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Supplementary Information

Anionic Ligand-Induced Chirality in Perovskite Nanoplatelets

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S1. Experimental Section

Materials

Lead(II) bromide ($PbBr_2$, 99.998% metals basis) was purchased from Thermo Scientific. Cesium carbonate (Cs_2CO_3, 99.9% trace metals basis), oleylamine (OLA, technical grade, 70%), oleic acid (OA, technical grade, 90%), octadecene (ODE, 90%) and hexane (HPLC grade, ≥98.5%) were purchased from Sigma Aldrich. Tert-butyl alcohol (t-ButOH, HPLC grade, ≥99.0%) was purchased from TCI America. All chemicals were used without further purification. (R)- and (S)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (R- and S-BNP) were synthesized with a procedure shown below.

Synthesis of BNP-$CsPbBr_3$ NPLs

Firstly, cesium precursor was prepared in a three-necked round-bottom flask by degassing 0.1018 g of Cs_2CO_3, 0.1088 g of BNP, 0.331 mL of OA and 5 mL of ODE at 110 ^oC for 1 hour to full dissolution. For BNP- $CsPbBr_3$ NPLs synthesis, 17.3 mg of $PbBr_2$, 70 mg of BNP, 0.125 mL of OLA and 5 mL of ODE were loaded in a three-necked round-bottom flask and degassed at 110 ^oC for 1 hour. For a complete dissolution of $PbBr_2$, the mixture was heated to 175 ^oC in nitrogen for 2 hours. OLA was used not only as surface capping ligand, but also to deprotonate BNP to improve its very low solubility in ODE.

Then, at 125 ^oC, 0.1 mL of cesium precursor was swiftly injected in the mixture which was quenched after 7 secs by immersing the flask in an ice water bath. When the mixture cooled to room temperature, 5 mL of t-ButOH was add to it and centrifuged at 7500 rpm for 10 min to purify the NPLs. The precipitate was dispersed in 2 mL of hexane and centrifuged at 5000 rpm for 5 min to remove big aggregated particles. R- and S-BNP- $CsPbBr_3$ NPLs were synthesized with the corresponding R- and S-BNP ligands.

Instrumentation

Absorption and photoluminescence spectra were measured by an Agilent Technologies Cary-60 UV-vis spectrometer and a Horiba FluoroMax Plus fluorometer, respectively. PL quantum yield was determined using Fluoromax plus fluorometer (Horiba) equipped with an integrating sphere at an excitation wavelength of 400 nm. PL decay was measured using a time-correlated single-photon counting (TCSPC) module (PicoHarp) with pulsed laser excitation at 405 nm. Transmission electron microscopy (TEM) and high angle annular dark field scanning TEM (HAADF-STEM) images were obtained by a Thermo Fisher-Talos microscope at an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) patterns were collected by Rigaku SmartLab Multipurpose Diffractometer with Cu Kα radiation (0.154059 nm). Fourier-Transform Infrared (FTIR) measurements were carried out with Nicolet Magna 560 spectrometer. CD measurements were performed by Chirascan V100 spectrometer with solution samples in in a 1 mm path length quartz cuvette at 20 °C, time-per-point 0.5 s, single scans and bandwidth 1 nm. Linearly polarized emission was measured using a FLS1000 photoluminescence spectrometer (Edinburgh Instruments) equipped with polarizers in both the excitation and the emission channels. The emission anisotropy values (r) are calculated using $r = \frac{G(\lambda_{\mathrm{em}})I_{VV}(\lambda_{\mathrm{em}}) - I_{VH}(\lambda_{\mathrm{em}})}{G(\lambda_{\mathrm{em}})I_{VV}(\lambda_{\mathrm{em}}) + 2I_{VH}(\lambda_{\mathrm{em}})}$ where I is the emission intensity and $G(\lambda_{\mathrm{em}})$ is the G-factor defined as $G(\lambda_{\mathrm{em}}) = \frac{I_{HH}(\lambda_{\mathrm{em}})}{I_{HV}(\lambda_{\mathrm{em}})}$. The first and second subscript V and H of I refer to vertically and horizontally polarized excitation and emission light, respectively; i.e. I_{VH} is the emission intensity detected with vertically polarized excitation polarizer and with horizontally polarized emission polarizer.

