator. The LCGDQD sample with the physical network of fibrous aggregates formed within the homogeneous LC texture (cooling from the isotropic phase without applying an electric field) is less scattering at the field-off state, which results in lower fluorescence emission than the sample prepared under the homeotropic LC texture. The QD dispersion in E7 without the gelator forming the physical network is not scattering and changes little the optical transmittance with voltage; consequently, no fluorescence amplification and no intensity modulation of CdSe/ZnS can be observed. Similar results were observed for doped E7 (CLC) without the gelator. The physical network formed by the nanofibres of the gelator is crucial to create the highly scattering LC in the cell at the field-off state.
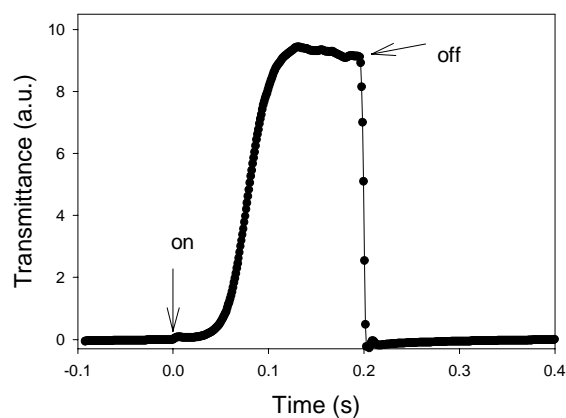

Figure S5

Figure S5 shows the electrooptical response of the sample in Fig. S1 upon application of a square-wave electric field between 0 and 100 V (200 ms duration). The realignment of LC molecules along the field direction gives rise to the rise in transmittance, while after removal of the field the transmittance drops due to the relaxation of LC molecules. The transmittance rise-time and drop-time, defined as the time required for change between 10 and 90% of the final and of the initial level, respectively, are 45 and 4 ms respectively. These are the switching times for the electrical modulation of the photoluminescence intensity of CdSe/ZnS in the LCGDQD.

3) Additional Results for LCGDQD with A Covalently Crosslinked Polymer
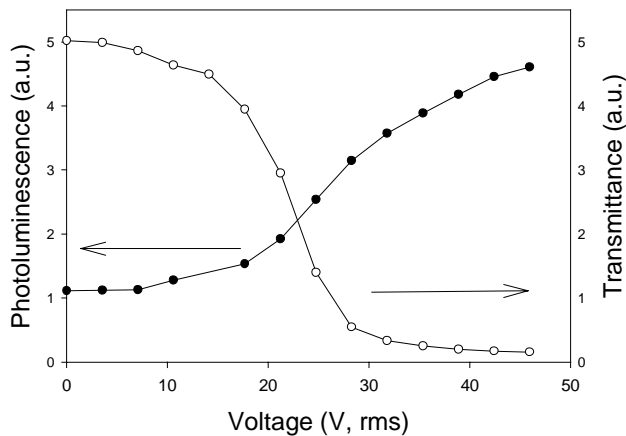

Figure S6

Figure S6 shows the plots of photoluminescence (measured at 604 nm with λ_{ex}=490 nm) and optical transmittance (measured using a probe light at λ=633 nm) vs. applied voltage (rms) for a sample containing 0.02% of CdSe/ZnS QD and 7% of crosslinked polymer (in a 25-μm gap cell). Contrary to the sample in Fig.S1, the transmittance drops as the planar texture of the CLC is destabilized by the electric field. This is accompanied by the rise of the fluorescence intensity. As compared to Fig. S1, the smaller contrast ratio of optical transmittance at field-off and field-on accounts for the smaller change in fluorescence intensity.
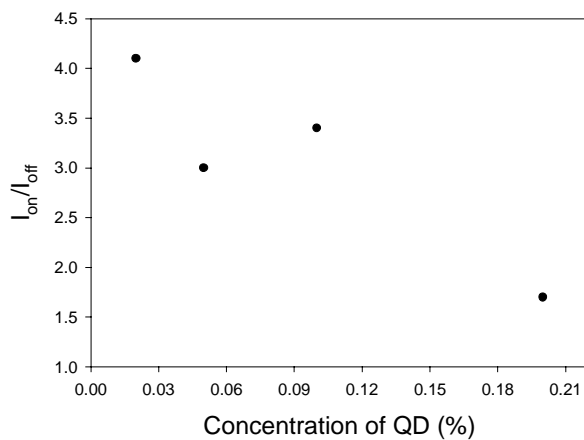

