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Supplementary Information

Polarization anisotropy losses due to morphological instability in CsPbX3 nanorods and strategies for mitigation

Authors: Michael Ng, Sunil B. Shivarudraiah, Jonathan E. Halpert*

Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay,
Kowloon, Hong Kong 999077, Hong Kong S.A.R

Synthesis

Synthesis of NR452. Synthesis of NR452 nanorods was prepared according to Amgar *et al.*[1] with some modifications. ***Cs-oleate (0.15 M).*** The Cs-oleate precursor was synthesized according to Lu *et al.*[2] where an increased amount of oleic acid was used in order to form a stable transparent liquid at room temperature. Cesium carbonate (0.200 g) was added to oleic acid (1.95 mL, OA) and 1-octadecene (6.2 mL, ODE) in a 50 mL 3-neck flask on a Schlenk line. The solutions was degassed for 1 h under vacuum at 120 °C. The solution was then purged with N_2 and heated to 150 °C until a transparent solution was formed. The solution was then cooled to room temperature naturally and kept under nitrogen flow for further use. ***Nanorod synthesis.*** ODE (1.25 mL), OA (0.125 mL), oleylamine (0.125 mL, 70%, OLAm), and HBr acid (5 µL, 48%) was added to a glass vial and stirred vigorously for 5 minutes. Cs-oleate (0.1 mL) and $PbBr_2$ (0.2 mL, 0.4 M, DMF) was then added and stirred for 5 minutes, upon which a faint turbid white solution formed. Acetone (5 mL) was then added and the solution was stirred for 10 minutes upon which the solution turns a pale green/yellow colour. The solution was then centrifuged at 3000 RPM for 5 minutes and the precipitate was redispersed in hexane (5 mL). The solution was then centrifuged at 15000 RPM for 5 minutes, the large aggregated material in the precipitate was then discarded and the supernatant was collected.

Synthesis of NR466. Synthesis of NR466 nanorods was prepared according to Seth e*t al.*[3] with some modifications. Oleic acid (0.5 mL, 90%) and oleylamine (40 µL, 98%) were added to ethyl acetate (4 mL) and stirred vigorously. $CsPbBr_3$ (0.2 mL, 0.0375 M CsBr and $PbBr_2$ in DMF) was added dropwise. The reaction was stirred vigorously for 15 hours and then centrifuged at 6000 RPM for 5 minutes. The precipitate was collected and redispersed in hexane.

Synthesis of NR515. Similar to NR452, except oleylamine was substituted for an equal moles of hexylamine (HAm). ODE (1.25 mL), OA (0.125 mL), HAm (0.05 mL), and HBr acid (5 µL) was added to a glass vial and stirred vigorously for 5 minutes. Cs-oleate (0.1 mL) and $PbBr_2$ (0.2 mL, 0.4 M, DMF) was then added and stirred for 5 minutes upon which a faint turbid white solution formed. Acetone (5 mL) was then added, and the solution was stirred for 10 minutes upon which the solution turned a pale green/yellow colour. The solution was then centrifuged at 3000 RPM for 5 minutes and the precipitate was redispersed in hexane (5 mL).

Synthesis of NR518. Synthesis of NR518 was prepared according to Yang *et al.*[4] ***Cs-oleate.*** Cesium carbonate (0.16 g), OA (1 mL), and ODE (16 mL) was added to a three-neck round bottom flask and degassed at 110 °C for 30 mins under vacuum. The solution was then heated to 150 °C under N_2 flow until a transparent clear solution has formed. ***Cs_4PbBr_6 nanocrystals.*** OLAm (1 mL), OA (1 mL), ODE (10 mL), and $PbBr_2$ (0.2 mmol) was added to a three-neck flask and degassed under vacuum at 80 °C for 30 mins. The solution was then heated to 140 °C under N_2 flow and Cs-oleate (4.4 mL) was injected. After 10 seconds the reaction was cooled to room temperature in ice bath. The solutions was then centrifuged at 6000 RPM for 10 mins and the precipitate was collected and redispersed in 10 mL cyclohexane. ***Nanorod synthesis.*** Cs_4PbBr_6 solution (2 mL) was added to water (2 mL) and left undisturbed for 42 hours. The solution was then centrifuged at 13000 RPM for 5 minutes and the supernatant was discarded. The precipitate was redispersed in cyclohexane and centrifuged at 8000 RPM for 3 mins and the precipitate was discarded.

Synthesis of NR520. Synthesis of NR520 was prepared according to Jing *et al.*[5] with some slight modifications. ***Cs_4PbBr_6 nanocrystals.*** ODE (10 mL), OA (2 mL), OLAm (2 mL), cesium acetate (0.2 mmol), and lead acetate (0.4 mmol) were degassed for 15 min under vacuum at 90 °C. Tetraoctylammonium bromide (0.4 mmol in 3 mL toluene) was then injected at 75 °C under N_2 flow. After 10 s the reaction was cooled in an ice bath. The nanocrystals was then collected by centrifugation at 6000 RPM for 5 mins and then redispersed in cyclohexane (10 mL). ***Nanorod synthesis.*** Cs_4PbBr_6 nanocrystal solution (2 mL) was added to water (2 mL) and left undisturbed for 1 week. Organic layer collected and centrifuged at 8000 RPM for 3 mins and redispersed in cyclohexane. Purification repeated 2 more times before being redispersed in cyclohexane or toluene.

Synthesis of NR581. PbI_2(0.2 mmol), OA (0.2 mL), and OLAm (0.2 mL) added to toluene (10 mL) and heated to 100 °C for 1 hour. The solution was cooled to room temperature naturally and used for anion exchange. PbI_2 solution (2 mL) mixed with 1 mL of NR452 (10 mg/mL). The solution was then stirred for 1 hour at 40 °C. Nanorods were then collected by centrifugation at 6000 RPM for 5 minutes. Precipitate redispersed in hexane and filtered using a 0.45 µm PTFE filter.

