Supporting Information

Dual-emitting dot-in-bulk CdSe/CdS nanocrystals with highly emissive core- and shell-based trions sharing the same resident electron

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Methods

Synthesis of dot-in-bulk (DiB) nanocrystals (NCs) and structural characterization

CdSe/CdS DiB NCs were synthesized following the procedure described in ref.[1]. Briefly, zincblende CdSe NCs were prepared using previously reported methods[2]. For the synthesis of CdSe (radius 1.5nm)/CdS NCs, 2×10^{-7} mol of CdSe NCs (purified twice) dispersed in 10 mL of 1-octadecene (ODE) were loaded into a 100 mL flask, degassed at 110°C for 1 h. The flask was filled with Ar and heated up to 300 °C for CdS shell growth. A 0.2 mmol sample of Cd-oleate and 0.2 mmol of 1-dodecanethiol were added slowly (0.1 mmol/min) and the reaction was maintained at the elevated temperature for 30 min to form a thin CdS buffer layer (~3 monolayers) on top of CdSe cores. For further CdS shell growth, a mixed solution of Cd-oleate and trioctylphospine-sulfur (0.5 M/0.5 M) in ODE was continuously added at a rate of 1 mmol/hour at 300°C. After the injection of precursors was completed, the reaction products were cooled to room temperature and purified repeatedly by a precipitation-and-redispersion method. The final products were dispersed in hexane for further characterization. Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 transmission electron microscope. This procedure produced DiB NCs with the 1.5 nm CdSe core radius and the 8.5 nm shell thickness.

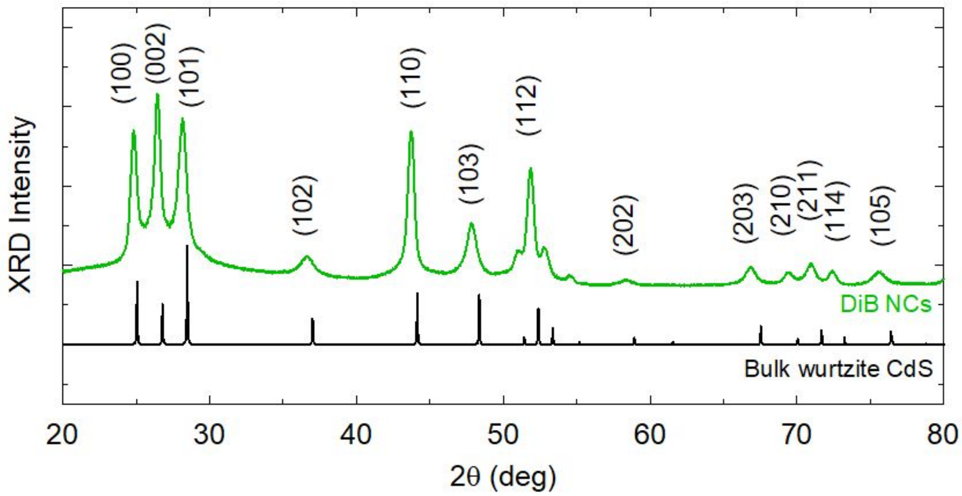
Spectroscopic studies

Steady-state and time-resolved photoluminescence (PL) spectra were obtained using excitation from a pulsed diode laser with the 3.06-eV photon energy (Edinburgh Inst. EPL 405, 40 ps pulse width) and a variable pulse repetition rate. The DiB NC samples were prepared as drop-cast films on glass substrates. For magneto-optical measurements, they were placed in a variable-temperature insert of a closed-cycle helium cryostat (T = 3.5 – 300 K). The emitted light was coupled into a 600 µm optical fiber and the PL signal was spectrally resolved with a TM-C10083CA Hamamatsu Mini-Spectrometer. The PL dynamics were studied with a Hamamatsu R943-02 time-correlated single-photon counting unit coupled to an Oriel Instruments Cornerstone 260 monochromator.

