Supplementary Information (SI) for Nanoscale.

Supplementary Information

Circular Dichroism Measurement of Single Anisotropic Chiral Nanostructure Using Scanning Circular Dichroism Microscopy

Jiaxin Du, †[a] Xujin Qin, †[b,c] Xinyu Li,[a] Hongyan Shi,[a,d] Yueling Zhang,[e] Pengfei Duan,[*f] and Bo Gao[*a,d]

a. Institute of Modern Optics, School of Physics, Key Laboratory of Micro-Nano Optoelectronic Information System, Ministry of Industry and Information Technology, Key Laboratory of Micro-Optics and Photonic Technology of Heilongjiang Province, Harbin Institute of Technology, Harbin 150001, China

b. Beijing National Laboratory for Molecular Sciences, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

c. University of Chinese Academy Sciences, Beijing 100049, China

d. Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China

e. State Key Laboratory for Animal Disease Control and Prevention, Harbin Veterinary Research Institute, Chinese Academy of Agricultural Sciences, Harbin 150069, China

f. CAS Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology (NCNST), Beijing 100190, China

* *Corresponding author:* gaobo@hit.edu.cn; duanpf@nanoctr.cn

† These authors contributed equally to this work

1. Derivation of the LDLB effect in the orientated single anisotropic chiral nanostructure

Figure S1 shows the scheme of Cartesian coordinate system used for the description of the optical effects. For the orientated single anisotropic chiral nanostructure, LD is the horizontal linear dichroism projection expressed as $LD=2\pi(k_x-k_y)\ l/\lambda$, LB is the horizontal linear birefringence projection expressed as $LB=2\pi\ (n_x-n_y)l/\lambda$, LD' is the 45° linear dichroism projection expressed as $LD'=2\pi\ (k_{45°}-k_{135°})\ l/\lambda$, and LB' is the 45° linear birefringence projection expressed as $LB'=2\pi\ (n_{45°}-n_{135°})l/\lambda$.[1-3]

If the orientation of the single anisotropic chiral nanostructure is β, LD_β is the linear dichroism of the single anisotropic chiral nanostructure expressed as $LD_\beta=2\pi\ (k_{\parallel}-k_{\perp})\ l/\lambda$. Besides, if the principal axes for LD and LB align, LD_β is the linear birefringence of the single anisotropic chiral nanostructure expressed as $LB_\beta=2\pi\ (n_{\parallel}-n_{\perp})\ l/\lambda$. In the single DBD and LBL chiral supramolecule, LD_β (LB_β) is the maximum value of the linear dichroism (linear birefringence). Therefore, k_x and k_y are the projections of $k_{\parallel}$ and $k_{\perp}$ with β, which can be expressed as $k_x=k_{\parallel}\cos^2\beta+k_{\perp}\sin^2\beta$, $k_y=k_{\parallel}\sin^2\beta+k_{\perp}\cos^2\beta$. Besides, $k_{45°}$ and $k_{135°}$ are the projections of $k_{\parallel}$ and $k_{\perp}$ with β, which can be expressed as $k_{45°}=k_{\parallel}\cos^2(45°\text{-}\beta)+k_{\perp}\sin^2(45°\text{-}\beta)$, $k_{135°}=k_{\parallel}\sin^2(45°\text{-}\beta)+k_{\perp}\cos^2(45°\text{-}\beta)$.

Hence, LD, LB, LD', and LB' can be expressed as $LD=2\pi(k_x-k_y)\ l/\lambda=LD_\beta\cos(2\beta)$, $LB=2\pi(n_x-n_y)l/\lambda=LB_\beta\cos(2\beta)$, $LD'=2\pi(k_{45°}-k_{135°})\ l/\lambda=LD_\beta\sin(2\beta)$, and $LB'=2\pi(n_{45°}-n_{135°})l/\lambda=LB_\beta\sin(2\beta)$. The term "$LBLD'-LB'LD$" can be expressed as

$$LBLD'-LB'LD=LB_\beta\cos(2\beta)\ LD_\beta\sin(2\beta)\text{-}LB_\beta\sin(2\beta)\ LD_\beta\cos(2\beta)=0 \tag{S1}$$

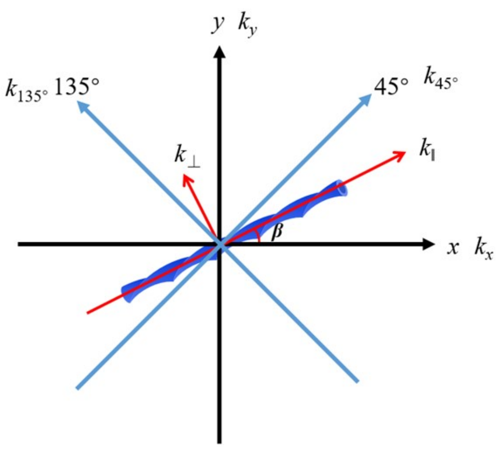

Figure S1 Scheme of Cartesian coordinate system used for the description of the optical effects.