Synthesis of NR587. PbI_2 (0.2 mmol), OA (0.2 mL), and OLAm (0.2 mL) added to toluene (10 mL) and heated to 100 °C for 1 hour. The solution was cooled to room temperature naturally and used for anion exchange. PbI_2 solution (2 mL) mixed with 1 mL of NR452 (10 mg/mL). The solution was then stirred for 1 hour at 40 °C. The solution was then centrifuged at 6000 RPM for 5 minutes and the supernatant was collected. The supernatant was left overnight undisturbed, upon which a precipitate was observed to have formed. The solution was then centrifuged at 6000 RPM for 5 mins and the precipitate was redispersed in hexane.

Synthesis of NR618. ***Oleylammonium iodide***. Oleylamine (6.25 mL, 98%) and ethanol (50 mL) added to the round bottom flask. Hydroiodic acid (5 mL, 57%) was then added dropwise and the solution was stirred overnight. Ethanol was then removed using a rotary evaporator. Diethyl ether was then added and the crystals were collected with a Buchner flask. The powder was then washed several times with cold diethyl ether. The powder was then dried overnight under a vacuum at 80 °C. ***Nanorod synthesis.*** OLAm-I (0.4 mmol), OA (0.2 mL), and OLAm (0.2 mL) was added to toluene (10 mL) and heated to 100 °C for 1 hour until all the precursors had dissolved. The OLAm-I solution (2 mL) was then added to 1 mL NR452 (10 mg/mL) and stirred vigorously at 40 °C for 1 hour. The nanorods were then collected by centrifugation at 8000 RPM for 5 mins, and the precipitate was redispersed in hexane.

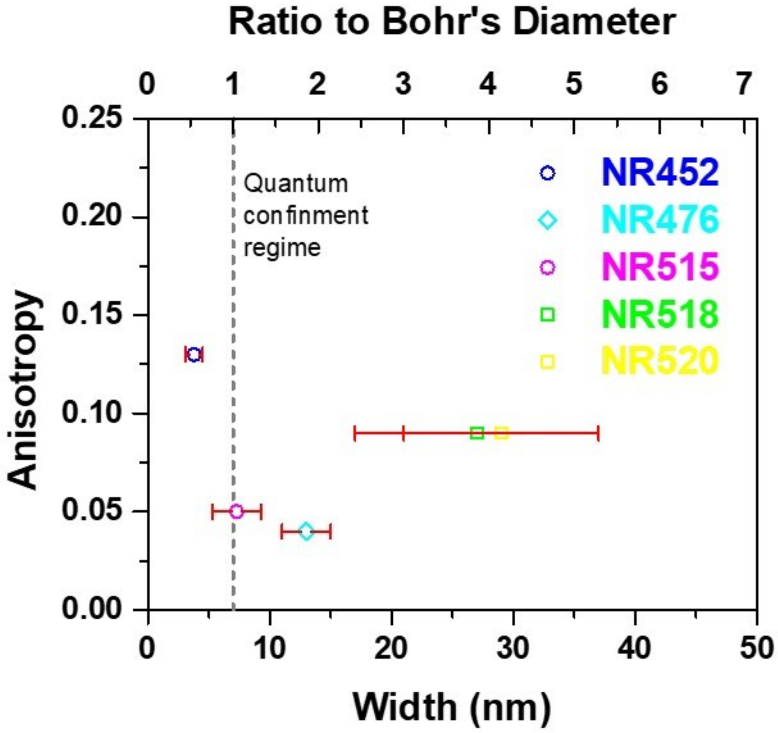

Figure S1. Comparison of anisotropy for $CsPbBr_3$ nanorods with different widths.

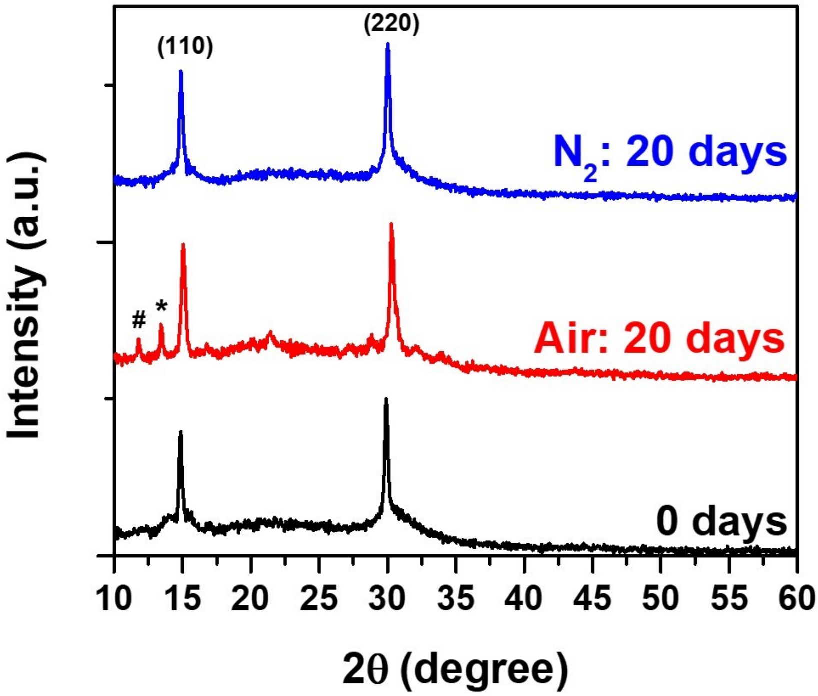

*Figure S2. XRD spectrum of NR452 dispersed in hexane and stored under air and nitrogen environment for 20 days. The peak at # corresponds to $CsPb_2Br_5$,[6] while the peak at * cannot be unambiguously assigned.*