For PL studies in high pulsed magnetic fields, the samples were mounted onto a custom fiber-coupled probe that, in turn, was loaded into a helium bath cryostat with a long tail extending into the bore of a 65 T-class pulsed magnet. Light was directed to and collected from the sample using a single 600 µm diameter multimode optical fiber. Thin film circular polarizers were used to select emitted light with a certain handedness of circular polarization. Full optical spectra were acquired every 1 ms continuously throughout the magnet pulse (~50 ms duration) using a fast CCD camera (Princeton Instruments Blaze). To switch between σ^+ and σ^- circular polarizations, we switched current direction in the magnet.

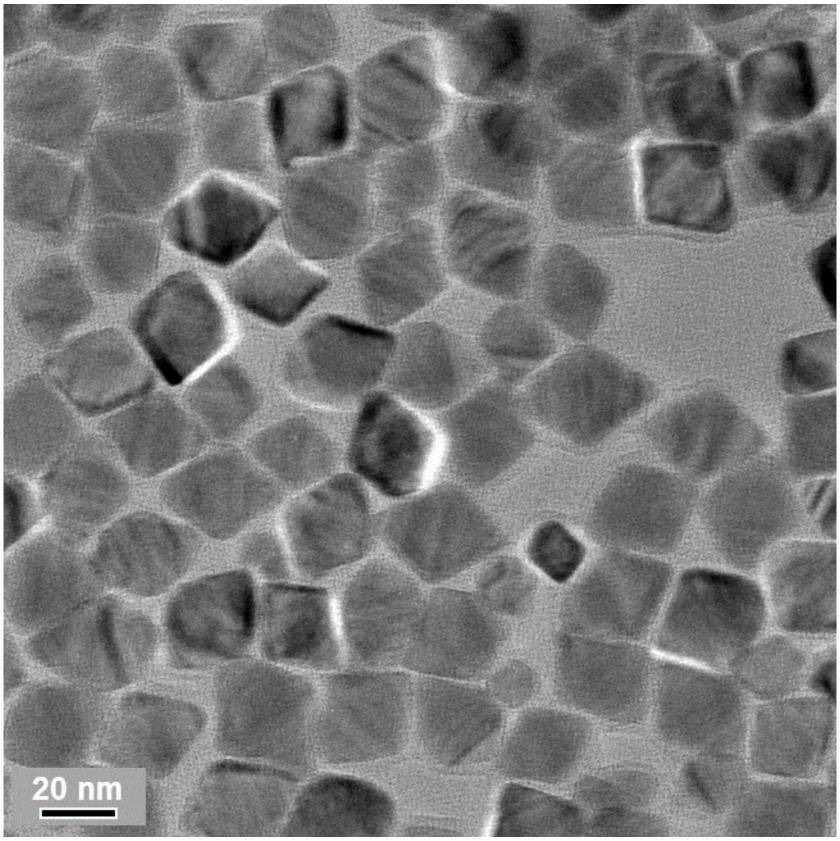
Magneto-optical measurements in a DC magnetic field (B) up to 15 T were performed using a magneto-optical setup based on a cryostat with a superconducting single-coil solenoid. An NC sample was kept in helium exchange gas at a 4.2 K temperature. Direct optical access to the sample was achieved using the top window. The B field was applied in the Faraday geometry wherein its direction was parallel to a wave vector of collected PL. The PL signal was dispersed using a 0.55-m spectrometer and detected by a liquid-nitrogen-cooled CCD or an avalanche Si-photodiode connected to a conventional time-correlated single-photon counting system. PL was excited with a pulsed diode laser (photon energy 3.06 eV, pulse duration 50 ps). The temporal resolution of this experiment was 100 ps.

Supporting Figure S1 – X-Ray Diffraction Pattern of CdSe/CdS dot-in-bulk (DiB) nanocrystals (NCs).