2. Relationship between $V_{d\text{-}2f}$ and incident polarization angles of the laser beam

Using the Mueller matrix approach, we analyzed the detected signals of scanning polarization modulation microscopy (SPMM).[4, 5] In this study, we determined the orientation angles β of the single chiral nanostructure under $2f$ modulation of PEM. When the reference of the lock-in amplifier is set at twice the resonant frequency ($2\omega_m$) of the PEM, the $2\omega_m$ component of intensity can be extracted

$$V_{\det-2f}(\omega_m) = -k_2 J_2(\delta_0) I_0 LD \sin\left[2(\theta+\beta)\right] \tag{S2}$$

where $k_2J_2(\delta_0)I_0$ could be determined by placing a polarizer between the PEM and the half-wave plate. Specifically, when the polarization is rotated to –45° concerning the i-axis of the PEM, the output of the lock-in amplifier is $V_{\text{ref-}2f}(2\omega_m) = T_g k_2 J_2(\delta_0) I_0$. T_g is the transmittance of the glass substrate, equal to 0.96. The detected signal $V_{d\text{-}2f} = T_g V_{\det\text{-}2f}(2\omega_m)/V_{\text{ref-}2f}(2\omega_m)$ can be simply expressed as follows:

$$V_{d-2f} = -LD \times \sin\left[2(\theta+\beta)\right] \tag{S3}$$

Therefore, we can determine the orientation angles β of the the single chiral nanostructure. Moreover, when the half-wave plate is at 0°, we can obtain the output signal expressed as:

$$V_{2f} = -LD \times \sin(2\beta) \tag{S4}$$

Figure S2 shows the obtained SPMM signals of the single DBD/LBL self-assembled chiral supramolecule with incident polarization angles θ from 0° to 180° clockwise in 10° increments. It can be seen that $V_{d\text{-}2f}$ signals are highly dependent on the incident polarization angles θ due to the anisotropy of the single DBD/LBL self-assembled chiral supramolecule. SPMM signals varied sinusoidally with incident polarization angles θ as shown in Figures S2(a) and (b). We determined the orientation angles of the single DBD/LBL self-assembled chiral supramolecule by fitting SPMM signals using Equation S3. The determined orientation angles of the single DBD self-assembled chiral supramolecule are –0.49°, 17.99°, 36.60°, 56.52°, 80.72°, 101.9°, 120.6°, 147.6°, 160.0°, and 175.4°, respectively (as shown in Figure S2(a)). Figure S2(b) shows the orientation angles of the single LBL self-assembled chiral supramolecule, determined separately to be 0.31°, 18.34°, 32.15°, 57.87°, 79.72°, 99.81°, 117.6°, 141.6°, 161.2°, and 176.1°. The orientation angles determined by SPMM are the same as those determined by SCDM, as shown in Figure 3.