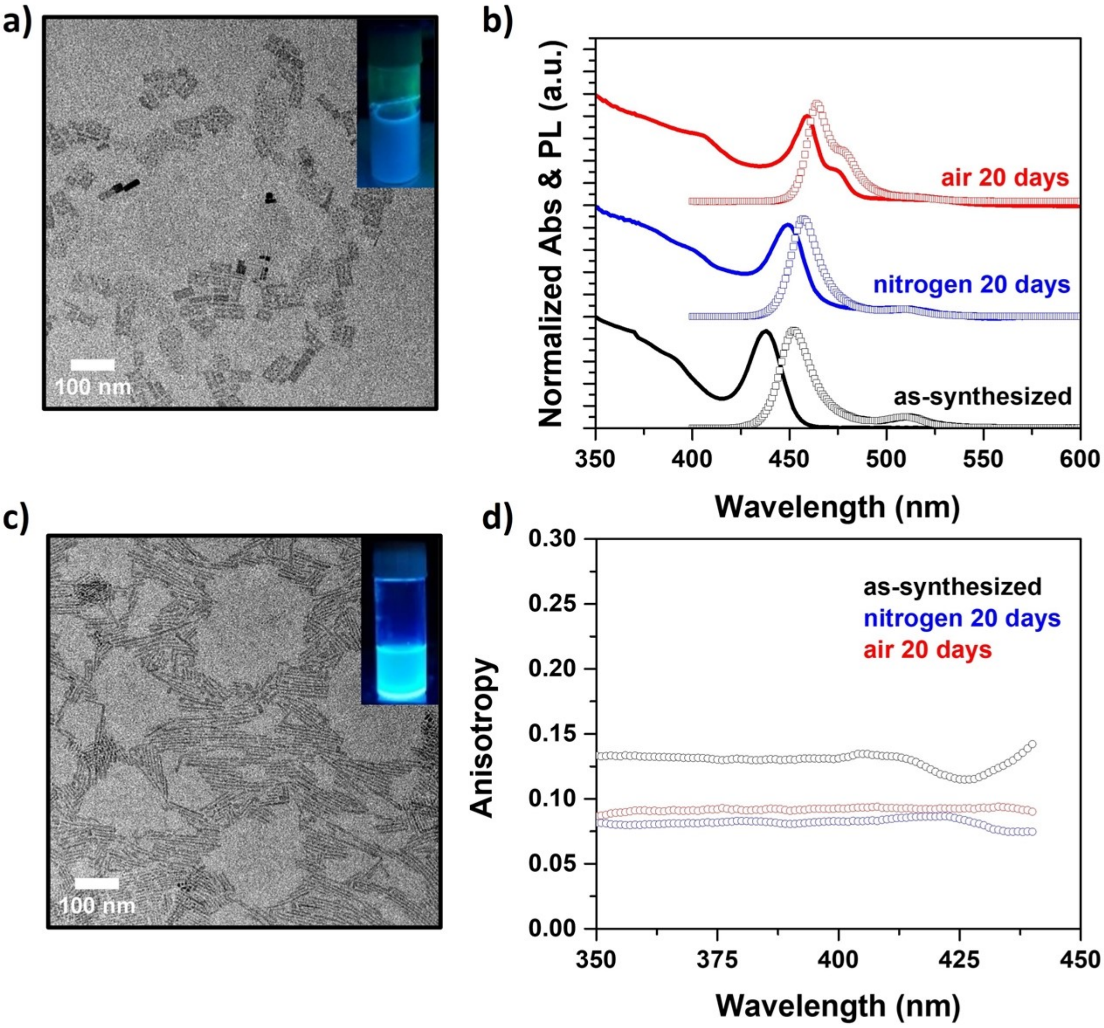

Figure S3. a) TEM micrographs of NR452 dispersed in anhydrous toluene (10 mg/mL) and stored in air for 20 days. Inset shows solution under UV light. b) UV-vis absorption and PL spectrum of NR452 dispersed in anhydrous toluene and stored in air and under nitrogen atmosphere for 20 days. c) TEM micrographs of NR452 dispersed in anhydrous toluene (10 mg/mL) and stored in nitrogen glovebox for 20 days. Inset shows solution under UV light. d) anisotropy of NR452 after 20 days in air and nitrogen.

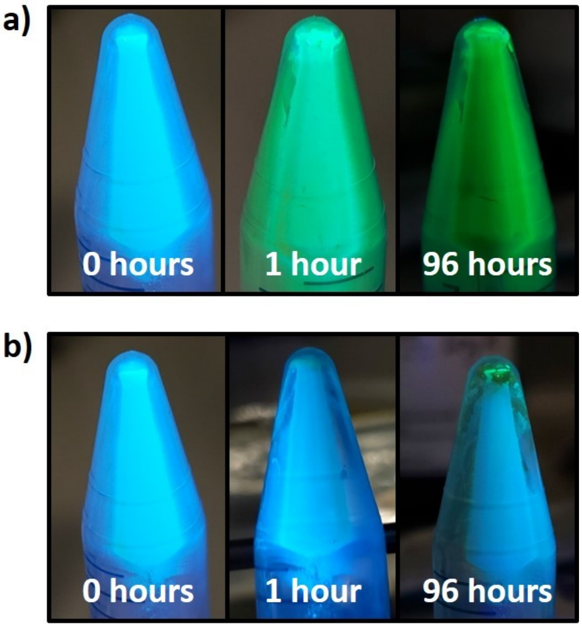

Figure S4. NR466 solid stored in a) air and b) under nitrogen environment under UV light.