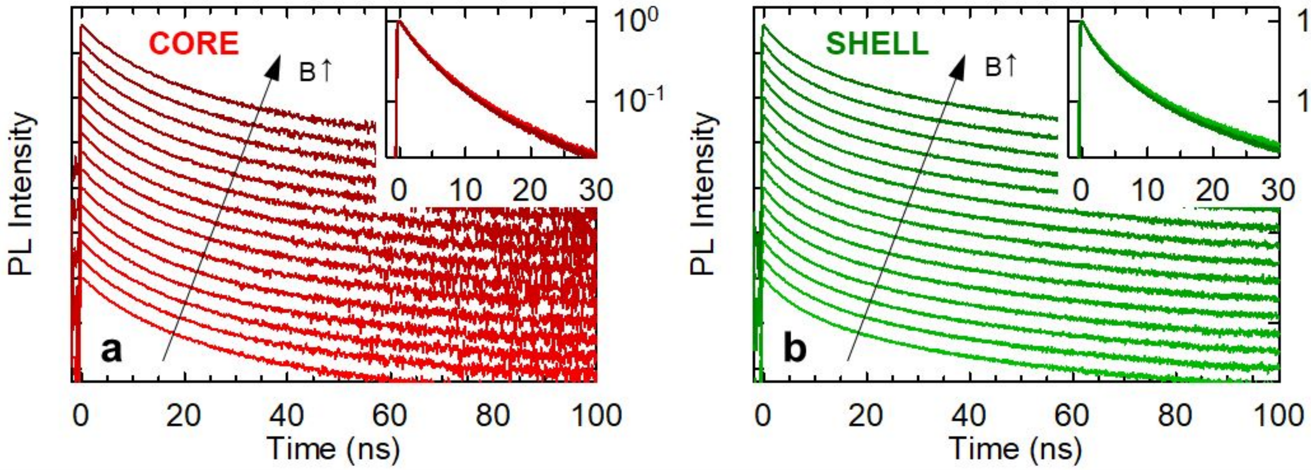
Supporting Figure S1 – The X-ray diffraction pattern of CdSe/CdS DiB NCs (green line) compared to the pattern of bulk CdS in wurtzite crystal structure (black line).

Supporting Figure S2 – Transmission Electron Microscopy Image of CdSe/CdS DiB NCs.



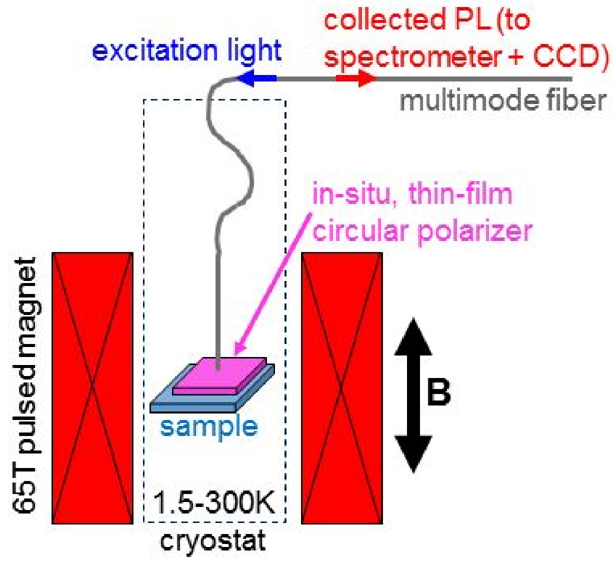
Supporting Figure S2 – Transmission electron microscopy (TEM) image of CdSe/CdS DiB NCs indicates a non-spherical shape due to the ultra-thick CdS shell (thickness of ~8.5 nm).

Supporting Figure S3 – Photoluminescence (PL) decay in DiB NCs as a function of Magnetic Fields.