Figure S7

Figure S7 is the plot of the fluorescence emission contrast ratio, defined as the high intensity at field-on over the low intensity at field-off (1.84 V μm^{-1}, rms), as a function of the concentration of CdSe/ZnS with the same amount of crosslinked polymer at 7%. As compared to LCGDQD with a self-assembled network, much lower concentrations of CdSe/ZnS are needed to obtain a significant modulation. A uniform dispersion of QD is more difficult to achieve in this mixture.
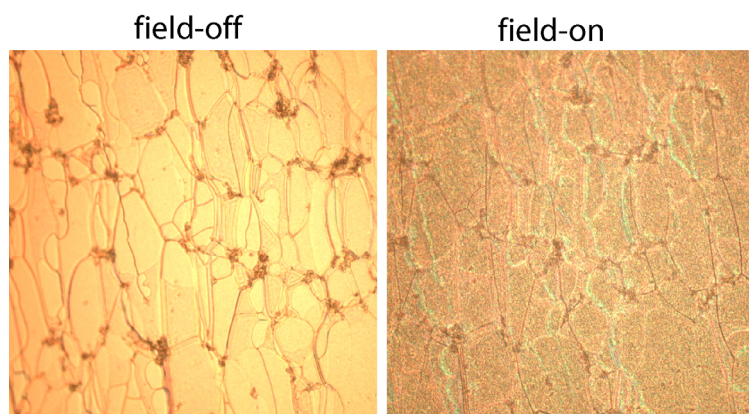
field-off   field-on

Figure S8

The polarizing optical micrographs in Figure S8 show the planar texture of CLC stabilized by the crosslinked polymer (7%) at the field-off state and the destabilization upon application of a voltage (2 V μm^{-1}). Due to the very low concentration of CdSe/ZnS QD in the mixture (0.02%), the dispersion of QD could not clearly be seen on a fluorescence microscope like in Fig. S3. Image area: 690×690 μm.
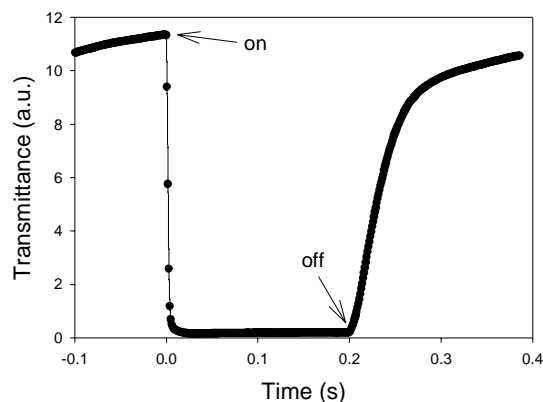

Figure S9

Figure S9 shows the electrooptical response of the sample in Fig. S6 upon application of a square-wave electric field between 0 and 50 V (200 ms duration). The destabilization of the planar texture results in the fast drop of the transmittance, while after removal of the voltage the planar texture can be recovered, but more slowly. The transmittance fall-time and rise-time, defined as the time required for change between 10 and 90% of the initial and of the final level, respectively, are 3 and 78 ms respectively.

References
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(3) Yang, D.-K.; Chien, L.-C.; Fung, Y. K. In *Liquid Crystals in Complex Geometries Formed by Polymers and Porous Networks*; Crawford, G. P.; Zumer, S. Ed.; Tayer&Francis Publishers, London, 1996, pp 103-142.
(4) C. Sanchez, B. Villacampa, R. Cases, R. Alcala, C. Martinez, L. Oriol, M. Pinol, *J. Appl. Phys.* **2000**, *87*, 274.