Supporting Information

Chiral Colloidal Molecules And Observation of The Propeller Effect

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Circular Differential Scattering

1. Calculations

All calculations are based on the analytical model first proposed by Bustamante et al. (*1*). We correct a small error that appears in their final expression for the circular differential scattering intensity(in Ref. (1)). We extend the calculations and also consider helical scatterers of finite thickness. Results from the corrected single helical scatterer (Ref. (1)) as well as the thick helix are shown.

The circular differential scattering intensity (CDSI) is defined as (2):

$$CDSI = \frac{I_l(\theta,\phi) - I_r(\theta,\phi)}{I_l(\theta,\phi) + I_r(\theta,\phi)} = \frac{\Delta I_{lr}}{TSI}, \tag{1}$$

where $I_{l,r}(\theta,\phi)$ are the intensities of the scattered light propagating in the direction defined by the polar angles (θ,ϕ) for left (l) or right (r) circularly polarized light incident upon the sample. In general, scattering can be modeled by considering a finite object to consist of point polarizabilities $\boldsymbol{\alpha_i}$ arranged in space. The scattered field at position $\boldsymbol{r}'$ is then given by:

$$\boldsymbol{E_s}(\boldsymbol{r}') = \frac{k^2}{r'} e^{-ikr'} \left(1 - \widehat{\boldsymbol{k}}\widehat{\boldsymbol{k}}\right) \cdot \sum_j \boldsymbol{e^{i\,\Delta k \cdot r_j}}\, \boldsymbol{\alpha_j} \cdot \boldsymbol{E_0} \tag{2}$$

where the electric field amplitude of the incident field is $\boldsymbol{E_0}$. The wave vector of the scattered radiation is $= {}^{2\pi}/_{\lambda}\ \widehat{\boldsymbol{k}}$, and $\Delta\boldsymbol{k} = \boldsymbol{k} - \boldsymbol{k_0}$. By expressing all quantities used in Eq.(2) in terms of a well-defined space-fixed and a scatterer-fixed coordinate systems it is possible to find an analytical expression for the rotationally averaged scattering intensity (averaging over all possible orientations of the scatterer). The isotropic differential scattering intensity ΔI_{lr} for a scatterer of arbitrary shape is then (*1*, *3*):

$$\langle \Delta I_{lr} \rangle = \frac{8\pi^4}{\lambda^4 r'^2} \sum_{i,j} \alpha_i^* \alpha_j \left(\hat{\boldsymbol{t}}_{\boldsymbol{j}} \times \hat{\boldsymbol{t}}_{\boldsymbol{i}}\right) \cdot \widehat{\boldsymbol{R}}_{\boldsymbol{ij}} \left[\left(\hat{\boldsymbol{e}}_{\boldsymbol{i}} \cdot \hat{\boldsymbol{e}}_{\boldsymbol{j}}\right) \left(\frac{j_2(q)}{q} - j_1(q) \right) - \left(\hat{\boldsymbol{t}}_{\boldsymbol{i}} \cdot \widehat{\boldsymbol{R}}_{\boldsymbol{ij}}\right)\left(\hat{\boldsymbol{t}}_{\boldsymbol{j}} \cdot \widehat{\boldsymbol{R}}_{\boldsymbol{ij}}\right) \left(\frac{5 j_2(q)}{q} - j_1(q) \right) \right] \left[\sin\frac{\theta}{2} + \sin^3\frac{\theta}{2} \right] \tag{3}$$

here r' is the distance between the scattering volume and the detector, and $\boldsymbol{R_{ij}} = \left|\boldsymbol{r_j} - \boldsymbol{r_i}\right| \widehat{\boldsymbol{R}}_{\boldsymbol{ij}}$ is the distance between the polarizabilities α_i and α_j with principle axes $\hat{\boldsymbol{t}}_{\boldsymbol{i}}$ and $\hat{\boldsymbol{t}}_{\boldsymbol{j}}$. The functions j_1 and j_2 are the spherical Bessel functions of the first kind of, respectively, first and second order. Their argument is defined by:

