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Great Amplification of Circular Polarization Sensitivity via Heterostructure Engineering of a Chiral Two-Dimensional Hybrid Perovskite Crystal with a Three-Dimensional MAPbl₃ Crystal

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ABSTRACT: Chiral hybrid perovskites have brought an unprecedented opportunity for circularly polarized light (CPL) detection. However, the circular polarization sensitivity of such a detector remains extremely low because of the high exciton recombination rate in those single-phase hybrid perovskites. Here, a heterostructure construction strategy is proposed to reduce the electron—hole recombination rate in a chiral hybrid perovskite and achieve CPL detectors with greatly amplified circular polarization sensitivity. A heterostructure crystal, namely, $[(R)-MPA]_2MAPb_2I_7/$ MAPbI₃ ((*R*)-MPA = (*R*)-methylphenethylamine, MA = methylammonium), has been successfully created by integrating a chiral two-dimensional (2D) perovskite with its three-dimensional counterpart via solution-processed heteroepitaxy. Strikingly, the sharp interface of the as-grown heterostructure crystal facilitates the formation of a built-in electric field, enabling the combined concepts of charge transfer and chirality



transfer, which effectively reduces the recombination probability for photogenerated carriers while retaining chiroptical activity of chiral 2D perovskite. Thereby, the resultant CPL detector exhibits significantly amplified circular polarization sensitivity at zero bias with an impressive anisotropy factor up to 0.67, which is about six times higher than that of the single-phase $[(R)-MPA]_2MAPb_2I_7$ (0.1). As a proof-of-concept, the strategy we presented here enables a novel path to modulate circular polarization sensitivity and will be helpful to design chiral hybrid perovskites for advanced chiroptical devices.

1. INTRODUCTION

Chiral photonics based on circularly polarized light (CPL) has been actively studied for applications such as optical spintronics, ellipsometric tomography, and quantum optics.¹⁻⁵ Developing the full potential of these technologies requires a chirality-active layer to create CPL detectors that are capable of distinguishing left-handed CPL (LCP) and right-handed CPL (RCP).^{6,7} The chiral medium, theoretically, needs to combine a high chiroptical response and efficient charge transport simultaneously. Currently, organic semiconductors such as helicene show promise in direct CPL detection owing to their high optical rotatory power and strong circular dichroism (CD).^{6,8–12} However, the operational wavelength of these organic molecules is generally in an ultraviolet regime. Metamaterials with engineered chirality can offer a specific response spanning the entire telecommunication regime, but their use remains limited due to fabrication challenges and optical losses.^{13,14} Therefore, it is of significant importance to explore a new system of semiconductor materials with large, easily accessible chiroptical activity for direct CPL detection.

Solution-processed organic–inorganic hybrid perovskites can fully meet the requirements. During recent years, they have been widely used in optoelectronics.^{15–20} The key advantage of such materials is their superior semiconductor properties, including high carrier mobility, large absorption coefficients, and low deep trap states.²¹⁻²³ Furthermore, the structure of hybrid perovskites often depends on the organic ligands, which allows one to control their band gap, composition, and dimensionality via chemical modification. Particularly, chiral organic ligands can be directly incorporated in hybrid perovskites.^{24–29} The resulting chiral one-dimensional (1D) and two-dimensional (2D) hybrid perovskites thereby possess intriguing chiroptical activity and excellent semiconductor properties, 30-32 opening a door to them for semiconductor properties, $^{30-32}_{33-35}$ opening a door to them for efficient CPL detection. $^{33-35}$ For example, Yuan et al. reported a direct CPL detector built on a chiral 2D perovskite crystal, showing a high responsivity of 3.8 A/W at 532 nm.³³ However, the large exciton binding energy and high exciton recombination rate in these low-dimensional single-phase perovskites limit the circular polarization sensitivity of their CPL detectors, with typically reported anisotropy factors of about 0.1. Very recently, Ishii and Miyasaka claimed that CPL detectors using chiral 1D perovskite films could achieve a remarkable

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anisotropy factor of up to 1.85 (calculated based on the reported $R_{\rm I}/R_{\rm R}$ of 25.4), owing to the optimized charge transport direction.³⁶ Despite such an advance, however, the search for chiral hybrid perovskites is still at a very early stage, and new strategies to design such materials with high circular polarization sensitivity are urgently desired.