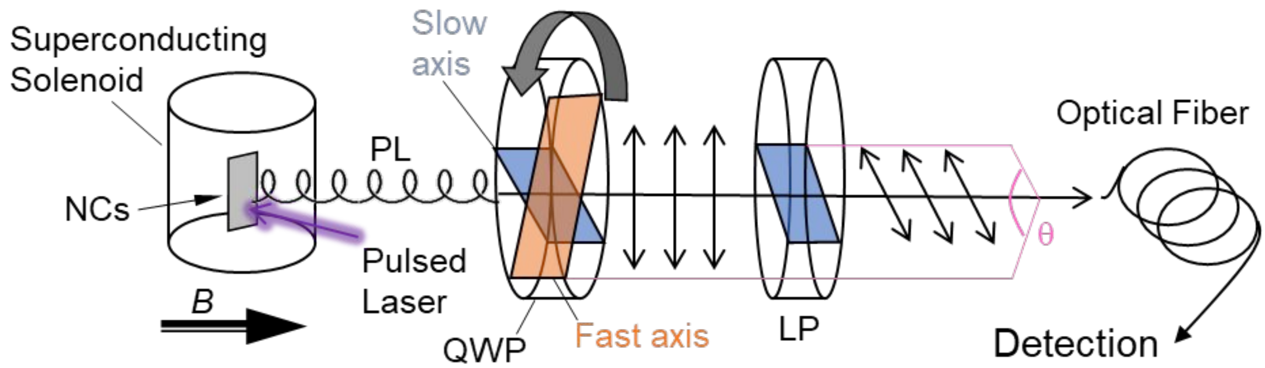
Supporting Figure S3 – (a) Core and (b) shell PL decays at increasing *B* (from 1 to 15 T with 1 T steps) and *T* = 4.2K. The PL traces are offset vertically for clarity. Insets: the expanded view of the first 30 ns of the same data; the PL traces are superimposed to highlight that no changes occur upon application of magnetic field. For the core PL decay, k_{rad}(1T) = 0.23 ns^{-1} and k_{rad}(15T) = 0.25 ns^{-1}, whereas for the shell PL decay, k_{rad}(1T) = 0.26 ns^{-1} and k_{rad}(15T) = 0.29 ns^{-1}.

Supporting Figure S4 – Schematic depiction of the high-field magneto-optical experiment.



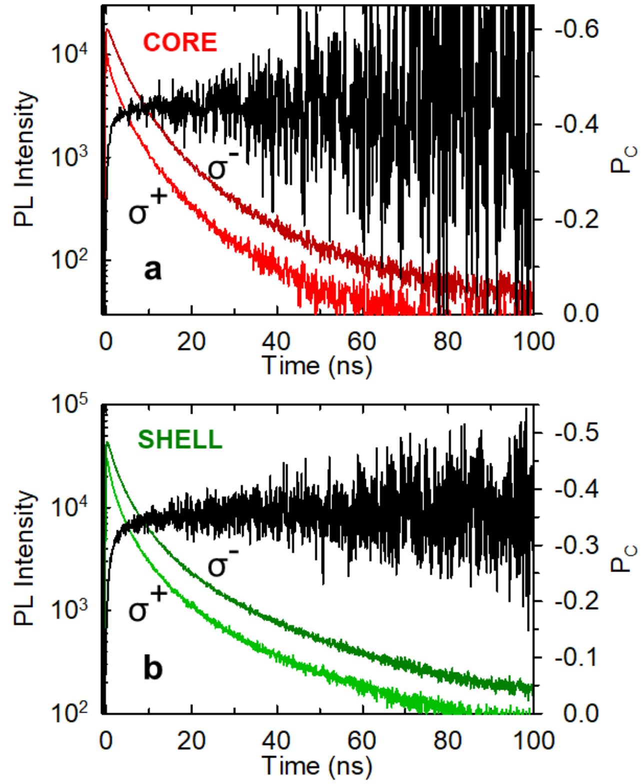
Supporting Figure S4 –The NCs samples are mounted onto a custom fiber-coupled probe residing in a He-bath cryostat with a long tail extending into the bore of a 65 T-class pulsed magnet. Pump laser light is directed towards the sample using a 600-μm diameter multimode optical fiber. The same fiber is used to collect the emitted PL. Thin film circular polarizers were used to select σ^- and σ^+ polarized PL. Full optical spectra are acquired every 1 ms continuously throughout the magnet pulse (~50 ms duration) using a fast CCD camera. To switch between different circular polarizations, we switched current direction in the magnet.