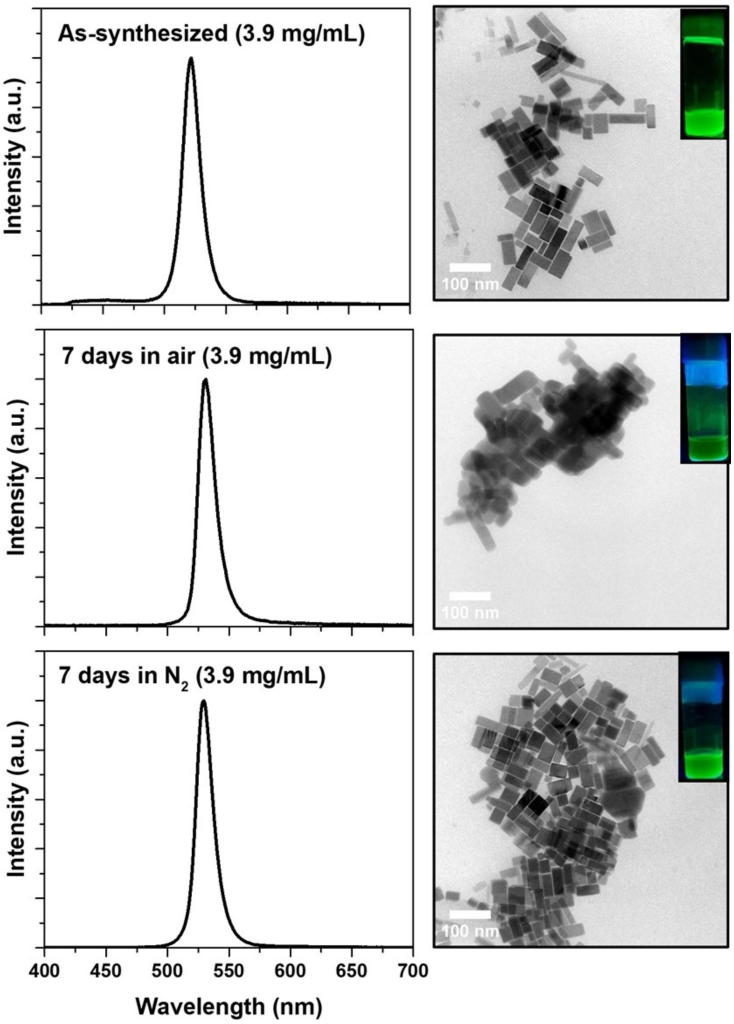

Figure S5. PL spectrum and corresponding TEM micrograph of NR518 stored in air and in nitrogen environment for 7 days.

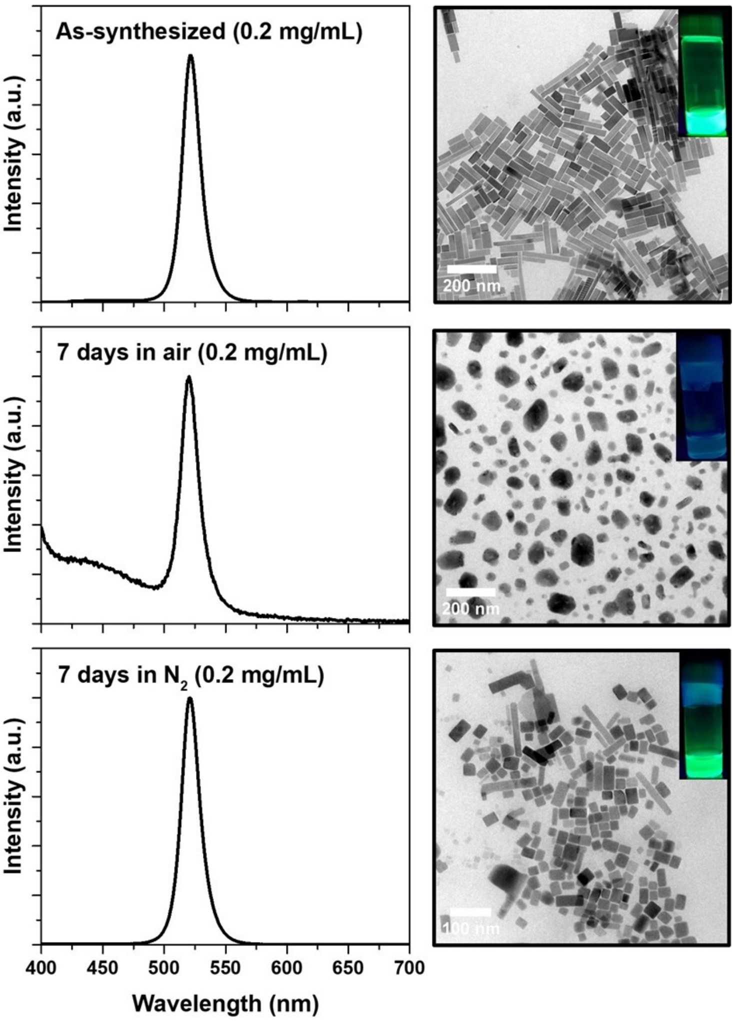

Figure S6. PL spectrum and corresponding TEM micrograph of NR520 stored in air and in nitrogen environment for 7 days.

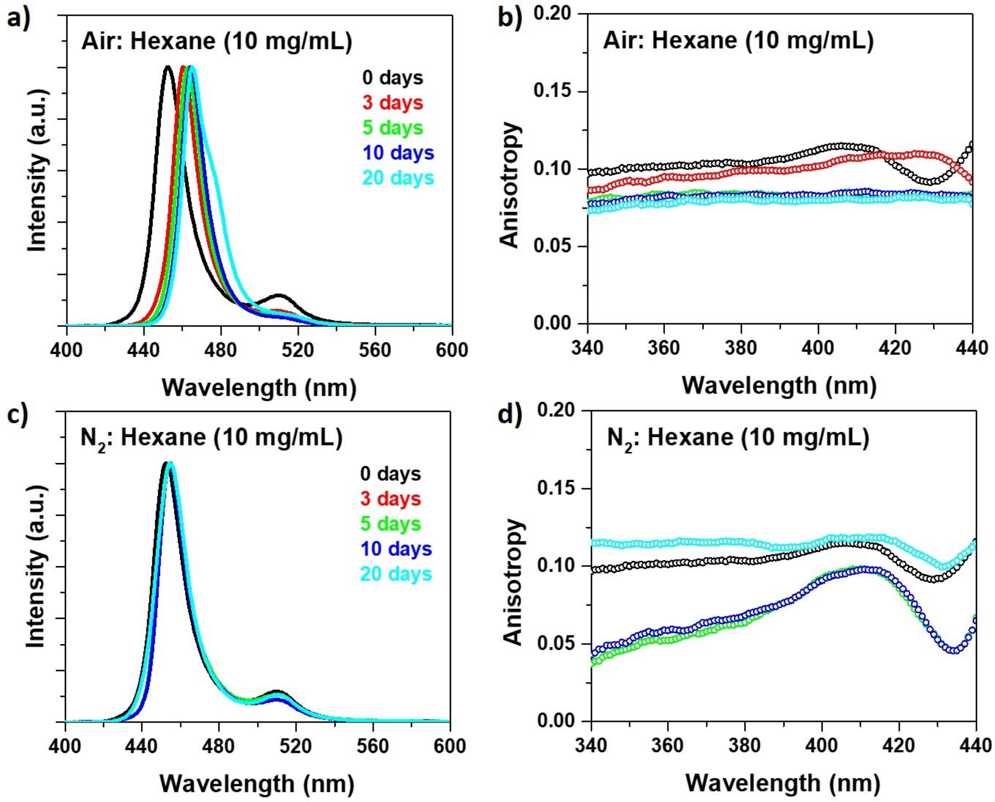

Figure S7. a) PL emission and b) optical anisotropy for NR452 dispersed in hexane (10 mg/mL) and stored in air. c) PL emission and d) optical anisotropy for NR452 dispersed in hexane (10 mg/mL) and stored in nitrogen.