S2. Synthesis and Characterization of Binaphthylphosphoric Acid

Chemicals:

Synthesis of R-Binaphthylphosphoric acid (R-BNP)

The synthesis was adapted according to a previously reported procedure.[1] To a flame-dried Schlenk flask fitted with a magnetic stirrer was 4.5 mL of dry pyridine added. While stirring, 1 g (0.0035 mol) of R-1,1'-Bi-2-naphthol (R-BINOL) was added. Then 0.45 mL (0.736 g, 0.0048 mol) of phosphorus oxychloride was added dropwise to the stirring solution. The temperature rose to about 80 °C. Most of the R-BINOL dissolved. Reaction was heated to 90 °C for complete dissolution. Then, it was allowed to cool to about 50 °C. White precipitate began to form. While stirring the suspension, 4 mL of water was added dropwise. Reaction was exothermic, and all the precipitate dissolved into a solution. Reaction was allowed to cool to about 60° C. Then, reaction mixture was transferred to a dropping funnel. The reaction flask was rinsed with 1 mL pyridine. The rinse was added to the reaction mixture and the whole mixture was added dropwise to 9 mL of 6 N hydrochloric acid with vigorous stirring. White precipitate was formed which was filtered by vacuum filtration. The wet white solid was transferred to a round bottom flask and refluxed with 4 mL of 6 N hydrochloric acid to de-solvate the binaphthylphosphoric acid. The mixture was cooled and the solid was filtered by vacuum filtration, washed with cold water and air-dried for several hours to get a white powder. It was then recrystallized in ethanol to obtain a white crystalline solid. Yield is 64% after recrystallization. ^{1}H NMR (DMSO, 400 MHz): δ (ppm): 3.69 (broad, -OH), 7.25 (d, *J* = 8.5 Hz, 1H), 7.37 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.52 (dd, *J* = 10.7, 8.2 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H). ^{31}P NMR (DMSO, 400 MHz): δ (ppm): 3.25 (s, 1P).

Synthesis of S-Binaphthylphosphoric acid (S-BNP)

The enantiomer (S-BNP) was synthesized according to the procedure reported above. A white crystalline solid was obtained. ^{1}H NMR (DMSO, 400 MHz): δ (ppm): 3.60 (broad, -OH), 7.24 (d, *J* = 8.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H). ^{31}P NMR (DMSO, 400 MHz): δ (ppm): 3.34 (s, 1P).