Constructing heterostructures between chiral hybrid perovskite and its 3D counterparts may provide a clue to address these challenges. This engineering strategy aims to, on the one hand, transfer chirality from the chiral component to the heterostructure, which as a higher free carrier density and stronger optical absorption; 37-40 on the other hand, it aims to generate a built-in electrical field at the junction. As is known, the built-in electrical field is efficient for charge transfer, which can facilitate photogenerated carrier separation/transport,^{41,42} reducing their recombination rate and thus improving the sensitivity of photodetectors.^{43,44} Hence, there is an exciting opportunity for chiral perovskite heterostructures to realize CPL detection with boosted circular polarization sensitivity. Herein, we apply a facile two-step solution-epitaxial method for creating a chiral perovskite heterostructure crystal, [(R)- $MPA]_2MAPb_2I_7/MAPbI_3$ ((R)-MPA = (R)-methylphenethylamine, MA = methylammonium). At zero bias, the CPL detector based on the heterostructure crystal exhibits greatly amplified circular polarization sensitivity as compared to the single-phase $[(R)-MPA]_2MAPb_2I_7$, with an impressive anisotropy factor of 0.67, indicating its promise for sustainable and sensitive CPL detection.

2. RESULTS AND DISCUSSION

2.1. Heterostructure Synthesis. Before the creation of a heterostructure, enantiomers of chiral 2D hybrid perovskites should be prepared first (Experimental Section in Supporting Information). In this step, large single crystals of [(R)-MPA]₂MAPb₂I₇ and $[(S)-MPA]_2MAPb_2I_7$ are grown via a temperature-cooling method (Figure 1a, Step 1), in which the structures are depicted in Figure S1a-c and Table S1.^{31,33} Scanning electron microscopy (SEM) measurements indicate the excellent single crystallinity of the grown crystal (Figure S1d). The absorption edge of the chiral 2D perovskite gives a bandgap of 2.0 eV by a direct-gap Tauc plot (Figure S2), consistent with the previous reports.^{31,33} In the next step, chiral 2D perovskite crystals are used as a substrate for epitaxial growth of MAPbI₃. We immersed half of the grown [(S)/(R)-MPA]₂MAPb₂I₇ crystal into a supersaturated MAPbI₃ solution at 60 °C for 90 s (Figure 1a, Step 2). Upon immersion, the surface of $[(R)-MPA]_2MAPb_2I_7$ (or $[(S)-MPA]_2MAPb_2I_7$) crystal underwent a rapid color change from bright red to shiny black, suggesting a surface layer of MAPbI₃ has grown onto the prior crystal and the corresponding heterostructure is formed. Though there is a large mismatch between the chiral perovskite (a = 12.4050 Å, b = 19.6581 Å, c = 23.3427 Å) and MAPbI₃ (a = 12.4050 Å, b = 19.6581 Å, c = 23.3427 Å)= b = 8.8725 Å, c = 12.547 Å), the soft nature of hybrid perovskites can relax this lattice mismatch strain and enables the MAPbI₃ heteroepitaxy.^{45,46} A reverse process that dips MAPbI₃ crystals in [(S)/(R)-MPA]₂MAPb₂I₇ solutions was also carried out. However, all $[(S)/(R)-MPA]_2MAPb_2I_7$ solutions were found to damage the existing crystal, and thus the reverse process is not feasible.

The growth mechanism of this two-step solution method is interpreted by a dissolution–nucleation diagram. Experimental solubility curves of [(S)/(R)-MPA]₂MAPb₂I₇ and MAPbI₃ are displayed in Figure 1b. It can be observed that the solubility of



Figure 1. (a) The synthesis process to create the 2D/3D heterostructure; (b) solubility curve of $[(R)/(S)-MPA]_2MAPb_2I_7$ and MAPbI₃ as a function of temperature in HI solution.