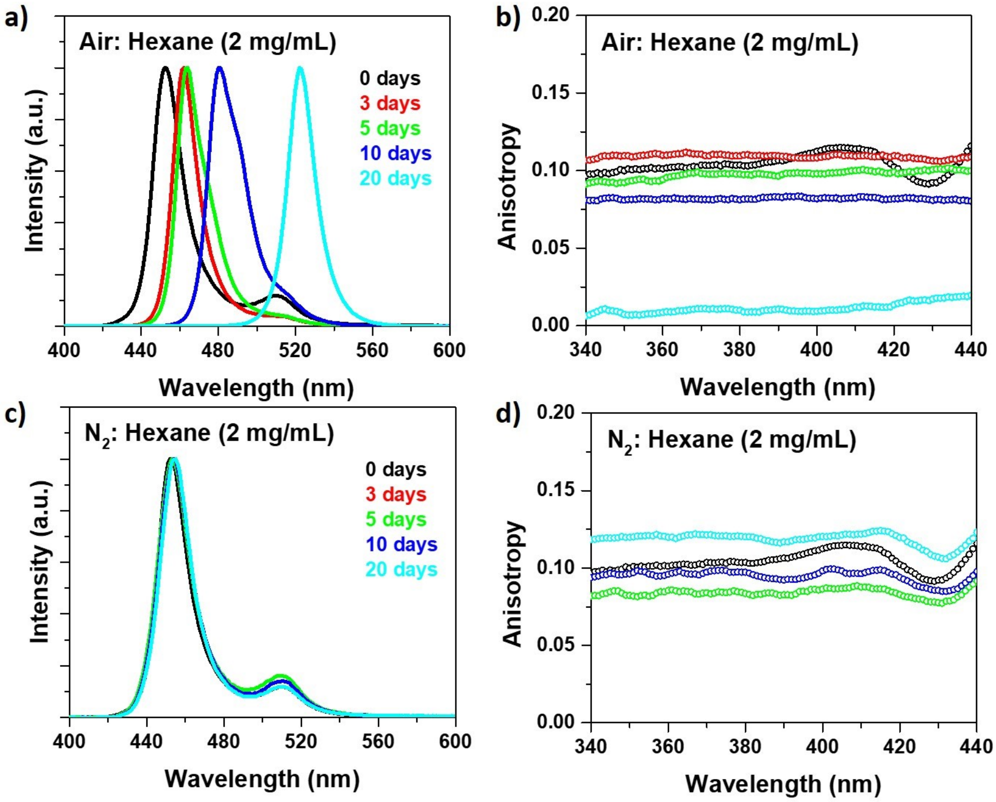

Figure S8. a) PL emission and b) optical anisotropy for NR452 dispersed in hexane (2 mg/mL) and stored in air. c) PL emission and d) optical anisotropy for NR452 dispersed in hexane (2 mg/mL) and stored in nitrogen.

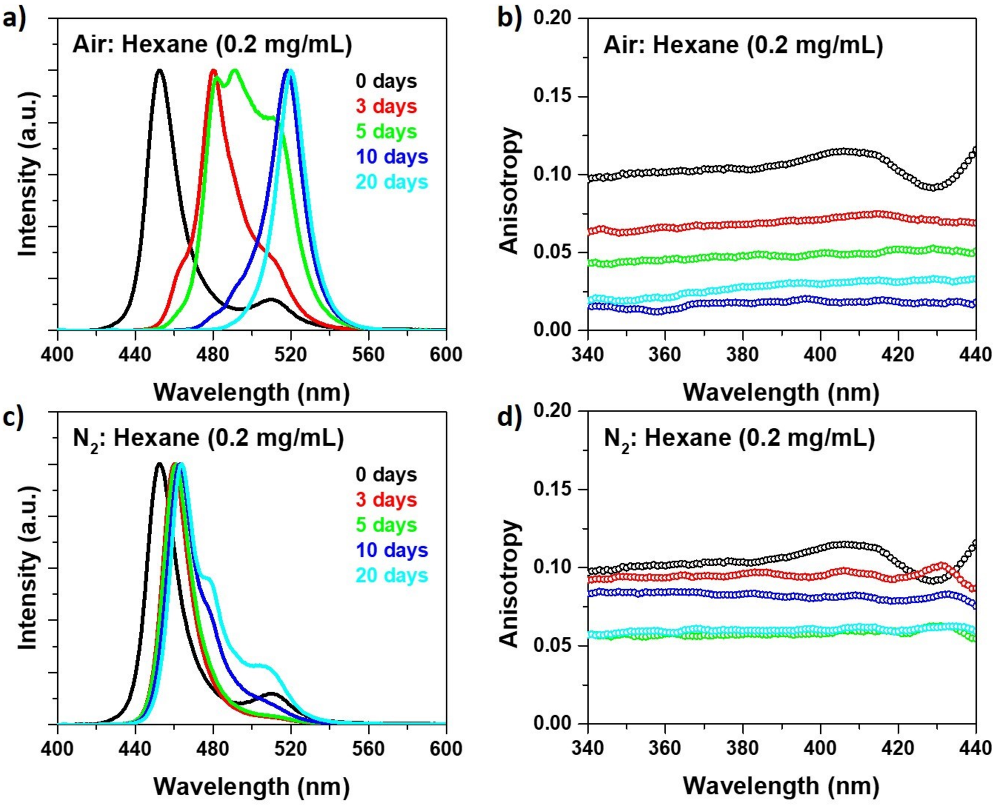

Figure S9. a) PL emission and b) optical anisotropy for NR452 dispersed in hexane (0.2 mg/mL) and stored in air. c) PL emission and d) optical anisotropy for NR452 dispersed in hexane (0.2 mg/mL) and stored in nitrogen.

