

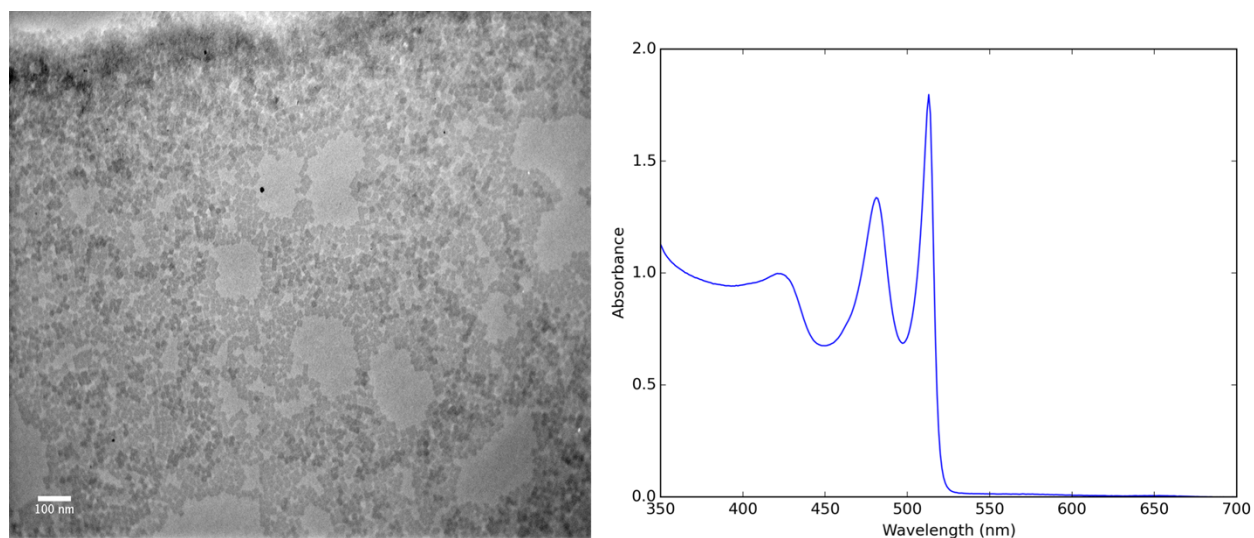
# Strain-controlled fluorescence polarization in a CdSe nanoplatelet / block copolymer composite.

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## Materials

The CdSe nanoplatelets synthesized for this study were synthesized as follows: 0.234 g of cadmium myristate and 0.024 g of selenium powder were mixed with 30 mL of octadecene in a three-neck round-bottom flask equipped with a condenser, a septum and a temperature controller. Under magnetic agitation, the mixture was then degassed under vacuum for 30 minutes and heated from ambient temperature to 240°C. When the temperature reached 200°C (after about 6 min 30 s), 0.160 g of cadmium acetate (in powder) was added to the solution after withdrawing the septum. When the salt is poured into the solution, the color of the solution turns from yellow to red. After 12 min at 240°C, heating was stopped and 1 mL of oleic acid was added. At this stage, the solution contained, as shown by UV-vis absorption, three populations of nanoparticles: platelets emitting at 460 nm, platelets emitting at 510 nm and quantum dots. To isolate the platelets emitting at 510 nm, a series of selective precipitation/centrifugation steps was performed. The raw product was separated in two centrifuge tubes and 20 mL of ethanol was added to each of the tubes. After centrifugation for 10 min at 5000 tr/min, the supernatant contained quantum dots while the precipitate contained only platelets. The latter was re-dispersed in hexane and this solution was centrifuged at 3000 tr/min for 10 minutes. The supernatant only contained platelets emitting at 510 nm while the larger platelets emitting at 460 nm precipitated. At last, ethanol was added to the solution to make the platelets precipitate, the supernatant was discarded and the precipitate was redispersed in hexane. The absorbance spectrum (figure S1) of the dispersion shows its purity with only one population of platelets 1.2 nm thick (4 CdSe monolayers)<sup>1</sup>. TEM examination shows a roughly square shape with an edge length close to 10 nm (figure S1).