^{1}H and ^{31}P NMR of R-BNP

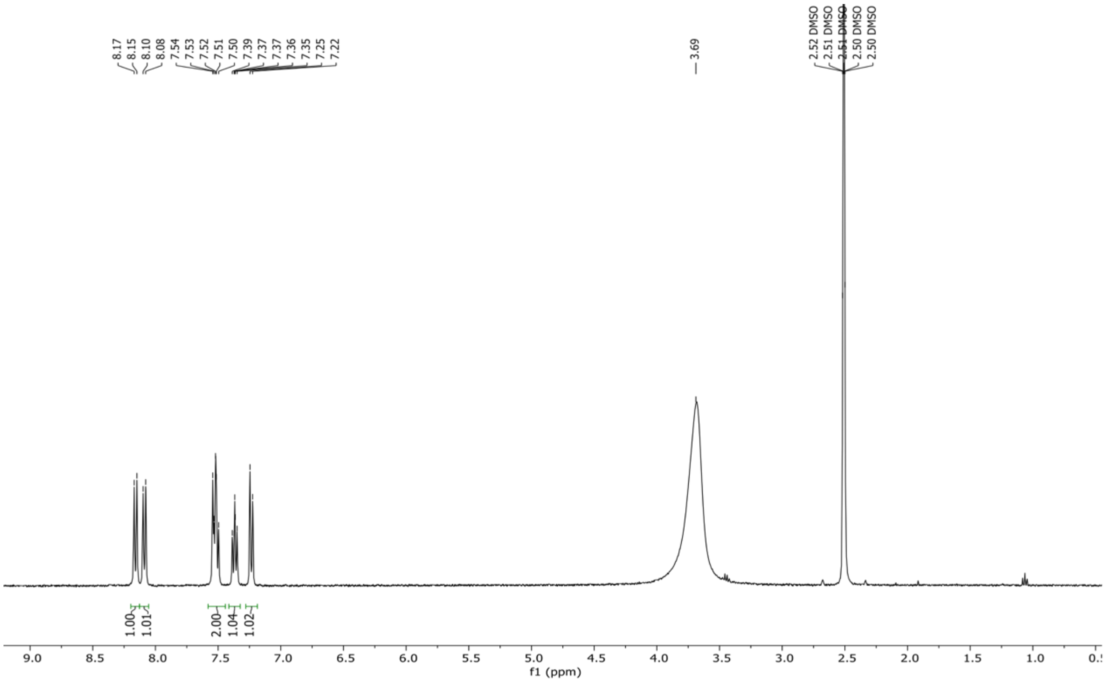

Figure S1. ^{1}H NMR of R-BNP

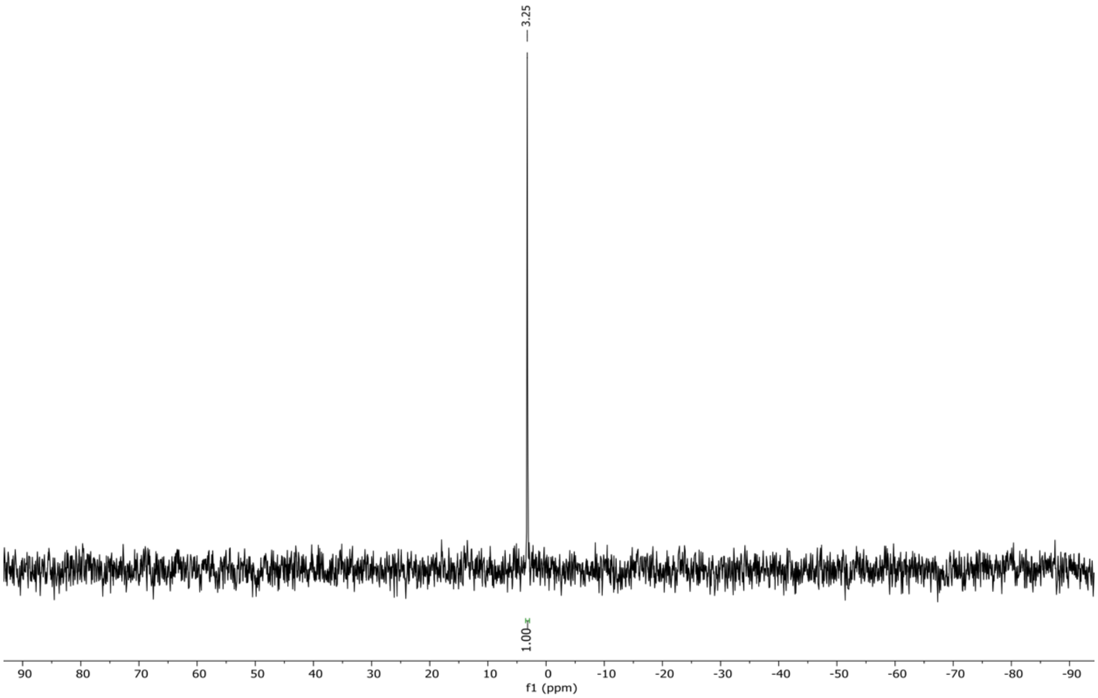

Figure S2. ^{31}P NMR of R-BNP

^{1}H and ^{31}P NMR of S-BNP

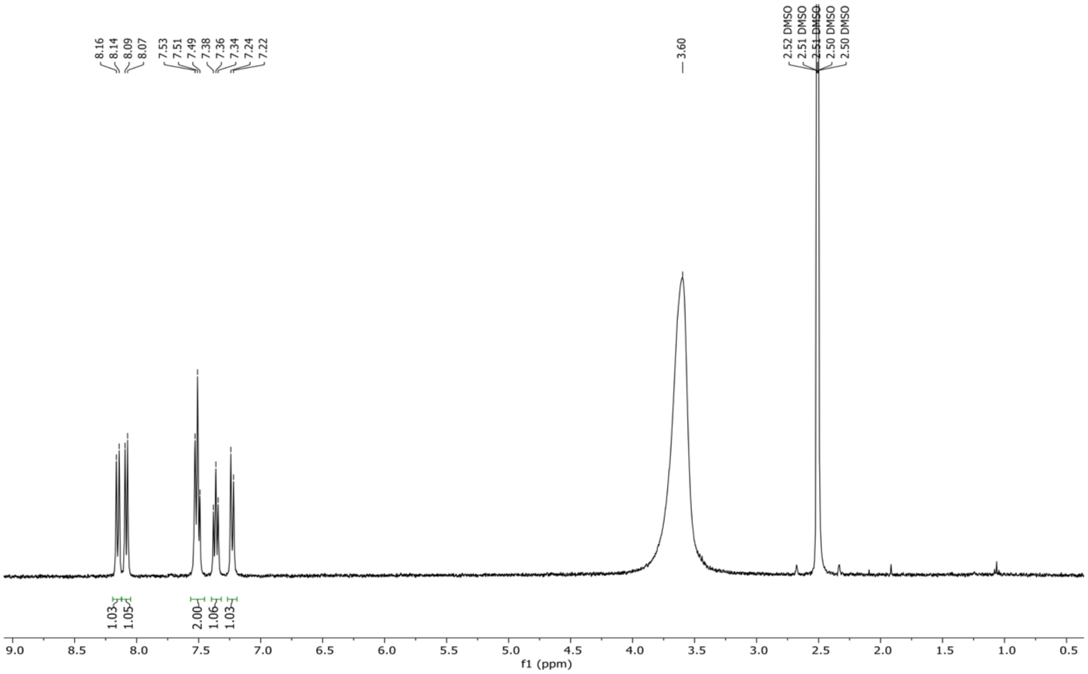

Figure S3. ^{1}H NMR of S-BNP

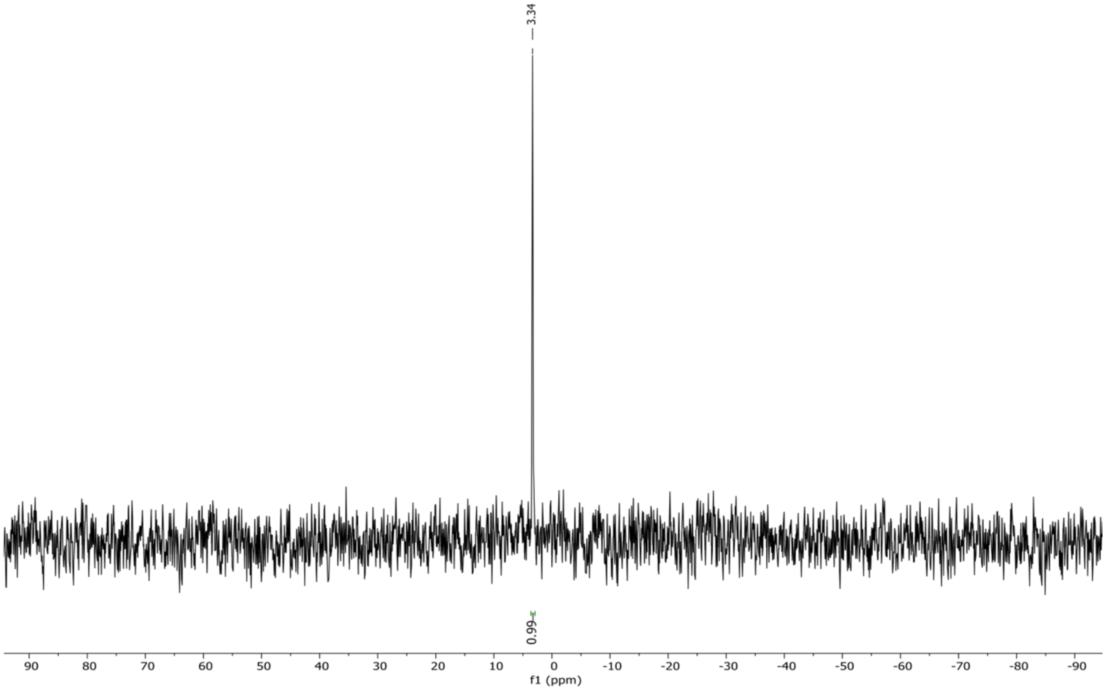