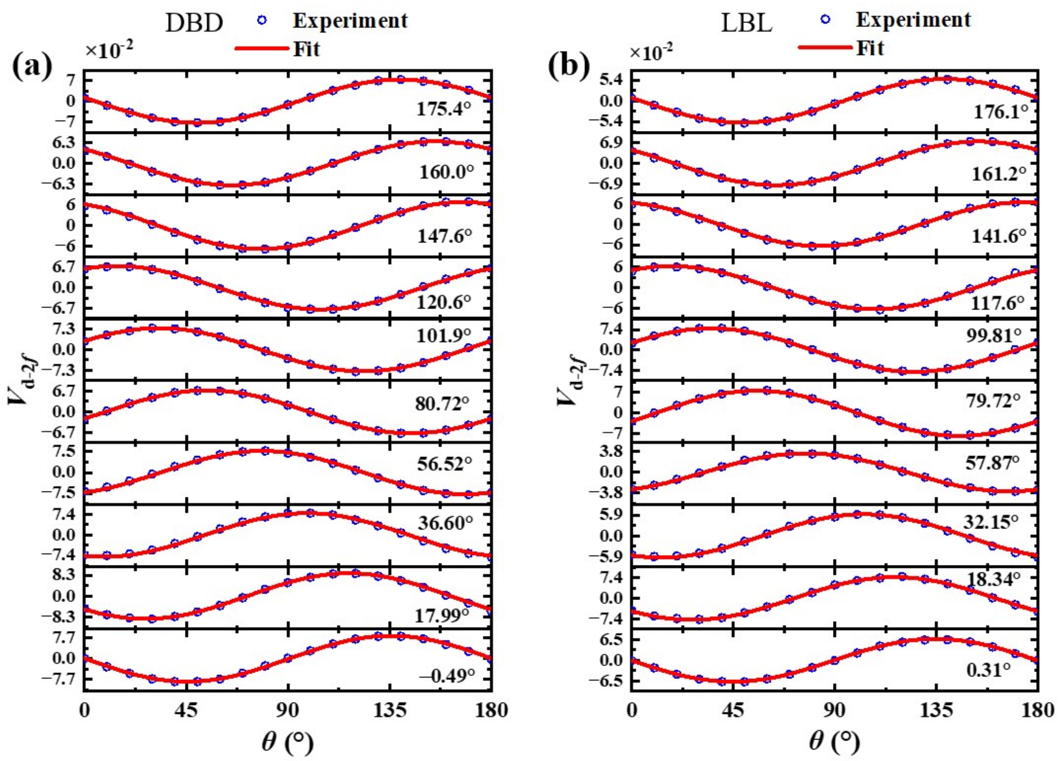

Figure S2. $V_{d\text{-}2f}$ signals as a function of incident polarization angles θ for the single (a) DBD and (b) LBL self-assembled chiral supramolecules at different orientation angles on a thin glass substrate, respectively. The incident polarization angles are from 0° to 180° in 10° increments. The blue points are the experimental data, and the red curves are the fit curves.

3. V_{2f} and optical images at different orientation angles

We rotated the single DBD/LBL self-assembled chiral supramolecule from 0° to 180° anticlockwise in 20° increments to detect SPMM signals. Figure S3 shows V_{2f} and optical images of the single DBD self-assembled chiral supramolecule with different orientation angles from 0° to 180° anticlockwise in 20° increments at 473 nm, respectively. V_{2f} images are highly dependent on the orientation angles due to the anisotropy of the single DBD self-assembled chiral supramolecule. V_{2f} images vary opposite compared to V_{1f} images (as shown in Figure 5), being negative when the orientation is between 0° and 90°, and positive between 90° and 180°. This behavior is consistent with a sine function having a period of 180°, as described in Equation S3. Similarly, Figures S4(a) and (b) show V_{2f} and optical images of the single LBL self-assembled chiral supramolecule at orientation angles from 0° to 180° anticlockwise in 20° increments.

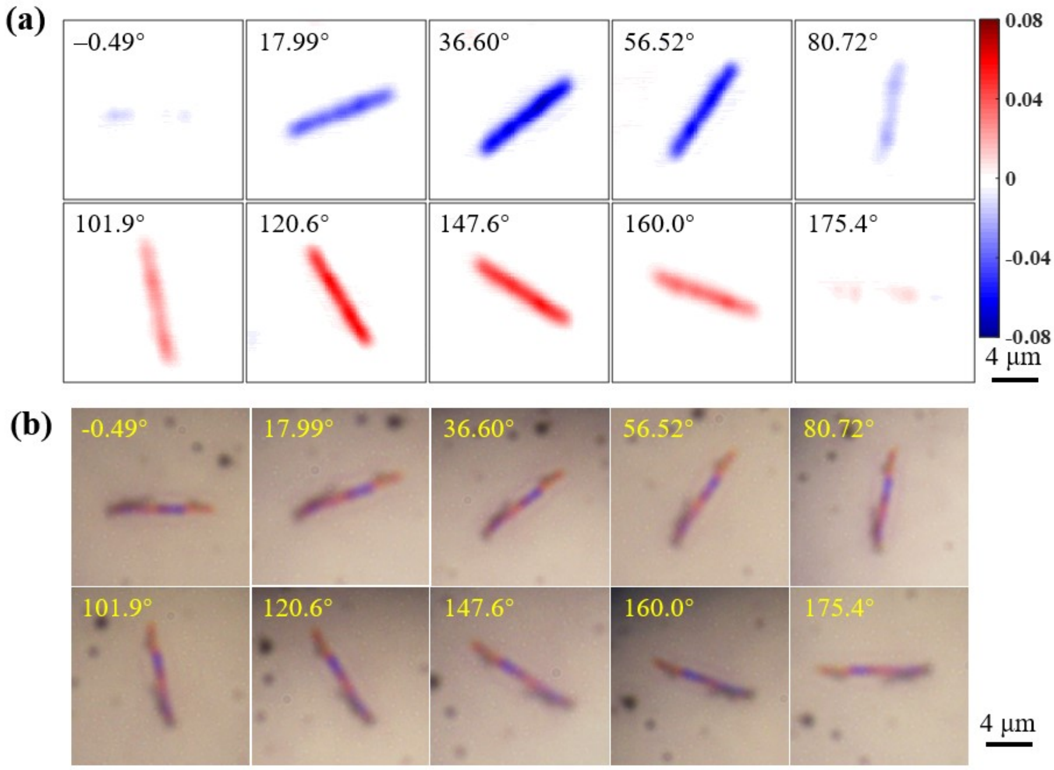

Figure S3. (a) V_{2f} and (b) optical images of the single DBD self-assembled chiral supramolecule at orientation angles from 0° to 180° anticlockwise in 20° increments.