Supporting Figure S5 –Schematic depiction of the 15T magneto-optical experiment.



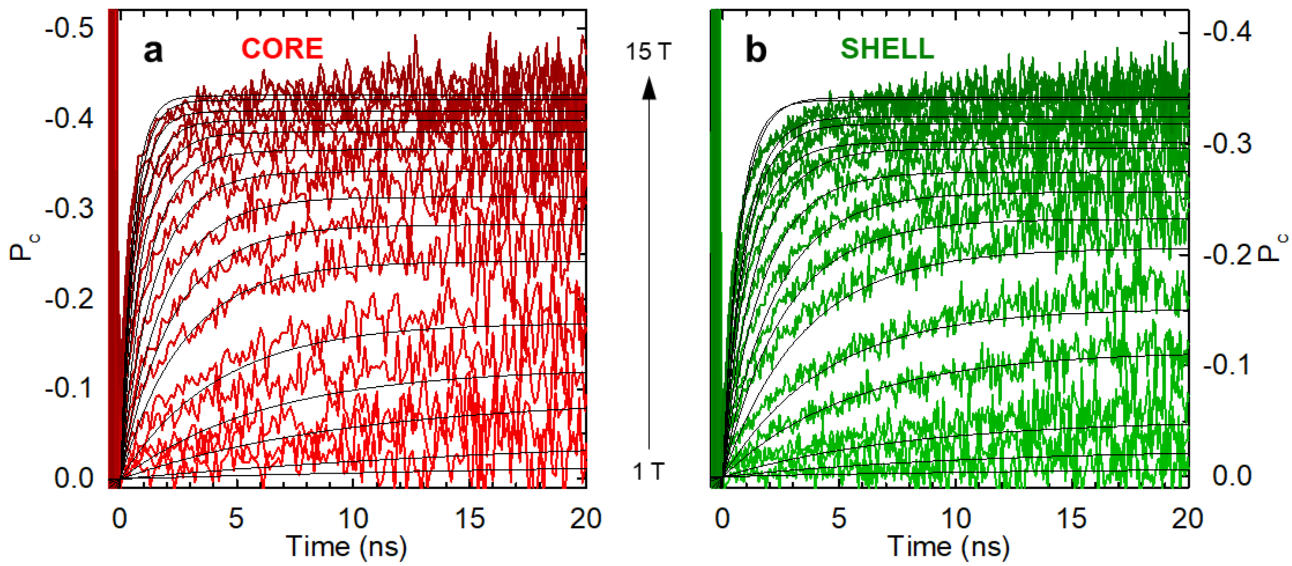
Supporting Figure S5 – Schematic of the circular-polarization resolves magneto-PL setup used in the 15T experiments. A film of DiB NCs dip-coated onto a glass substrate is mounted in a single-coil superconducting solenoid with direct optical access and is excited with a pulsed ultraviolet laser (photon energy is 3.06 eV). The emitted two-color light is resolved for its handedness by the quarter wave plate (QWP) and the linear polarizer (LP) mounted before a light-collecting input of an optical fiber coupled to a 0.55 m spectrometer and a charge-coupled-device detector. Right- and left-handed photons are selected by adjusting the angle θ between the fast axis of the QWP and the optical axis of the LP.