Figure S4. ^{31}P NMR of S-BNP

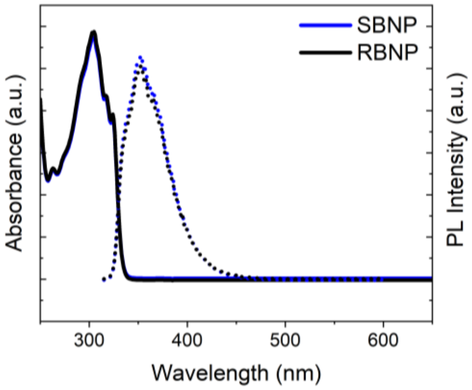

Figure S5. Absorption and PL spectra of BNP molecules

S3. Additional Characterization of BNP-$CsPbBr_3$ NPLs and Nanocubes

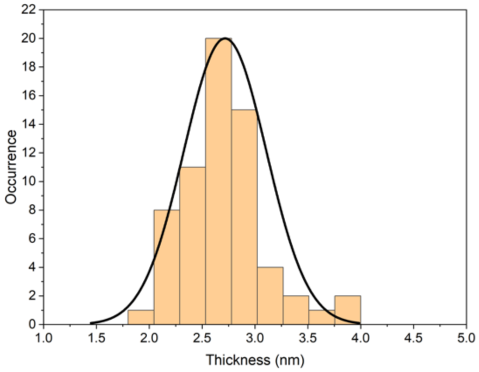

Figure S6. Thickness distribution of BNP-$CsPbBr_3$ NPLs (n=68)