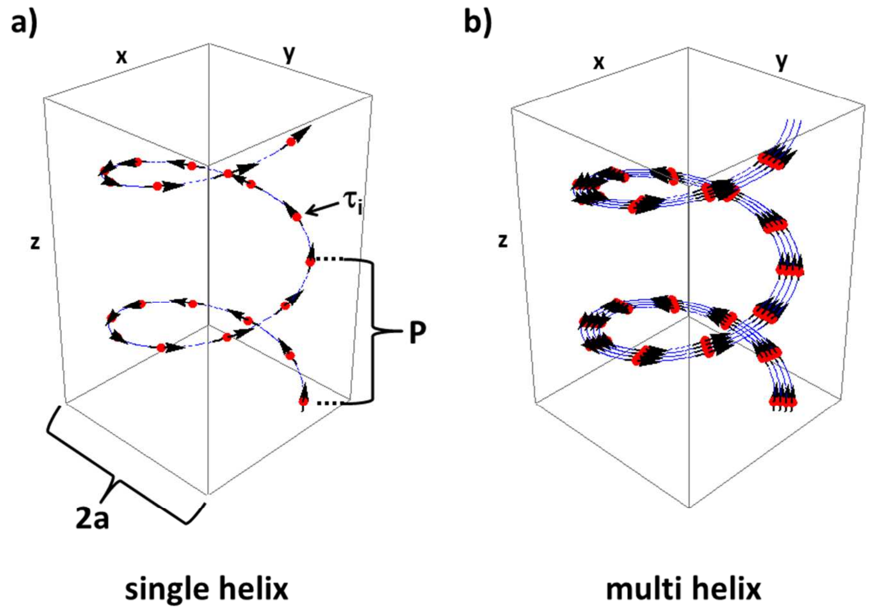

Fig. SI-1: a) Depicted is a thin helix, pitch *P* and radius *a*, composed of uniaxial point polarizabilities (red dots). b) Shows a multi helix stack with the same pitch, but increasing radius. The direction of the principal axes is indicated by the arrows. See text for details.

$$q = \left(\frac{4\pi R_{ij}}{\lambda}\right) \sin\frac{\theta}{2} \tag{4}$$

Similarly, an expression for the total scatted intensity TSI can be derived (see (*1*)). A number of simplifications can be made if the helical geometry is expressed in terms of the radius a and pitch *P*, and if the uniaxial point polarizabilities are evenly spaced along the helix with their principle directors aligned tangential to the helix (as seen in Fig. SI-1a). We can then write $\boldsymbol{r_i}$ and $\boldsymbol{\hat{t}_i}$ as a function of a and *P*:

$$\begin{aligned} \boldsymbol{r_i} &= a\cos(i\tau_0)\boldsymbol{e_1} + a\sin(i\tau_0)\,\boldsymbol{e_2} + i\frac{P\tau_0}{2\pi}\boldsymbol{e_3} \\ \boldsymbol{\hat{t}_i} &= -\frac{a}{M}\sin(i\tau_0)\,\boldsymbol{e_1} + \frac{a}{M}\cos(i\tau_0)\,\boldsymbol{e_2} + \frac{P}{2\pi M}\boldsymbol{e_3}, \\ &\text{with } M = \sqrt{a^2 + \tfrac{P^2}{4\pi^2}} \end{aligned} \tag{5}$$

here τ_0 is the angular distance between subsequent polarizabilities i and *i+1* in radians. Using Equation (5) and $\tau_{ij} = (j-i)\tau_0$ we can write:

$$\begin{aligned} \langle \Delta I_{lr}\rangle_h = \frac{2\pi^3 a^2 P}{M^4\lambda^4 r'^2}\sum_{ij}\frac{\alpha_i^*\alpha_j}{\sqrt{G_{ij}}}\left(4\sin^2\frac{\tau_{ij}}{2} - \tau_{ij}\sin\tau_{ij}\right)\Bigg[\left(a^2\cos\tau_{ij} + \frac{P^2}{4\pi^2}\right)\left(\frac{j_2(q)}{q} - j_1(q)\right) \\ - \frac{1}{G_{ij}}\left(a^2\sin\tau_{ij} + \frac{P^2}{4\pi^2}\tau_{ij}\right)^2\left(\frac{5j_2(q)}{q} - j_1(q)\right)\Bigg]\left\{\sin\frac{\theta}{2} + \sin^3\frac{\theta}{2}\right\} \end{aligned} \tag{6}$$

where

$$G_{ij} = \left|\boldsymbol{R_{ij}}\right|^2 = 4a^2\sin^2\frac{\tau_{ij}}{2} + \left(\frac{P\,\tau_{ij}}{2\pi}\right)^2$$

Due to the helical symmetry we can replace the double summation by $\sum_{k=1}^{N-1}(N-k)$, where *N* is the total number of polarizabilities.