**Figure 1: left: TEM image of the nanoplatelet dispersion before insertion in the copolymer. Right: absorbance spectrum of the platelet dispersion**

SBS is a triblock copolymer commercially available from PolymerSource (QC, Canada) with a narrow polydispersity index (PDI) of 1.04 and almost equal molecular weights of PS ( $39.7 \text{ kg.mol}^{-1}$ ) and PB ( $41.0 \text{ kg.mol}^{-1}$ ). This molecular weight composition leads to a microphase separation with a lamellar morphology. Mixtures with different concentrations of CdSe were prepared by adding different volumes of nanoplatelet suspension in hexane to 30 mg SBS in 1 ml toluene. The CdSe concentration was checked by the UV-visible absorption of the mixtures. Composite films were then obtained by solvent-casting. Annealing was performed for 12 hours at  $110^\circ\text{C}$  under argon atmosphere. Hybrid films with typical thickness of  $100 \mu\text{m}$  and diameter of 10 mm were prepared. Good dispersions with nanoplatelet volume fractions ranging from 2 to 20% were obtained. In this work, we focus on the results obtained with the intermediate volume fraction of 10%.

### **Transmission electron microscopy**

Cross-sectional TEM specimens of 50 nm thickness were cut in the composite films using a Leica EM UC6/FC6cryo-ultramicrotome at -100 °C and a 35-degree Diatome diamond knife. Cryosections were collected on Quantifoil S7/2 grids coated by a continuous thin carbon film. The sections were stained by exposure to OsO<sub>4</sub> vapor for 15 min. The specimens were examined with a JEOL JEM 2011 TEM using a 200kV acceleration voltage. Images were acquired using a Gatan ultrascan CCD camera. OsO<sub>4</sub> reacts preferentially with the unsaturated carbon double bond in the polybutadiene block, which is why the PB regions appear darker than the PS ones in bright-field TEM images. Moreover, due to their high electronic density, CdSe platelets appear very dark.

### **Small-Angle X-ray Scattering.**

We used a laboratory SAXS setup equipped with a rotating copper anode generator (wavelength  $\lambda = 0.154$  nm) and an Osmic Ni/C multilayered optics.<sup>3</sup> The sample to detector distance was 1.07 m for experiments at small scattering vectors and 0.41 m for experiments at medium scattering vectors. The accessible range of scattering vector modulus  $q$  ( $q = (4\pi\sin\theta)/\lambda$ ), where  $2\theta$  is the scattering angle) was  $0.09 < q < 1.3$  nm<sup>-1</sup> in the first case and  $0.25 < q < 3.5$  nm<sup>-1</sup> in the second. The scattered X-rays were detected by a Princeton CCD camera and exposure times typically ranged from 5 to 15 minutes. 2-dimensional images are presented as such, whereas 1-dimensional  $I(q)$  curves of the scattered intensity versus  $q$  were obtained by angular averaging of the scattering patterns. Using well-documented procedures,<sup>4</sup> the platelet alignment, quantified by the nematic order parameter  $S$ , was derived from the dependence versus azimuthal angle of the scattered intensity at fixed  $q$  value in the SAXS patterns.

### **Fluorimetry**

Photoluminescence measurements were performed by irradiating the films with unpolarized excitation light at 400 nm in a Horiba FluoroMax 4 fluorimeter. A narrow strip, 10 mm long and 2 mm wide was cut out from the films and set horizontal in the spectrometer. An analyzer was inserted after the sample. The fluorescence intensity was measured with the analyzer axis either in horizontal orientation, i.e. parallel to the film,  $I_h$ , or in vertical orientation, i.e. perpendicular to the film,  $I_v$ . The ratio of these raw intensities  $I_v/I_h$  was corrected from the detector response by a factor  $G$ , so that  $I_{\perp}/I_{\parallel} = 1/G \cdot I_v/I_h$ . The value of the correction factor  $G$  (0.8) was measured using a dilute solution of nanoplatelets in toluene. For measurements upon stretching, each end of the film was glued on a small rubber band which was stretched to reach the desired strain.

The nematic order parameter  $S$  of the CdSe platelets can be deduced from the anisotropy of their fluorescence emission. Indeed, for the intensity of the fluorescent emission of a uniaxial object (a platelet or a stack of platelets) with axis  $u$ , we can write quite generally:  $I_{fl}(u) = (i^T \bar{\alpha} u)^2 (u^T \bar{\beta} f)^2 I_0$ , where  $I_0$  is the excitation intensity and unit vectors  $i$  and  $f$  are the polarization of the incident and the detected signal, respectively. Since in our experiments the excitation light is unpolarized (which corresponds to an average over the orientations of  $i$  in the plane normal to the direction of incidence), one can reasonably assume that the first factor does not depend on  $u$ . Furthermore, we can express the second factor in terms of the tensor components:  $\beta_{ij} = \sqrt{\beta_{\parallel}}$  for  $i = j$  and  $\beta_{ij} = \sqrt{\beta_{\perp}}$  for  $i \neq j$ , leading to:

$$I_{fl}(u) = \langle \alpha \rangle^2 \{ \beta_{\parallel} (u \cdot f)^2 + \beta_{\perp} [1 - (u \cdot f)^2] \} I_0$$