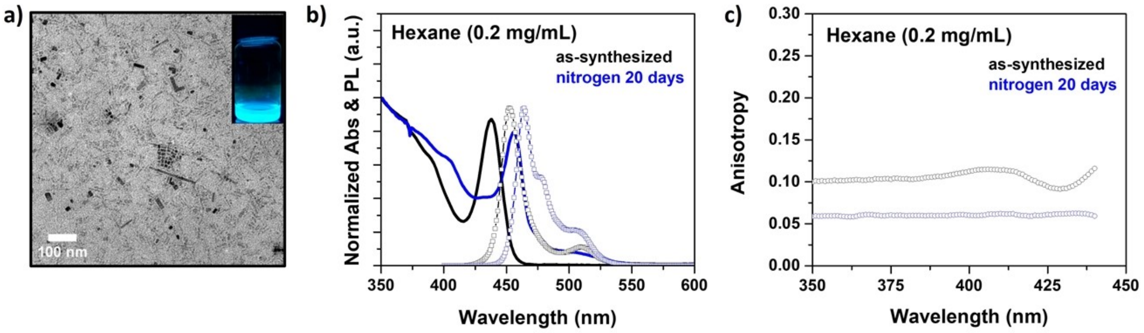

Figure S10. a) TEM micrographs of NR452 dispersed in anhydrous hexane (0.2 mg/mL) and stored in nitrogen environment for 20 days. Inset shows solution under UV light. Corresponding b) UV-vis absorption and PL, and c) optical anisotropy.

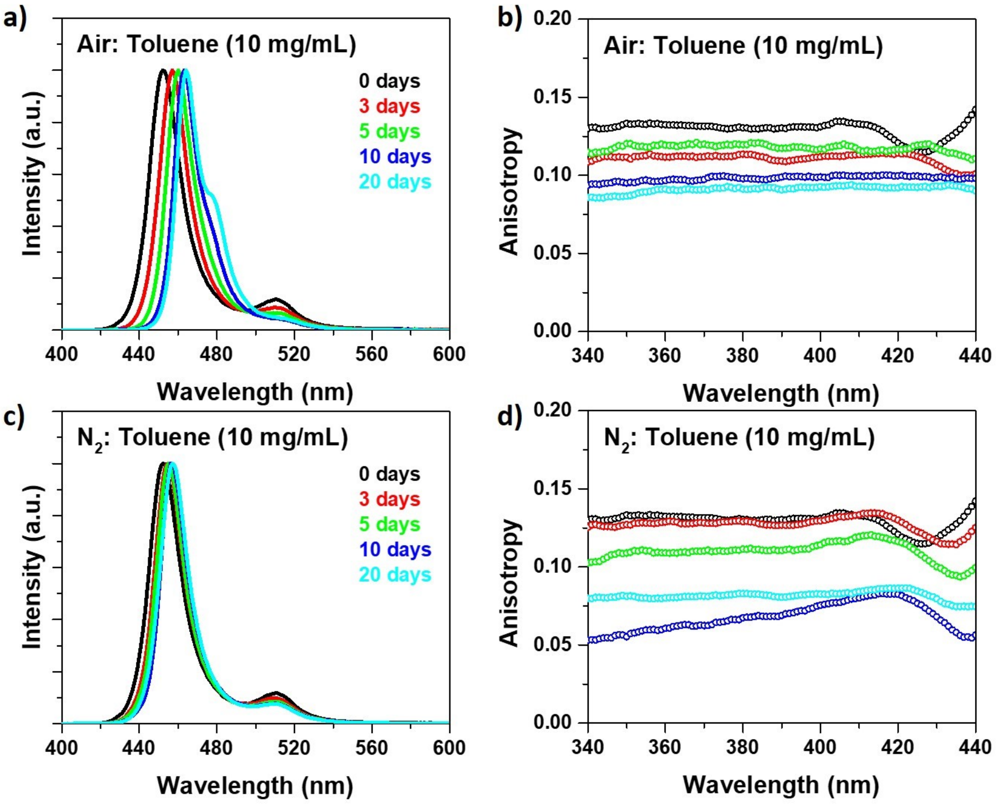

Figure S11. a) PL emission and b) optical anisotropy for NR452 dispersed in toluene (10 mg/mL) and stored in air. c) PL emission and d) optical anisotropy for NR452 dispersed in toluene (10 mg/mL) and stored in nitrogen.