both 2D and 3D perovskites in HI solution increases upon heating, and at any fixed temperature, the solubility of MAPbI₃ is always much higher than that of $[(S)/(R)-MPA]_2MAPb_2I_7$. This may explain the fact that MAPbI₃ crystals are easily dissolved when dipped in $[(S)/(R)-MPA]_2MAPb_2I_7$ solution. Generally, for a solution with a concentration above the solubility curve (i.e., supersaturated), spontaneous nucleation will occur and corresponding growth rate is high.⁴⁷ Therefore, in experimental step 1 mentioned above, a stable unsaturated region was chosen to grow large 2D perovskite crystals, as denoted by the green dot and characterized by the presence of sizable crystals in a slow temperature-cooling procedure. For step 2, we note that only supersaturated MAPbI₃ solution gives the quick epitaxial growth of the surface layer. A less concentrated solution can either lead to second phase formation or etch the 2D perovskite crystal surface. It has been reported that epitaxial growth as well as ion diffusion may occur simultaneously in such a solution process.^{48,49} In our case, however, the use of a rigid π -conjugated organic spacer can efficiently suppress the ion interdiffusion, and hence it is deduced that the epitaxial growth dominates the heterostructure construction.⁴⁶ Moreover, the thickness of the MAPbI₃ surface layer can be controlled by the dipping time, and the initial growth rate of MAPbI₃ is estimated to be 70 nm/s (Figure S3). Schematic illustration of the heterostructure is shown in Figure 2a and Figure S4a. We conclude that the key to this heterostructure synthesis is the spontaneous nucleation of MAPbI₃ on the $[(S)/(R)-MPA]_2MAPb_2I_7$ crystal surface, which can be controlled by MAPbI₃ solution concentration and dipping time. Our convenient and costeffective approach for heterostructure construction may provide a handle for better control of the interface integrity and the associated optoelectronic properties.



Figure 2. (a) Schematic illustration of the [(R)-MPA]₂MAPb₂I₇/MAPbI₃ heterostructure. The purple, green, blue, and gray spheres represent I, Pb, N, and C, respectively. For clarity, H atoms are omitted. (b) SCXRD diffraction patterns of the heterostructure crystal at the [001] plane; (c) SCXRD diffraction patterns of the chiral 2D hybrid perovskite in the [001] plane. Inset: SCXRD diffraction patterns of MAPbI₃ at the [001] plane; (d) SEM image of the as-grown heterostructure. Inset: Optical microscopy image of the heterostructure; (e) SEM image of the surface layer MAPbI₃; (f) AFM image of the surface layer MAPbI₃; (g) SEM image of cross sections of heterostructure crystal. Inset: Magnified cross-section SEM image at the heterostructure interface; (h) I-V measurements according to the SCLC method.

2.2. Heterostructure Characteristics. Phase purity of the heterostructure is evidenced by power X-ray diffraction (PXRD, Figure S4b). To study the interface structure of the as-fabricated $[(R)-MPA]_2MAPb_2I_7/MAPbI_3$ heterostructure (R-HS) crystal, we performed single crystal X-ray diffraction (SCXRD) measurements (Figure 2b,c). After the integration of 3D MAPbI₃, we observed a significant further increase in the peak intensities of the [001] reflections in the SCXRD image and the appearance of characteristic reflection peaks of MAPbI₃, suggesting that the stable heteroepitaxy between $[(R)-MPA]_2MAPb_2I_7$ and MAPbI₃ is out-of-plane (vertical) connected along the [001] direction. And the strain is probably relaxed through rearrangement of the organic cations.⁴⁶ Figure S5 displays the SEM image of the heterostructure with dimensions of about 1.5 mm \times 1.5 mm \times 260 μ m and shows a clear MAPbI₃ surface layer (Figure 2d). Notably, no visible grain boundaries or pin holes are observed in the surface layer (Figure 2e), suggesting few surface defects, which is consistent with atomic-force microscopy (AFM) characterization (Figure 2f). More importantly, cross-sectional SEM images in Figure 2g display a quite sharp interface between MAPbI₃ and [(R)-MPA]₂MAPb₂I₇. This nearly atomically sharp interface suggests negligible ion diffusion across the interface, supporting the vertically epitaxial growth of MAPbI₃. For practical optoelectronic applications, such a sharp interface is highly desirable because it can facilitate the formation of a built-in electrical field, which is necessary to improve the performance and for sustainable devices.⁵⁰ To quantitatively evaluate the trap density (n_{trap}) of the heterostructure crystal,

we performed a space-charge-limited current (SCLC) technique (Supporting Information). The n_{trap} is calculated to be as low as 7.8×10^{10} cm⁻³ (Figure 2h), comparable to the high-quality MAPbX₃ (X = Br, I; $n_{trap} = 3 \times 10^{10}$ cm⁻³) crystals.²¹ The above observations suggest the heteroepitaxy between the two distinct perovskites is of high crystalline quality, which will potentially benefit the carrier transport and optoelectronic performance.