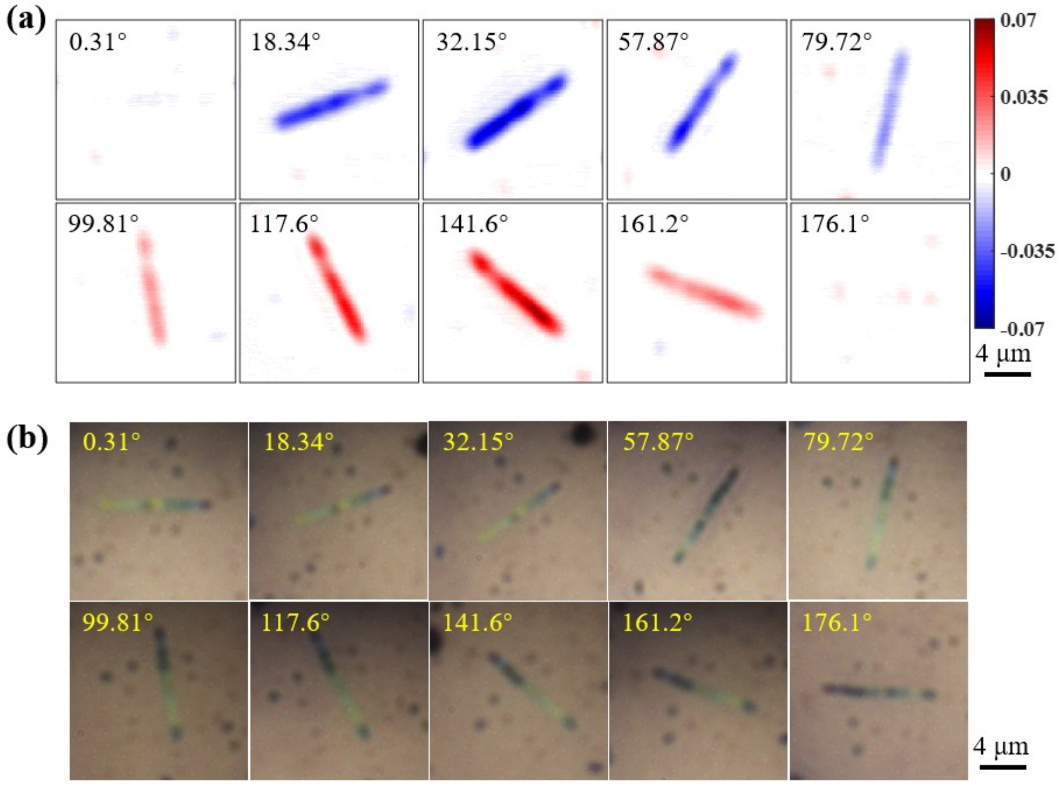

Figure S4. (a) V_{2f} and (b) optical images of the single LBL self-assembled chiral supramolecule with orientation angles from 0° to 180° anticlockwise in 20° increments.

4. Measurement through both backward and forward of the single DBD chiral supramolecule

Figure S5 shows both optical microscopy and AFM images of the single DBD self-assembled chiral supramolecule. The single DBD self-assembled chiral supramolecule, with an approximate height of 181 nm, displays a left-handed helix.

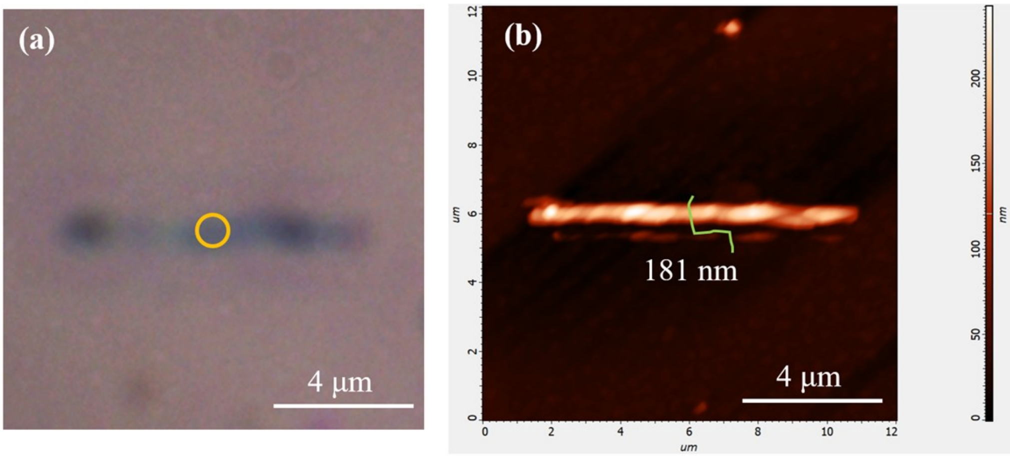

Figure S5 (a) Optical microscopy (OM) and (b) AFM images of the single DBD self-assembled chiral supramolecule. From the AFM image, the single DBD self-assembled chiral supramolecule is left-handed.