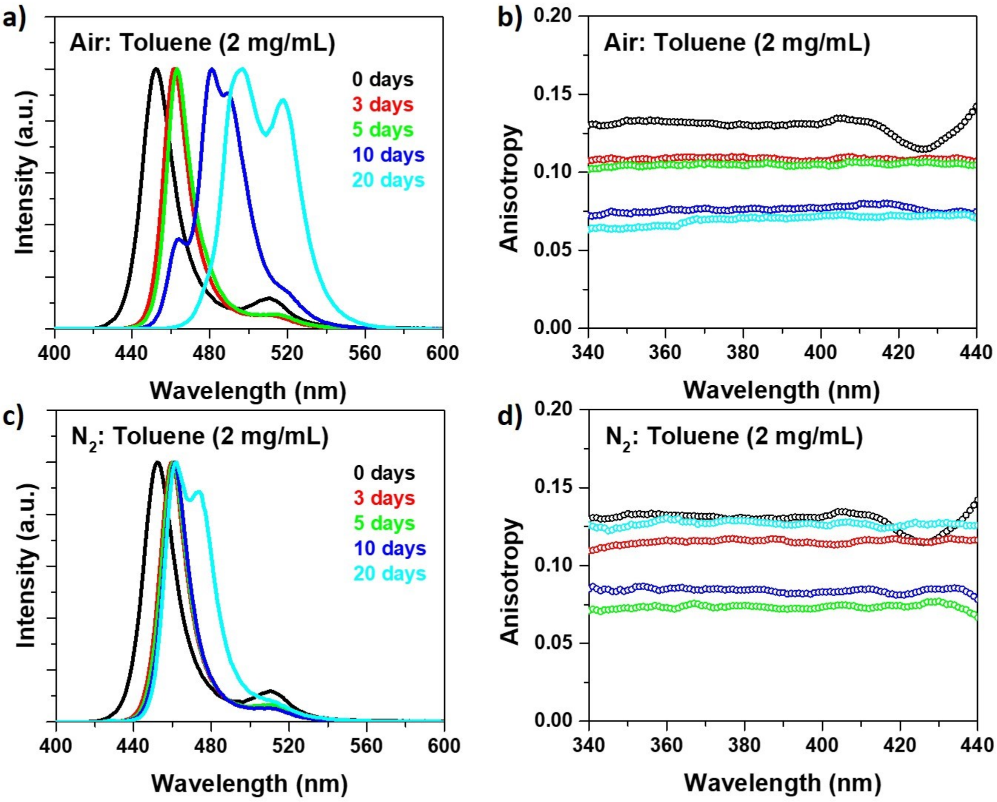

Figure S12. a) PL emission and b) optical anisotropy for NR452 dispersed in toluene (2 mg/mL) and stored in air. c) PL emission and d) optical anisotropy for NR452 dispersed in toluene (2 mg/mL) and stored in nitrogen.

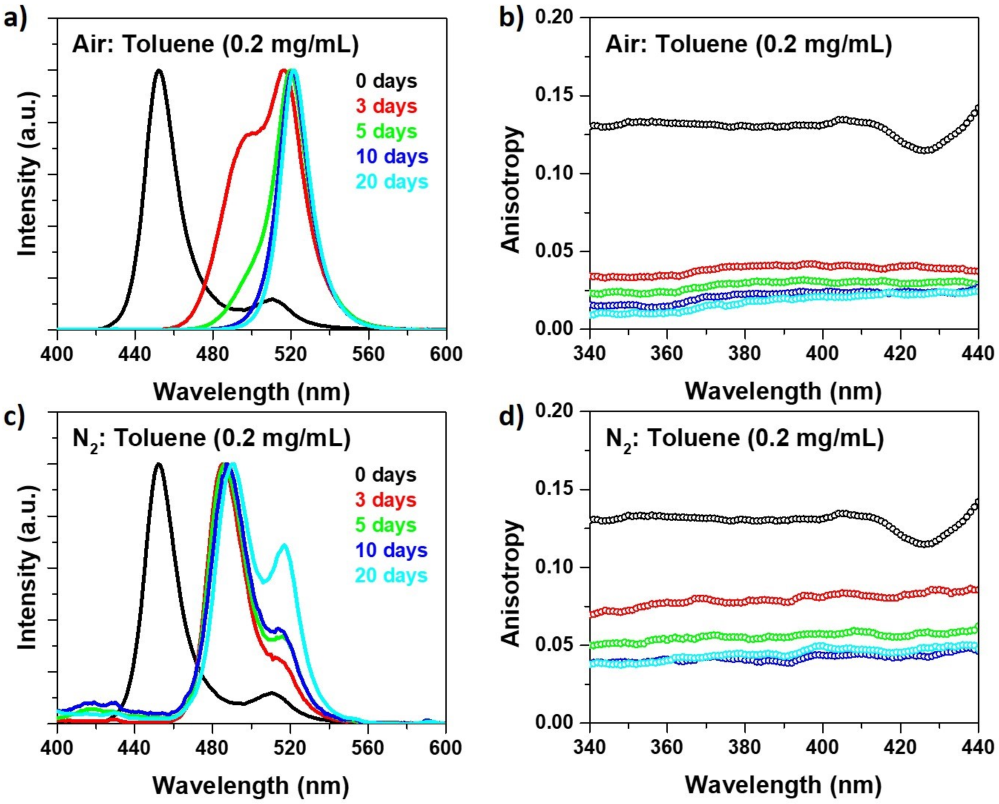

Figure S13. a) PL emission and b) optical anisotropy for NR452 dispersed in toluene (2 mg/mL) and stored in air. c) PL emission and d) optical anisotropy for NR452 dispersed in toluene (2 mg/mL) and stored in nitrogen.