Further, we conducted photoluminescence (PL) spectroscopy, ultraviolet-visible (UV-vis) absorption spectroscopy and CD spectroscopy to study the optical properties of our chiral perovskite heterostructures. The PL profile of the vertical heterostructure contains two distinct emission peaks at 560 and 800 nm, corresponding to $[(R)/(S)-MPA]_2MAPb_2I_7$ and MAPbI₃, respectively (Figure 3a). A consistent phenomenon is observed in UV-vis spectra, with an enhanced optical absorption after integration of MAPbI₃ (Figure 3b). CD spectra provide the ground state chiral information for chiral 2D perovskites and the corresponding heterostructures. As illustrated in Figure 3c, the R-HS crystal shows an obvious CD signal peaking at 540 and 570 nm, indicating a preferential absorption of R-CPL; a mirror CD spectrum is observed for the S-HS crystal. This result implies the ability of the heterostructure to discriminate between left- and right-handed CPL, and the handedness of chiral 2D perovskite controls the handedness of CPL to which it responds (Figure 3d). Interestingly, as compared to single-phase chiral 2D perovskites, the CD signal peaks red shift (~25 nm) after the formation of the heterostructure. Ben-Moshe et al. found that



Figure 3. (a) PL spectra and (b) optical absorption spectra of [(R)/(S)-MPA]₂MAPb₂I₇, MAPbI₃, and the heterostructure; (c) CD spectra of the (*R*)-HS and (*S*)-HS; (d) CD spectra of [(R)-MPA]₂MAPb₂I₇ and [(S)-MPA]₂MAPb₂I₇.

the CD spectra are based on split excitonic transition states, and each CD peak has a corresponding excitonic transition.⁵¹ The observed red shift in CD spectra may be ascribed to electrical coupling between the two phases, as has been observed in heterostructures based on chiral organic semiconductors.⁹ However, the precise mechanism for this phenomenon still requires further investigation. The high crystalline quality together with chiroptical activity will offer exciting opportunities for our heterostructures in CPL detection.

2.3. Device Fabrication and Performance. Previous to examining the CPL detection capability, the *R*-HS crystal is first introduced as a photoactive semiconductor in a photodetector to investigate its optoelectronic properties. The device with the structure of Au/2D [(*R*)-MPA]₂MAPb₂I₇-3D MAPbI₃/Au is shown in Figure 4a. An electrical transport

study clearly demonstrated an obvious rectifying behavior (Figure S6a), indicating a built-in perpendicular electric field has been formed in the vertical $[(R)-MPA]_2MAPb_2I_7/MAPbI_2$ heterostructure. Under illumination, the device exhibits excellent photocurrent generation characteristics with a photovoltage of ~0.23 V (Figure S6b-d). The observation of the photovoltaic effect supports the existence of a built-in electrical field and implies that the present device can act as a self-driven photodetector operating at zero external bias. The excellent performance of the R-HS photodetector encourages us to further investigate its CPL detection capability in a selfdriven mode. As shown in Figure 4a, the CPL is controlled by a linear polarizer and a quarter-wave $(\lambda/4)$ plate and then incident at the heterostructure crystal. Considering the UV-vis absorption spectrum, CD spectrum, and the available laser in our lab, a laser of 520 nm is chosen. By continuously rotating the $\lambda/4$ plate from 0° to 360°, the incident light (520 nm, 2.5 mW/cm²) is tuned from linear to left- and right-handed circular polarization.⁵² The photovoltage response under different polarization angles is displayed in Figure 4b and Figure S7, where no mirror plane with 180° rotation angle is observed, experimentally indicating that chirality activity of $[(R)-MPA]_2MAPb_2I_7$ has been successfully transferred to the heterostructure of its constituents. According to the recent mCP-AFM and MR studies, this chirality transfer is expected to originate from the selective spin-polarized carrier transport between chiral 2D perovskites and 3D perovskite.^{30,37,53-55} The selective spin-polarized carrier transport is the manifestation of a chiral-induced spin selectivity (CISS) effect which occurs when chiral cations of chiral perovskites only allow the one of the spin states (up-spin or down-spin state) to transport through the organic spacer while blocking the other one. Under CPL illumination, photogenerated carriers in [(R)-MPA]₂PbCl₄ are highly spin-polarized in which the spin orientation is determined by the R-MPA cation. The continuous separation and transport of those spin-polarized carriers thus leads to anisotropic photovoltage that is highly