We performed measurements through both the back and the front of the single DBD self-assembled chiral supramolecule using the home-built SCDM setup at 473 nm as you recommended. We varied both the incident polarization angles θ and the orientation angles β of the single DBD self-assembled chiral supramolecule at 473 nm. First, to collect SCDM ($V_{d\text{-}1f}$) signals of the incident light from the backward and forward directions of the single DBD self-assembled chiral supramolecule shown in Figures S6(a) and S6(b), the half-wave plate was rotated to vary the incident polarization angles θ from 0° to 360° clockwise in 10° increments, as indicated by the orange circles in Figure S5(a), respectively. Next, to further analyze the chiral behavior, we rotated the orientation angles β of the single DBD self-assembled chiral supramolecule from 0° to 180° in 20° increments and measured the $V_{d\text{-}1f}$ signal at each orientation.

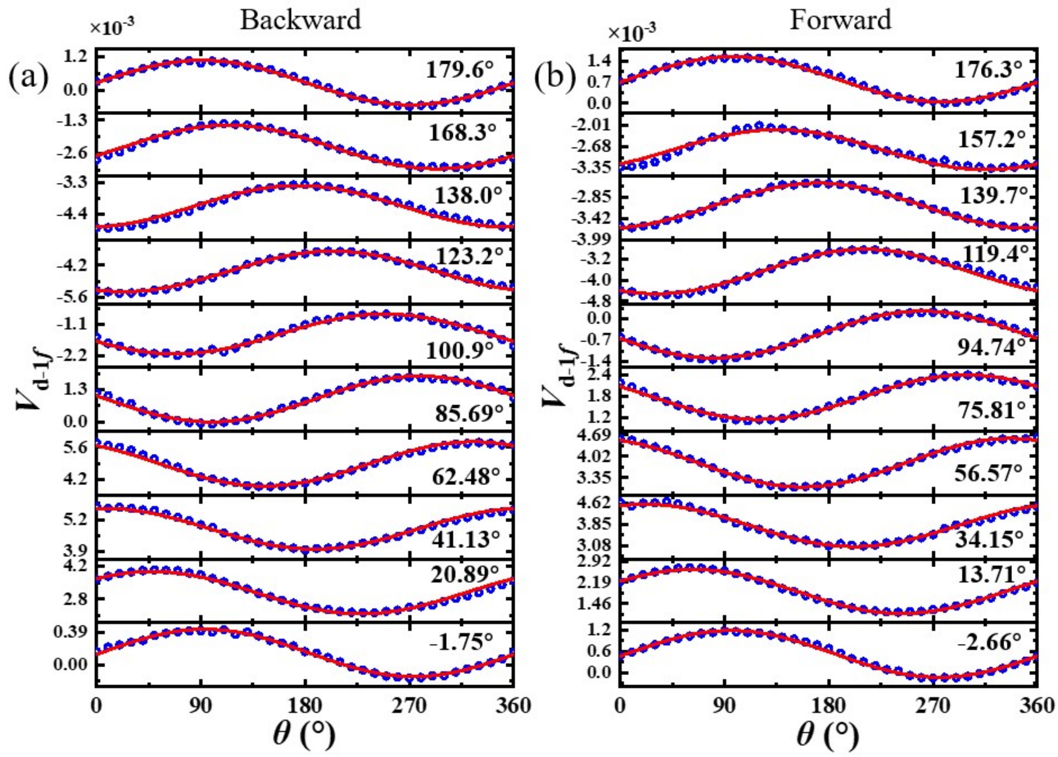

Figure S6 $V_{d\text{-}1f}$ signals as a function of incident polarization angles θ for the incident light directed from the backward and forward sides of the single DBD self-assembled chiral supramolecule at different orientation angles on a thin glass substrate, respectively. The incident polarization angles are from 0° to 360° in 10° increments. The blue points are the experimental data, and the red curves are the fit curves.

$V_{d\text{-}1f}$ signals showed a strong dependence on the incident polarization angles θ, reflecting the anisotropy of the single DBD self-assembled chiral supramolecule. We determined the orientation angles of the single DBD self-assembled chiral supramolecule by analyzing these $V_{d\text{-}1f}$ signals. Figure S6(a) shows the $V_{d\text{-}1f}$ signals of the incident light from the backward direction of the single DBD self-assembled chiral supramolecule, with the orientation angles determined to be –1.75°, 20.89°, 41.13°, 62.48°, 85.69°, 100.9°, 123.2°, 138.0°, 168.3°, and 179.6°, respectively. Besides, Figure S6(b) displays the $V_{d\text{-}1f}$ signals of incident light directed from the forward side, with the orientation angles recorded as -2.66°, 13.71°, 34.15°, 56.57°, 75.81°, 94.74°, 119.4°, 139.7°, 157.2°, and 176.3°, respectively. These results were consistent with those obtained from SPMM analysis, as shown in Figure S7.