This gives the following expression for the differential scattering intensity of a thin helix:

$$\langle \Delta I_{lr} \rangle_h = \frac{2\pi^3 a^2 P}{M^4 \lambda^4 r'^2} \sum_{k=1}^{N-1} \frac{(N-k)|\alpha_k|^2}{\sqrt{G_k}} \left(4\sin^2\frac{k\tau_0}{2} - k\tau_0 \sin k\tau_0\right) \left[\left(a^2\cos k\tau_0 + \frac{P^2}{4\pi^2}\right)\left(\frac{j_2(q)}{q} - j_1(q)\right) - \frac{1}{G_k}\left(a^2 \sin k\tau_0 + \frac{P^2}{4\pi^2}k\tau_0\right)^2 \left(\frac{5j_2(q)}{q} - j_1(q)\right)\right]\left\{\sin\frac{\theta}{2} + \sin^3\frac{\theta}{2}\right\} \quad (7)$$

In order to model chiral colloids with a finite thickness, i.e. an inner and outer radius (a_{in}, a_{out}), we consider a stack of n_h concentric "thin" helices with the same pitch but increasing radius ($a_{in} \le a \le a_{out}$)(Fig. SI-1b). The CDIS value for the colloid is either calculated by independently simulating each thin helix using Eq.(7) or by summing a helix stack. For the latter approach Eq. (7) has to be slightly modified. First, we define the radius as a function of the index i, the number of turns T, the number of polarizabilities per turn n_p and the number of helix n_h:

$$a[i] = a_{\mathrm{in}} + \left\lfloor \frac{i}{T\,n_p} \right\rfloor \left(\frac{a_{out} - a_{in}}{n_h}\right) \quad (8)$$

Here $\lfloor x \rfloor$ is the floor function giving the greatest integer less than or equal to x. Next we use $a[i]$ and Eq.(5) to redefine the following parameters:

$$\begin{aligned}
\boldsymbol{r_i} &= a[i]\cos(i\tau_0)\boldsymbol{e_1} + a[i]\sin(i\tau_0)\,\boldsymbol{e_2} + c_i\frac{P\tau_0}{2\pi}\boldsymbol{e_3} \\
\hat{\boldsymbol{t}}_{\boldsymbol{i}} &= -\frac{a[i]}{M_i}\sin(i\tau_0)\,\boldsymbol{e_1} + \frac{a[i]}{M_i}\cos(i\tau_0)\,\boldsymbol{e_2} + \frac{P}{2\pi M_i}\,\boldsymbol{e_3} \\
M_i &= \sqrt{a[i]^2 + \frac{P^2}{4\pi^2}}, \qquad c_{ij} = (c_j - c_i)\tau_0, \qquad c_i = i - \left\lfloor \frac{i}{T\,n_p} \right\rfloor T\,n_p \\
G_{ij} &= a[i]^2 + a[j]^2 - 2a[i]a[j]\cos\tau_{ij} + \left(\frac{Pc_{ij}}{2\pi}\right)^2
\end{aligned} \quad (9)$$

Finally using the equations above we can express the spatially averaged differential intensity for the multi-helix stack:

$$\langle \Delta I_{lr} \rangle_{mh} = \frac{2\pi^3 P}{\lambda^4 r'^2} \sum_{ij} \frac{\alpha_i^* \alpha_j}{\sqrt{G_{ij}}\, M_i^{\,2} M_j^{\,2}} \left(a[i]^2 + a[j]^2 - a[i]a[j]\left(2\cos\tau_{ij} + c_{ij}\sin\tau_{ij}\right)\right) \left[\left(a[i]a[j]\cos\tau_{ij} + \frac{P^2}{4\pi^2}\right)\left(\frac{j_2(q)}{q} - j_1(q)\right) - \frac{1}{G_{ij}}\left(a[i]a[j]\sin\tau_{ij} + \frac{P^2 c_{ij}}{4\pi^2}\right)^2\left(\frac{5j_2(q)}{q} - j_1(q)\right)\right]\left\{\sin\frac{\theta}{2} + \sin^3\frac{\theta}{2}\right\} \quad (10)$$

In Fig. SI-2 both models are compared and CDSI intensities are computed for a variety of helix geometries.