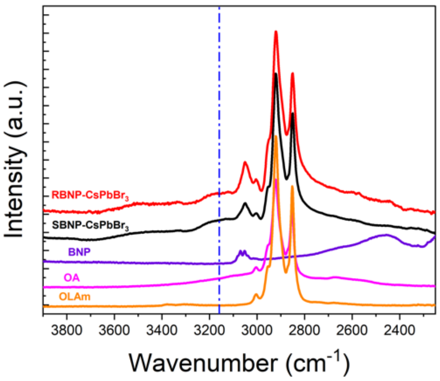

Figure S7. FTIR spectra of OLAm, OA, and BNP-$CsPbBr_3$ NPLs at 3900 – 2250 cm^{-1}. The dashed line denotes 3159 cm^{-1}.

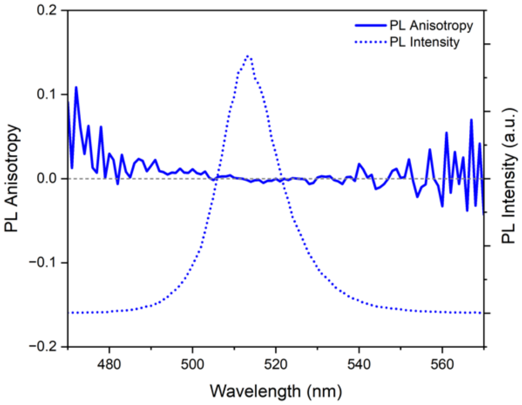

Figure S8. Fluorescence anisotropy of $CsPbBr_3$ nanocubes prepared following ref.[2].

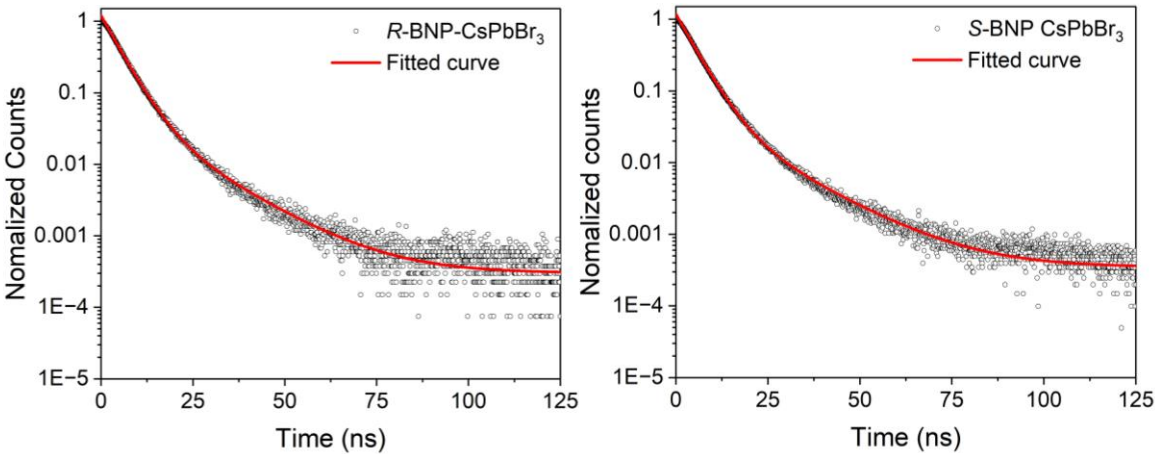

Figure S9. PL decay measurement curves and bi-exponential fitting curves for (a) *R*- and (b) *S*- BNP NPLs

Table S1. PL decay fitting parameters of *R*- and *S*- BNP NPLs. The decays are fitted to bi-exponential function: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + y_0$. The average lifetime is determined by $\tau_{avg} = ((A_1 \times \tau_1^2) + (A_2 \times \tau_2^2)) / ((A_1 \times \tau_1) + (A_2 \times \tau_2))$.

Samples	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_{avg} (ns)
R-BNP NPLs	4.51	1.15	14.26	0.06	5.89
S- BNP NPLs	4.55	1.13	15.16	0.06	6.14

Reference

1 J. Jacques and C. Fouquey, in *Organic Syntheses*, pp. 1–1.

2 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett*, 2015, **15**, 3692–3696.