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

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In a recent paper[1] we reported the discovery that a fluorescent self-assembled liquid-crystal gel (LCG) can have its fluorescence intensity modulated through electric-field-controlled LC orientation. The fluorescence came from the fibrous aggregates formed by a gelator exhibiting the unusual aggregation-induced enhanced emission.[2] The LC orientational state-controlled internal scattering of the excitation light has been suggested to be at the origin of the phenomenon. In the present study, we have applied the suggested mechanism to liquid-crystal gel-dispersed quantum dots (LCGDQD) and achieved the reversible electrical modulation and switching of the photoluminescence intensity of QD. We demonstrate that by controlling the LC orientational state with the use of either a self-assembled physical network or a covalently crosslinked polymer, it is possible to switch the photoluminescence of QD in two different ways, namely, switching between high intensity at field-off and low intensity at field-on, and vice versa. In view of the considerable interest in the photoluminescence of QD for a broad range of applications, our study on LCGDQD introduces a general approach of controlling the emission intensity of QD by means of an electric field. This may open the door to new exploitation for applications of QD such as emission-based liquid-crystal display (LCD).

The compounds used are shown in Figure 1. A cholesteric liquid crystal (CLC) was obtained by doping the nematic E7 with 3−5% of a chiral dopant R811 (both from Merck). E7 has a nematic−isotropic transition temperature $T_{ni} = 60$ °C. A gelator, G1,[3] and a LC diacrylate monomer, RM257 (Merck), were utilized for obtaining a self-assembled physical network and a crosslinked polymer in the CLC/QD dispersion, respectively. The QD used was the core−shell CdSe/ZnS nanocrystals (diameter ≈ 4 nm) having the fluorescence emission maximum at ~600 nm in toluene (Evident Technologies). We have first prepared LCGDQD whose emission intensity can be diminished by an electric field. Figure 2 shows how this was achieved. In the example, a homogeneous mixture of G1 (1 wt %), QD (0.2%), and CLC (98.8%) was obtained (see Supporting Information for preparation conditions). The mixture warmed at ~60 °C was flow-filled into a nonrubbed, indium tin oxide (ITO)-coated cell with a gap of 50 μm (E.H.C. Japan). After being heated to 65 °C (in the isotropic phase of CLC), it was cooled to the chiral nematic phase at 50 °C and a voltage (2.4 V μm^{-1}, rms) was applied to align LC molecules perpendicularly to the substrate surfaces (homeotropic orientational state). At this point, the gelator remained soluble in the CLC. Then, under voltage the mixture was cooled to room temperature to allow the aggregation of gelator molecules to form a physical network of fibrous aggregates[4,5] within the homeotropic LC orientational state. While turning off the electric field, LC molecules relaxed, and randomly aligned LC domains in the presence of the physical network gave rise to a highly scattering LCGDQD; the cell appeared opaque. Upon application of a voltage, the sample became transparent as LC molecules were realigned by the electric field (Figure 2a). The
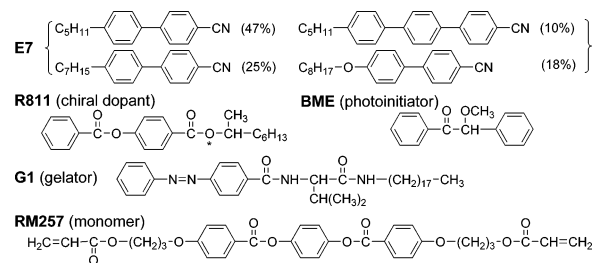

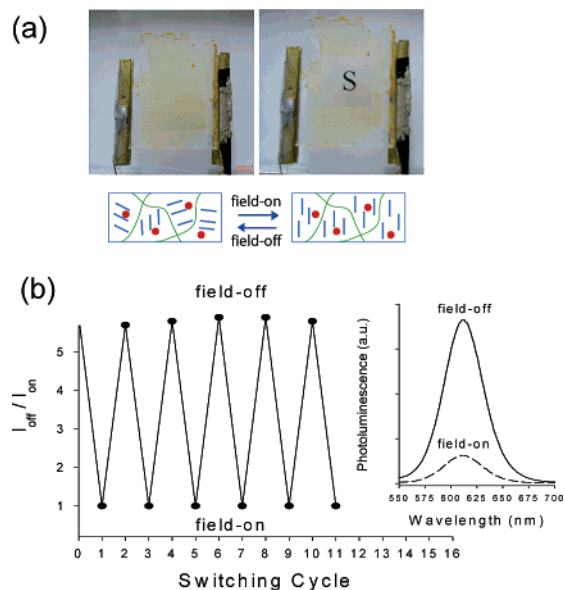**Figure 1.** Chemical structures of the used compounds.

Figure 2. LCGDQD with a self-assembled physical network: (a) photos and the schematic showing the electrically controlled liquid-crystal orientation and the resultant change in transparency (scattering at the field-off state); (b) reversible switching of photoluminescence intensity of CdSe/ZnS (measured at 610 nm, $\lambda_{ex} = 490$ nm); the inset shows the emission spectra at field-off (0 V) and field-on (2.4 V μm^{-1}, rms).