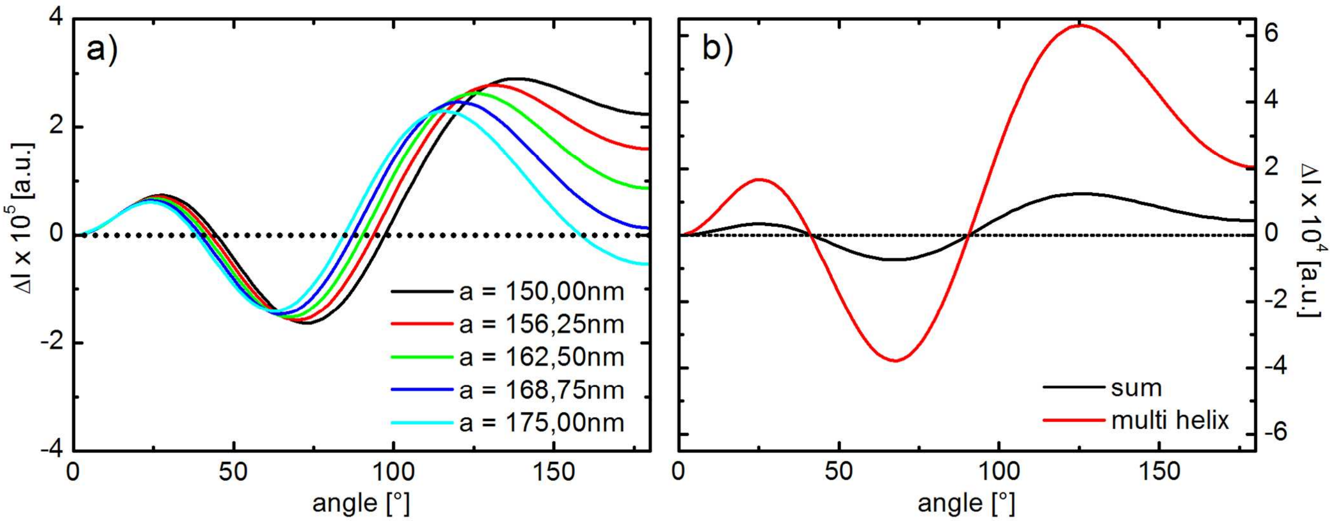

Fig SI-2: Calculation of ΔI for a single helix a) with increasing radius. The sum of these signals (black line) is shown on the right and compared to a multi helix composed of the same single helices.

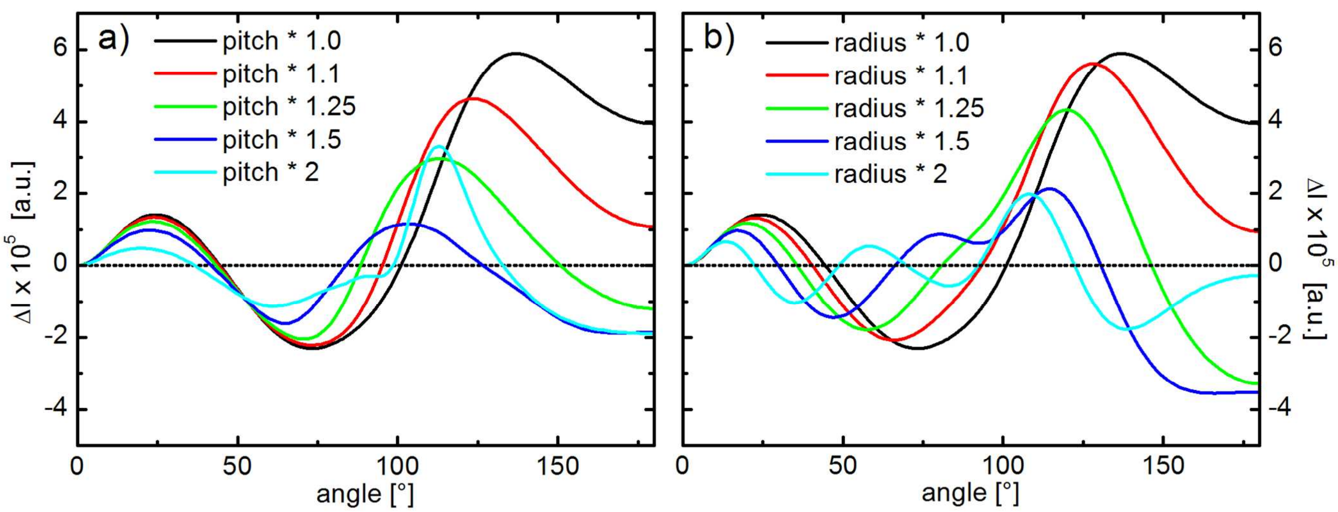

Fig. SI-3: Calculation of ΔI for a single helix with increasing pitch (left) and radius (right). It can be seen that the difference in the scattering intensities is sensitive to small changes in the geometrical parameters of the helix.