Figure 4. (a) Illustration of the CPL detector of the $[(R)-MPA]_2MAPb_2I_7/MAPbI_3$ heterostructure crystal; (b) photovoltage of the heterostructure device as a function of the rotation angle of $\lambda/4$ plate. The right- and left-handedness of light is colored blue. (c) Photovoltage under RCP and LCP illumination; (d) short-circuit current of the heterostructure device as a function of the rotation angle of $\lambda/4$ plate; (e) SC of the device under RCP and LCP illumination; (f) g_{Isc} and photovoltage as a function of RCP light intensity.

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sensitive to the excitation light helicity. The photovoltage under RCP and LCP irradiation is shown in Figure 4c. More interestingly, this photovoltage dissymmetry fully translates to a correspondingly large distinction in the short-circuit current (SC) for LCP and RCP light (Figure 4d). As expected, the SC achieved under RCP illumination is much higher than that under LCP illumination, demonstrating an excellent distinguishability between RCP and LCP photons (Figure 4e). We note that the heterostructure has a large resistance under zero bias, which makes its photovoltage change more slowly than that of the photocurrent.

The circular polarization sensitivity of SC is evaluated by the anisotropy factor (g_{lsc}) , which is determined by eq 1:

$$g_{\rm Isc} = 2 \frac{I_{\rm sc}^{\rm R} - I_{\rm sc}^{\rm L}}{I_{\rm sc}^{\rm L} + I_{\rm sc}^{\rm R}}$$
(1)

where I_{SC}^{L} and I_{SC}^{R} represent short-circuit current under LCP and RCP illumination, respectively.³³ The g_{Isc} is calculated to be 0.67, which is greatly enhanced as compared to that of the pristine chiral [(R)-MPA]₂MAPb₂I₇ crystal (0.1, Figure S8).³³ This value is significantly higher than many recent reports of direct CPL detectors using either chiral hybrid perovskites or organic semiconductors, which typically achieve $g \leq 0.1$ and require operating voltages to produce photocurrent (Table S2). The 2D/3D heterostructure crystal construction strategy demonstrated here allows us to achieve amplified g_{Isc} without an external energy supply and could be applied to a broad range of chiral materials with varied structures. gisc under a different excitation intensity is shown in Figure 4f, which shows a trend of first increasing and then decreasing with varied excitation powers. Since our device is operated at zero bias, the increasing of g_{Isc} at lower light intensities can be ascribed to the photovoltage increasing, which offers a stronger effective electric field for exciton separation (Figure 4f). The sequent decrease may originate from the enhanced recombination of photogenerated carriers by defects at higher light powers, and the gradual saturation of photocurrent may lead to a slight decline in g_{Isc} .

In a heterostructure active layer as the ones explored here, the greatly amplified circular polarization sensitivity as compared to the single-phase $[(R)-MPA]_2MAPb_2I_7$ crystal can be mainly ascribed to a spin-selective interfacial charge transfer process.⁴⁰ As is known, the large exciton binding energy (of about 0.2–0.5 eV) in 2D hybrid perovskites may cause a high exciton recombination rate, which impedes the exciton separation and carrier transport, making it difficult for these materials to achieve a high circular polarization sensitivity.^{24,56}