reversible change in the LC orientational state, viewed along the field direction (cross section of the cell), is schematized. The inset in Figure 2b, shows the corresponding fluorescence emission spectra ($\lambda_{ex} = 490$ nm). The emission intensity of CdSe/ZnS QD dispersed in the CLC at the field-off state is six times greater than that in the field-on state. The reversible switching of intensity in response to several cycles of field-off (0 V) and field-on (2.4 V μm^{-1}) is shown. This modulation of photoluminescence intensity of CdSe/ZnS is due to the different internal scattering of the excitation light. At the highly scattering state, excitation photons undergo multiple scattering before they can get out of the cell, which increases the probability for them to hit and be absorbed by the dispersed QD. At the transparent state, most photons go straight through the cell, reducing the probability for the QD to be excited. By varying the
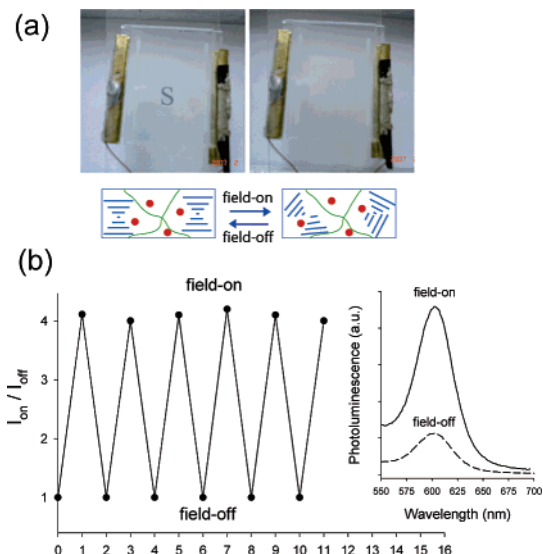
Figure 3. LCGDQD with a crosslinked polymer: (a) photos and the schematic showing the electrically changeable liquid-crystal orientation and the resultant change in transparency (scattering at the field-on state); (b) reversible switching of photoluminescence intensity of CdSe/ZnS (measured at 604 nm, $\lambda_{ex} = 490$ nm); the inset shows the emission spectra at field-off (0 V) and field-on (1.84 V μm^{-1}, rms).

voltage, the fluorescence intensity can be set to any intermediate values (Supporting Information). The excitation wavelength of 490 nm was chosen to minimize the possible interference from CLC and the gelator.

To reverse the modulation of the photoluminescence intensity of QD, that is, to increase the intensity upon application of a voltage, the electrooptical response of the LCGDQD should be reversed. It needs to be transparent at field-off and opaque at field-on. Figure 3 explains the way to achieve this control and shows an example of the results. Here we prepared a dispersion of CdSe/ZnS QD in a polymer-stabilized CLC. Instead of a self-assembled physical network, a covalently crosslinked polymer was utilized. In this case, a homogeneous mixture comprising CLC (91.48%), RM257 (7%), MBE (1.5%), and CdSe/ZnS QD (0.02%) was prepared and introduced into a rubbed, ITO-coated cell with a gap of 25 μm. Upon the formation of the planar texture by the CLC at 30 °C, in which the helices formed by LC molecules are aligned perpendicular to the substrate surfaces, the mixture was exposed to UV light ($\sim$340 nm, 0.07 mW cm^{-2}) for 8 h to photopolymerize the LC monomer. After subsequent cooling to room temperature, the LCGDQD remained transparent due to the stabilization of the homogeneous planar texture by the covalent polymer network.[6] Upon application of a voltage, the helices are destabilized resulting in a highly scattering state. The photos in Figure 3a show the opposite change in transparency as compared to the sample in Figure 2. Likewise, the reversible change in the LC orientational state is schematized. Indeed, the fluorescence emission spectra of this LCGDQD (inset of Figure 3b) confirmed the reverse intensity modulation. The emission intensity increased fourfold upon application of a voltage (1.84 V μm^{-1}). The repeated switching over several cycles of field-off (0 V) and field-on (1.84 V μm^{-1}) is shown in Figure 3b.

The photoluminescence switching times of LCGDQD are determined by the switching times of LC molecules between the field-off and field-on states. For the sample in Figure 2, the

photoluminescence drop-time (field-on) was $\sim$45 ms and the rise-time (field-off) was 4 ms. For the sample in Figure 3, the rise-time (field-on) was $\sim$3 ms while the drop-time (field-off) was 78 ms. In both cases, the disordering of CLC texture leading to the scattering state is much faster than the ordering process. We have also investigated the effects of a number of variables for the two types of LCGDQD, (Supporting Information). A uniform QD dispersion in LC was a particular concern, and we had to keep the concentration of CdSe/ZnS QD low. It is conceivable that if the QD is decorated with a molecule that promotes the miscibility in LC, higher concentrations can be used. On the other hand, the contrast ratio of photoluminescence between field-off and field-on can be optimized by exploiting the extensive knowledge about LCD regarding the contrast ratio of optical transmittance. The lowest photoluminescence is expected with the highest transmittance (minimized internal scattering and excitation of QD), while the strongest photoluminescence should be obtained with the lowest transmittance (maximized internal scattering and excitation of QD). If the LC texture can be configured to effectively confine or to hold as long as possible the excitation light through multiple internal scattering, an even larger amplification of the photoluminescence intensity of QD can be obtained.

To summarize, we present the first study of using the electric-field controllable LC orientation to modulate and switch the photoluminescence intensity of QD. By using a self-assembled physical network and a covalently crosslinked polymer to configure the changes in the LC orientational state in response to an electric field, we succeeded in demonstrating two ways of switching the photoluminescence of CdSe/ZnS QD dispersed in a CLC. By virtue of the internal scattering-based mechanism, the approach obviously is general and can easily be applied to other QD and other systems such as nanorods and dyes. With QD of various sizes (thus various emission wavelengths), it would be possible to obtain white-light emission of electrically switchable intensity. Study is underway in our laboratory to exploit the many ways of switching LC orientational state to achieve the control of photoluminescence emission.

Supporting Information Available: Experimental details, fluorescence and polarizing optical microscope images, switching time measurements, and more data on the electrical modulation of photoluminescence intensity. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0711720