2. Geometrical parameters of measured samples

The geometrical parameters of the measured samples shown in the main text (Fig. 3) have been determined from SEM images. The results are shown in Tab. SI-4.

Table SI-4. Geometrical Parameters of measured Colloids

Sample	d_{bead}	$d_{helix\ i}$	$d_{helix\ o}$	l_{helix}	l_{total}	#t	p
left-handed helix	0.43 ± 0.03	0.23 ± 0.02	0.35 ± 0.04	1.386 ± 0.008	1.832 ± 0.003	5	0.277 ± 0.002
right-handed helix	0.31 ± 0.02	0.212 ± 0.011	0.34 ± 0.02	1.323 ± 0.011	1.630 ± 0.006	5	0.265 ± 0.002
achiral rod	0.33 ± 0.02	------------------	---------------	-----------------	2.314 ± 0.004	--	------------------

Geometrical parameters of the colloids which have been used for the calculations. Diameter of bead (d_{bead}), inner diameter of helix ($d_{helix\ i}$), outer diameter of helix ($d_{helix\ o}$), length of helix (l_{helix}), total length of colloid (l_{total}), number of turns (*#t*), pitch of helix (*p*).

3. Control measurement of racemic mixture

In Fig. SI-5 we also measured a racemic mixture of the aqueous solutions of the left- and right handed helices. As expected the CDIS signal almost vanishes whereas the TSI signal does not change significantly. Moreover, the CDIS signal of the racemate is in good agreement with the mean value of the signals for both helices, which is also shown for comparision.

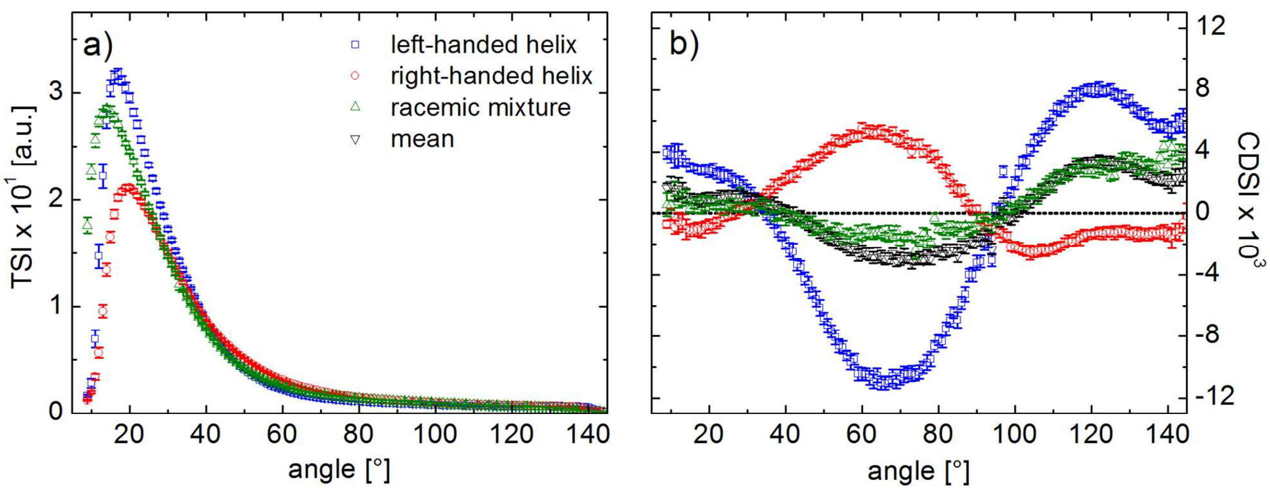

Fig. SI-4: a) Total Scattered Intensity (TSI) and b) Circular differential scattering signal (CDSI) for a racemic mixture of the left- and right handed helices. The CDIS values for the enantioclean solutions are also shown as well as the mean value of these signals.

Chiral separation

1. Video 1

Video 1 shows the separation of a racemic mixture of right- (red tracks) and left-handed (green tracks) particles in a magnetic field of 20 Gauss rotating at a frequency of 20 Hz, over a time interval of 30 s, played at 3x speed. The scale bar is 20 μm.

Notes

The Table of Contents graphic was in part drawn with the free web application "DIY molecules".[4]

REFERENCES

(1) Bustamante, C. Circular intensity differential scattering of light. IV. Randomly oriented species. *The Journal of Chemical Physics* **1982**, *76*, 3440.

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(4) Herráez, A., *Do-It-Yourself Molecules: from 2D to 3D,* http://biomodel.uah.es/en/DIY/ **2010**.