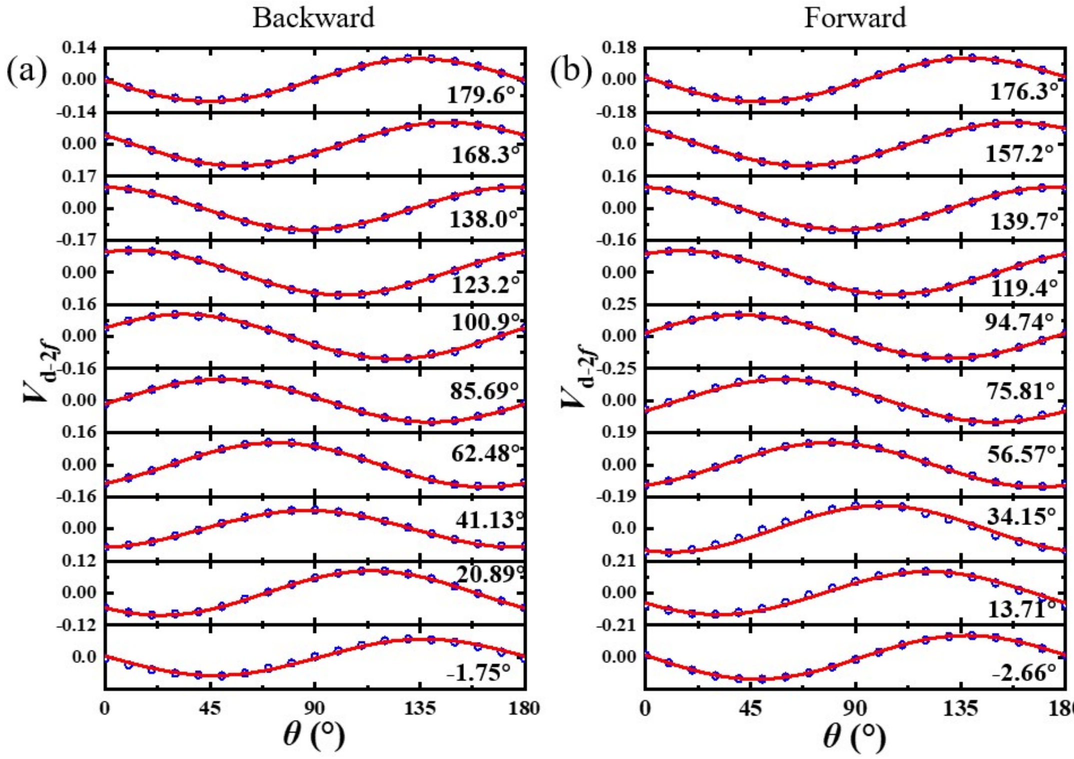

Figure S7 $V_{d\text{-}2f}$ signals as a function of incident polarization angles θ for the incident light directed from the backward and forward sides of the single DBD self-assembled chiral supramolecule at different orientation angles on a thin glass substrate, respectively. The incident polarization angles are from 0° to 180° in 10° increments. The blue points are the experimental data, and the red curves are the fit curves.

Then, in order to obtain the "intrinsic" CD signal of the single DBD self-assembled chiral supramolecule shown in Figure S8, we calculated V_{1f} signals which are the values of "$CD+\frac{1}{2}(LBLD'-LB'LD)$" corresponding to shifts in longitudinal coordinates of the $V_{d\text{-}1f}$ signals from Figure S6, respectively. V_{1f} signals still contain contributions from "artifact" signals. To extract the " intrinsic" CD signal of the single DBD self-assembled chiral supramolecule, V_{1f} signals were obtained at different orientation angles, accounting for the impact of β. Figure S8 illustrates that the V_{1f} signals are highly dependent on the orientation angles β of the single DBD self-assembled chiral supramolecule. This confirms that the V_{1f} signals are strongly influenced by "artifact" signals inherent to the single DBD self-assembled chiral supramolecule. Additionally, the V_{1f} signal follows a sine function with respect to β with a period of 180°, reflecting the periodic nature of the "*LBLD'*–*LB'LD*" interaction with the orientation angles. As shown in Figure S8(a), the signal shifts upward relative to the zero point, and in Figure S8(b), it also shifts upward, reflecting the left-handedness of the single DBD self-assembled chiral supramolecules. Figure S8(a) shows V_{1f} signals with the incident light from the backward side of the single DBD self-assembled chiral supramolecule. In contrast, V_{1f} signals were obtained with the incident light the forward side of the same single DBD self-assembled chiral supramolecule as shown in Figure S8(b). Based on the curve fitting using the equcation: $V_{1f} = CD + \frac{1}{2}(LBLD' - LB'LD)$, the calculated "intrinsic" CD signal of the incident light from the backward side of the single DBD self-assembled chiral supramolecule is 2.5×10^{-4} at 473 nm. For the incident light from the forward side, it is calculated as 2.7×10^{-4} at 473 nm. Accordingly, the "intrinsic" CD signal of the single DBD self-assembled chiral supramolecule for the incident light from the backward side is 8.3 mdeg at 473 nm, while for incident light from the forward side, the "intrinsic" CD signal is 8.8 mdeg at 473 nm.