The orientation of the individual objects  $u$  being symmetric around the vertical axis  $z$ , it is characterized by the distribution function  $f(\theta)$  which depends only on the angle  $\theta = (u, z)$ . The

macroscopic fluorescence signal is obtained by averaging  $u$  over  $f(\theta)$  for a given value of  $f$ . In particular, for  $f \parallel z$  and  $f \parallel y$ :

$$I_z \propto \langle \beta_{\parallel} u_z^2 + \beta_{\perp} (1 - u_z^2) \rangle_{f(\theta)} = \beta_{\parallel} \frac{1+2S}{3} + \beta_{\perp} \frac{2-2S}{3} \text{ and } I_y \propto \beta_{\parallel} \frac{1-S}{3} + \beta_{\perp} \frac{2+S}{3},$$

where the order parameter  $S = \left\langle \frac{3\cos^2 \theta - 1}{2} \right\rangle_{f(\theta)}$ .

The anisotropy parameter is defined by:  $r = \frac{I_z - I_y}{I_z + 2I_y} = S \frac{\beta_{\parallel} - \beta_{\perp}}{\beta_{\parallel} + 2\beta_{\perp}}$ .<sup>5</sup> Previous experiments<sup>6</sup> have shown that the fluorescence is mainly emitted in the plane of the platelets:  $\beta_{\perp} \gg \beta_{\parallel}$ . In this limit, we obtain  $r = -\frac{S}{2}$  as given in the main text.

### Reversibility of the anisotropy

The reversible orientation of the NPLs upon stretching was verified by measuring the photoluminescence as described above, for a film which was alternatively stretched and relaxed. Figure 2 below shows that each time the film is relaxed (odd test number), the value of  $I_{\perp}/I_{\parallel}$  comes back to virtually the same level ( $\approx 0.85$ ) as before any mechanical stress (test #1). Therefore, the orientation of the NPLs is very nicely reversible.

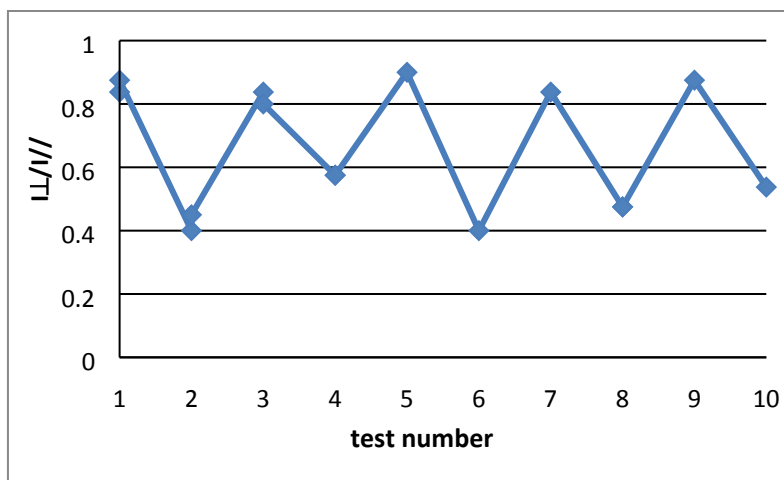


Figure 2: values of  $I_{\perp}/I_{\parallel}$  of the hybrid film subjected to successive cycles of stretching (even test number) and relaxation (odd test number).

### Optical fluorescence microscopy

The homogeneity of the fluorescence intensity was observed with a Olympus BX51 fluorescence microscope equipped with a FITC filter (excitation  $480 \pm 20\text{nm}$ ; emission  $535 \pm 50\text{ nm}$ , beamsplitter at 505 nm). Images were recorded with a Nikon D200 digital camera.

1. B. Mahler, B. Nadal, C. Bouet, G. Patriarche and B. Dubertret, *J Am Chem Soc*, 2012, **134**, 18591-18598.
2. S. Ithurria and B. Dubertret, *J Am Chem Soc*, 2008, **130**, 16504-16505.
3. M. Imperor-Clerc and P. Davidson, *European Physical Journal B*, 1999, **9**, 93-104.
4. E. Paineau, I. Dozov, A. M. Philippe, I. Bihannic, F. Meneau, C. Baravian, L. J. Michot and P. Davidson, *J Phys Chem B*, 2012, **116**, 13516-13524.
5. J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer, Baltimore, USA, 2006.
6. B. Abecassis, M. D. Tessier, P. Davidson and B. Dubertret, *Nano Lett*, 2014, **14**, 710-715.