According to ultraviolet photoelectron spectroscopy (UPS) measurements, our chiral heterostructure adopts a type-II band alignment. This band alignment favors charge transfer, which can serve to spatially separate the photogenerated electron–hole pairs and reduce their recombination probability.⁴¹ The charge transfer process is evidenced by the decrease of the emission intensity and PL lifetime at the junction area (Figure Sa, Figure S9). Upon illumination, spin-polarized electrons are generated in [(R)-MPA]₂MAPb₂I₇ and move to achiral MAPbI₃, while holes move to [(R)-MPA]₂MAPb₂I₇ (Figure Sb). The direct result of this is the recombination probability for electrons and holes during their motion to the opposite electrodes can be significantly reduced. Further, in our device structure as mentioned in Figure 4a, the chiral [(R)-



Figure 5. (a) PL lifetime spectrum for heterostructure at 560 nm emission. Inset: Photoluminescence lifetime spectrum for $[(R)-MPA]_2MAPb_2I_7$ at 560 nm emission; (b) schematic illustration of the band alignment of the chiral perovskite heterostructure and the motion of the photogenerated carriers.

MPA]₂MAPb₂I₇ crystal is placed parallel to the substrate, while the chiral organic cations are perpendicular. Therefore, the helical distribution of the electron cloud in chiral [(R)-MPA]₂MAPb₂I₇ is perpendicular to the 3D MAPbI₃ and more importantly, parallel to the built-in electric field direction (Figure 5b). In this way, the built-in electric field can efficiently separate/transport those spin-polarized excitons with particular spin orientation, which reduces their recombination rate and results in pronounced $I_{SC}^{R,37}$ Thus, the circular polarization sensitivity can be greatly amplified. On the basis of the above results, we conclude that the chirality in the single-phase chiral hybrid perovskite can be transferred to the heterostructure, and the spin-selective interfacial charge transfer results in the amplification of circular polarization sensitivity.

Temporal response of the device with RCP irradiation (at 0 V bias, $\lambda = 520$ nm) indicates an ultralow dark current of 2 × 10^{-14} A together with a high on/off ratio of 10^5 (Figure 6a). Such an on/off ratio is about 2 orders of magnitude higher than the values reported for other perovskite-based photo-detectors.^{57–59} Further, three important parameters, responsivity (*R*), external quantum conversion efficiency (EQE), and detectivity (*D**), are introduced to appraise the detection capability. As shown in Figure 6b, the *R* value of 1.2 mA/W is achieved under an incident light density of 0.2 mW/cm². At the same light intensity, EQE is estimated to be 2.8% (Figure S10). Significantly, the highest *D** value of 1.1×10^{12} Jones is comparable to the excellent CPL detectors based on chiral 2D hybrid perovskites.³³ Figure 6c shows that the device can work without obvious attenuation after a long-term repetition of



Figure 6. (a) Photocurrent measured with different incident light intensities under RCP illumination; (b) incident-light power dependence of R and D^* ; (c) time-dependent switching cycles of photoresponse for the CPL detector; (d) the response time of the self-driven CPL detector.

RCP light—on/off, indicating the antifatigued attributes of our device. On the basis of the definition of response speed, the rise and decay time are estimated to be 2 and 2.4 ms, respectively (Figure 6d). Besides, device stability is another important figure-of-merit. We find that the heterostructure device is stable without an obvious photoresponse loss after 30 days of storage in air (Figure S11), demonstrating its favorable stability.

3. CONCLUSIONS

In summary, for the first time, we have demonstrated a selfdriven CPL detector using a chiral 2D perovskite-based heterostructure crystal, which is created via a delicate two-step solution-epitaxial method. The as-synthesized heterocrystal features high crystalline quality and a nearly atomically sharp interface. Benefiting from the combination of chirality transfer and charge transfer, the resultant CPL detector can easily distinguish LCP and RCP with a significantly amplified circular polarization sensitivity at zero bias. Strikingly, the anisotropy factor of the device can reach up to 0.67, which is much higher than that of the pristine single-phase chiral 2D perovskite (0.1), surpassing many other CPL detectors based on chiral semiconductors. Our heterostructure construction strategy for integration of functional hybrid perovskites is an important step forward, which can widen the range of potential material combinations for the design of chiroptical active materials in application of CPL detectors, as well as other advanced optoelectronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.1c00649.

Experimental details; bulk crystals and growth morphology; experimental bandgap; photoelectronic measurements of heterostructure (PDF)

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Notes

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