Supporting Figure S6 – Circular-polarization-resolved PL decays and time-dependent P_c.



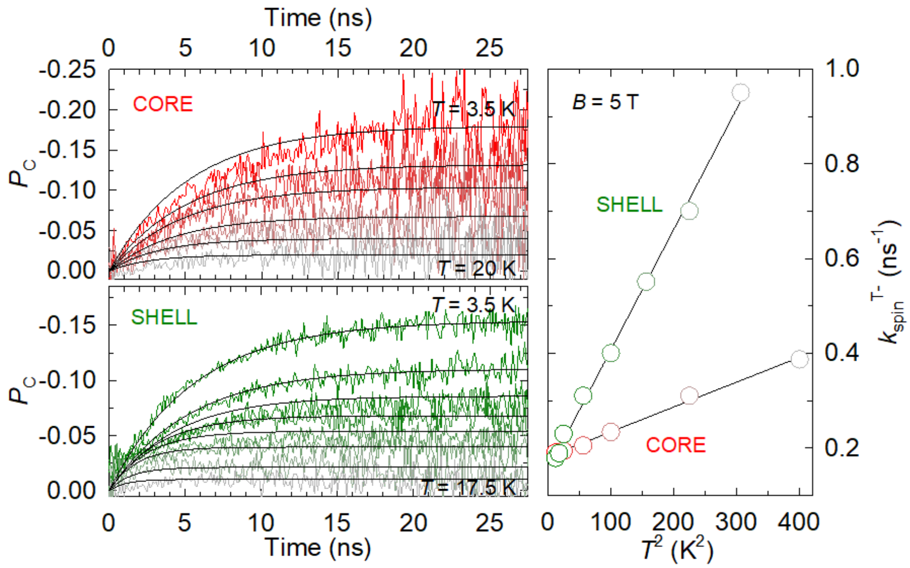
Supporting Figure S6 – (a) Core and (b) shell CP-resolved PL decays acquired at $B = 15$ T and $T = 4.2$ K. Dark red and green curves refer to left-handed circularly polarized PL decays, whereas light red and green curves refer to right-handed circularly polarized PL decays. The black curves are the respective time-dependent P_c values, calculated using **Equation (1)**.

Supporting Figure S7 – Complete set of time-dependent P_c data in different magnetic fields.



Supporting Figure S7 –Complete sets of time-resolved P_c curves for core (a) and shell (b) emissions for B increasing from 1 T to 15 T with 1 T steps. The black curves are the results of fitting with **Equation (2)**.

Supporting Figure S8 – Time-dependent P_c data at different temperatures (B=5T).



Supporting Figure S8 – Left panels: Complete sets of time-resolved P_c curves for core (top) and shell (bottom) emissions for T increasing from 3.5K to 20K (B=5T). The black curves are the results of fitting with **Equation (2)**. Right panel: Spin-flip rate values extracted from the P_C dynamics as a function of T^2.

Supporting Table S1 – Parameters obtained by fitting k_{spin} versus B with Equation (3) (T = 4.2 K).

	CORE	**SHELL**
$k_{spin,0}^{T-}$[ns^{-1}]	2×10^{-2}	5×10^{-2}
α [ns^{-1}T^{-2}]	6.9×10^{-3}	5.6×10^{-3}

Supporting Table S2 – Parameters obtained by fitting P_c^{eq} and P_c^{int} versus B with Equations (5) and (7), respectively.

	CORE	**SHELL**
hole g-factor	-0.85	-1.2
i	0.245	0.185
f	0.255	0.195

References

1. Galland, C.; Brovelli, S.; Bae, W. K.; Padilha, L. A.; Meinardi, F.; Klimov, V. I.; *Nano Lett.* **2013,** 13, (1), 321-328.
2. Yang, Y. A.; Wu, H.; Williams, K. R.; Cao, Y. C.; *Angew. Chem.* **2005,** 117, (41), 6870-6873.