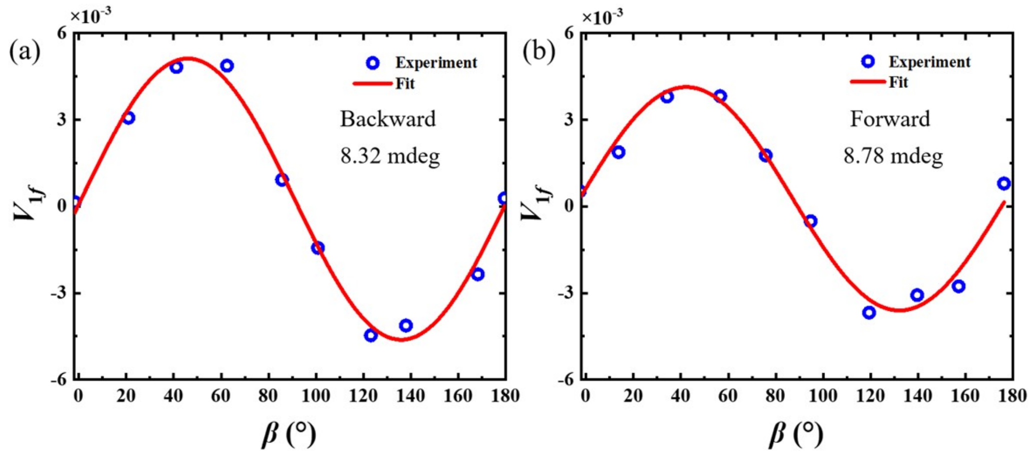

Figure S8 V_{1f} signals as a function of orientation angles β for the incident light directed from the backward and forward sides of the single DBD self-assembled chiral supramolecule on a thin glass substrate at 473 nm, respectively. The orientation angles are from 0° to 180° anticlockwise in 20° increments. The blue points are the experimental data, and the red curves are the fit curves.

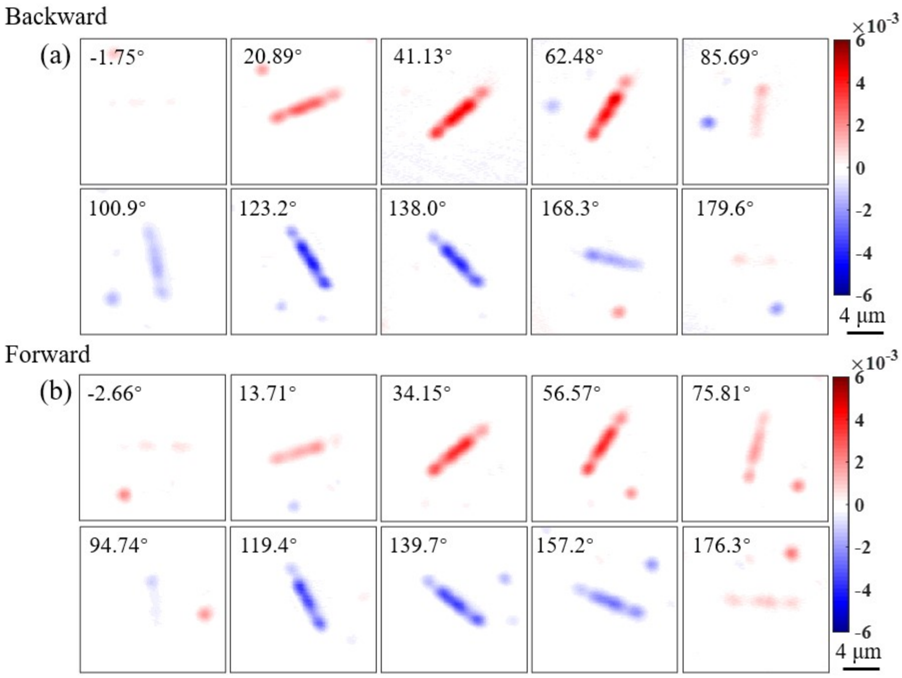

Figure S9. V_{1f} images with laser from (a) backward and (b) forward of the single DBD self-assembled chiral supramolecule at orientation angles from 0° to 180° anticlockwise in 20° increments.