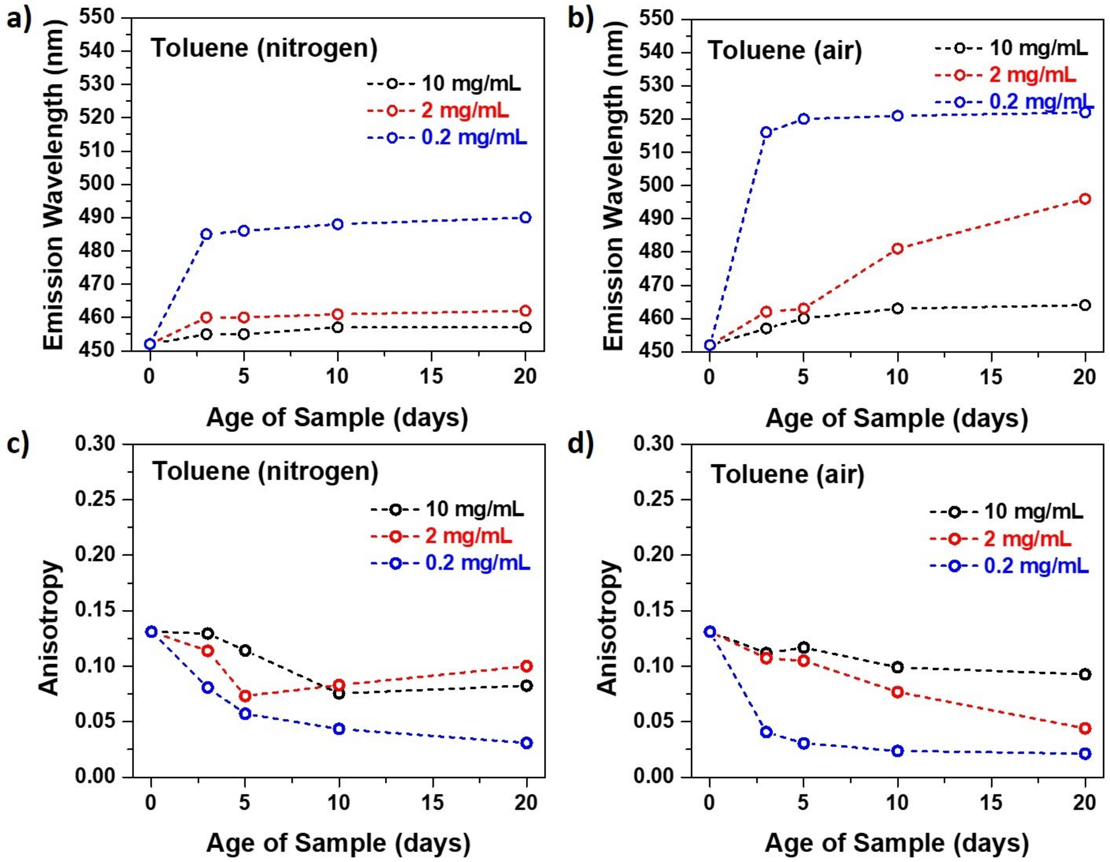

Figure S14. Comparison of emission wavelength with age of sample with different concentrations stored in a) nitrogen and b) air for NR452 dispersed in toluene. Comparison of anisotropy with age of sample with different concentrations stored in a) nitrogen and b) air.

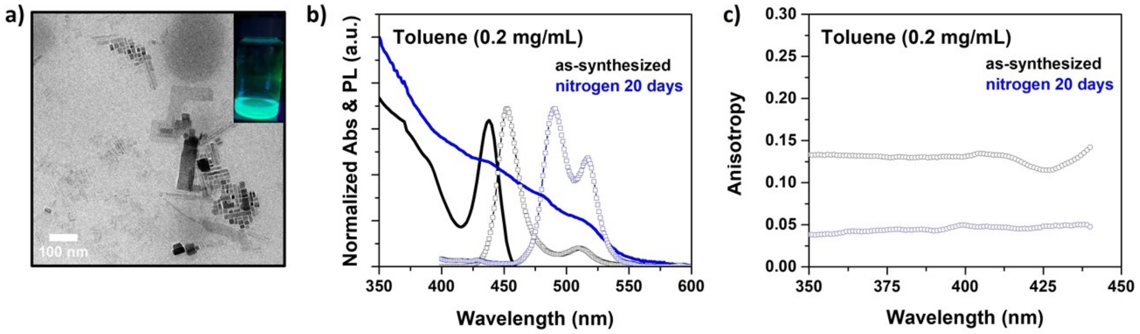

Figure S15. a) TEM micrographs of NR452 dispersed in anhydrous toluene (0.2 mg/mL) and stored in nitrogen environment for 20 days. Inset shows solution under UV light. Corresponding b) UV-vis absorption and PL, and c) optical anisotropy.

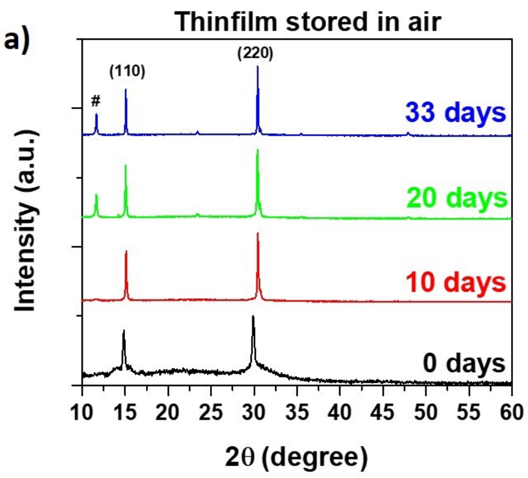

Figure S16. XRD spectrum of thin films stored in a) air and b) under nitrogen environment. The peak at # corresponds to $CsPb_2Br_5$.[6]

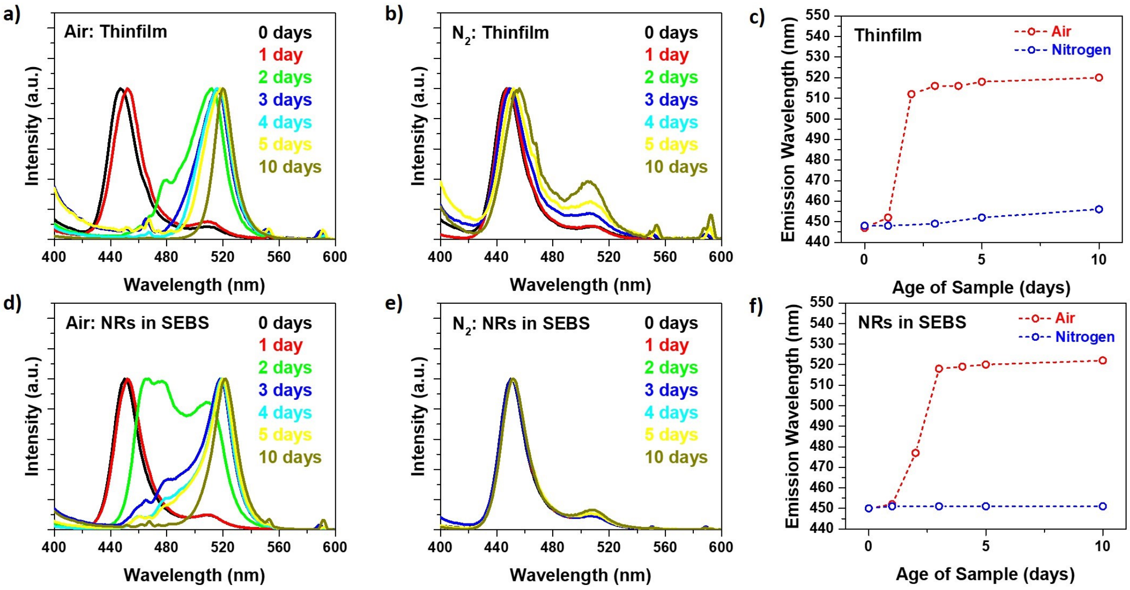

Figure S17. PL spectrums of thin films stored in a) air and b) under nitrogen c) PL peak emission shift of thin film stored in air and nitrogen. PL spectrum of polymer matrix thin film (10% NRs in SEBS) stored in d) air and e) under nitrogen. f) peak emission wavelength shifts for polymer matrix thin film (10% NRs in SEBS).

References

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