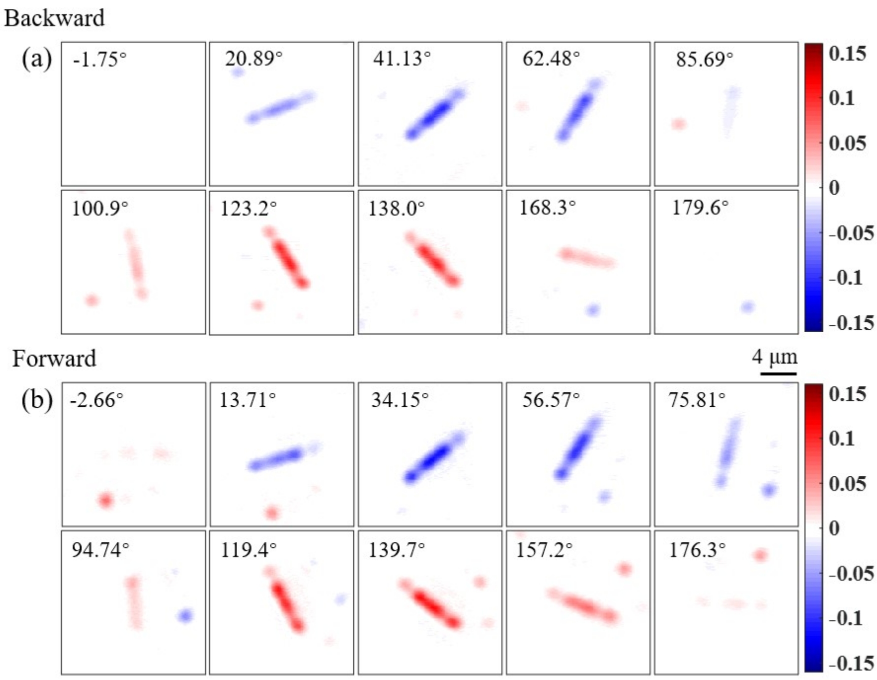

Figure S10. V_{2f} images with laser from (a) backward and (b) forward of the single DBD self-assembled chiral supramolecule at orientation angles from 0° to 180° anticlockwise in 20° increments.

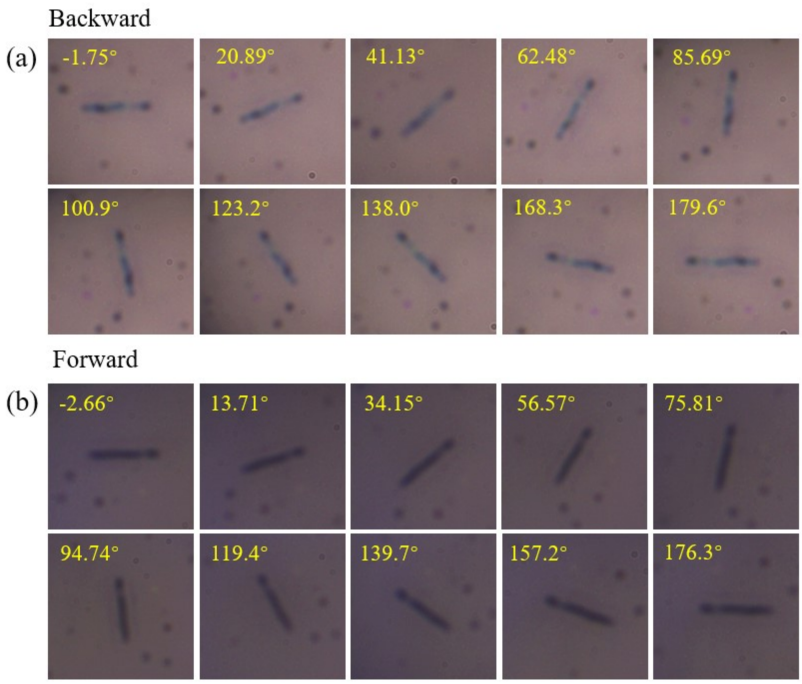

Figure S11. OM images with laser from (a) backward and (b) forward of the single DBD self-assembled chiral supramolecule at orientation angles from 0° to 180° anticlockwise in 20° increments.

5. Noise and Experimental Error

As shown in Figure S12, the noise level in our experiment is on the order of 10^{-5}, and the experimental error is well within this noise level, further supporting the reliability of the measured signals.

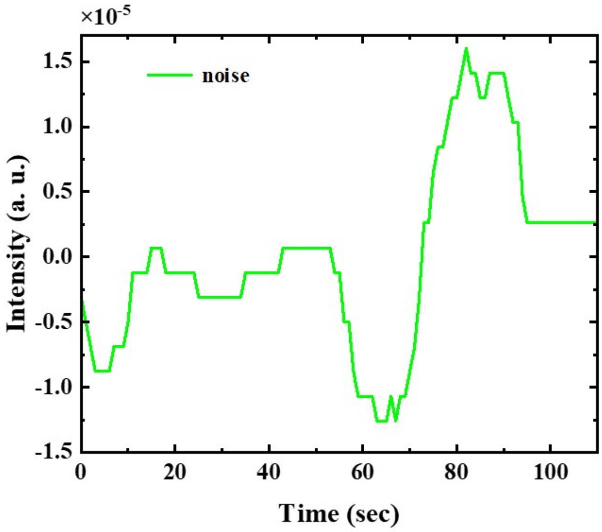

Figure S12. Noise level of SCDM measurement on the thin glass substrate at 473 nm.

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