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Supplementary Materials for

Resolving enantiomers using the optical angular momentum of twisted light

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The PDF file includes:

Supplementary Figures

Supporting figure 1

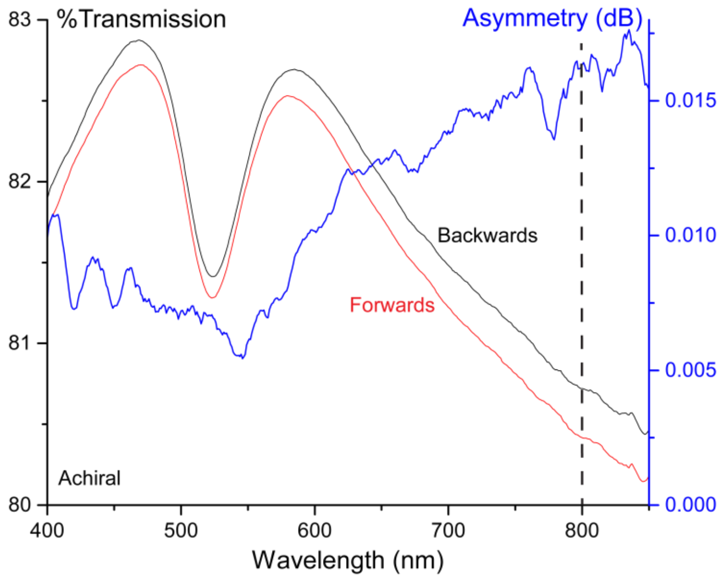

Fig. S1: Transmission and asymmetry of transmission spectra for the achiral sample. Broadband asymmetric transmission, i.e. a difference in transmission for forward and backward direction, is observed for the achiral plasmonic nanoparticle aggregate. This implies the generation of strong electric quadrupole fields.

Supporting figure 2

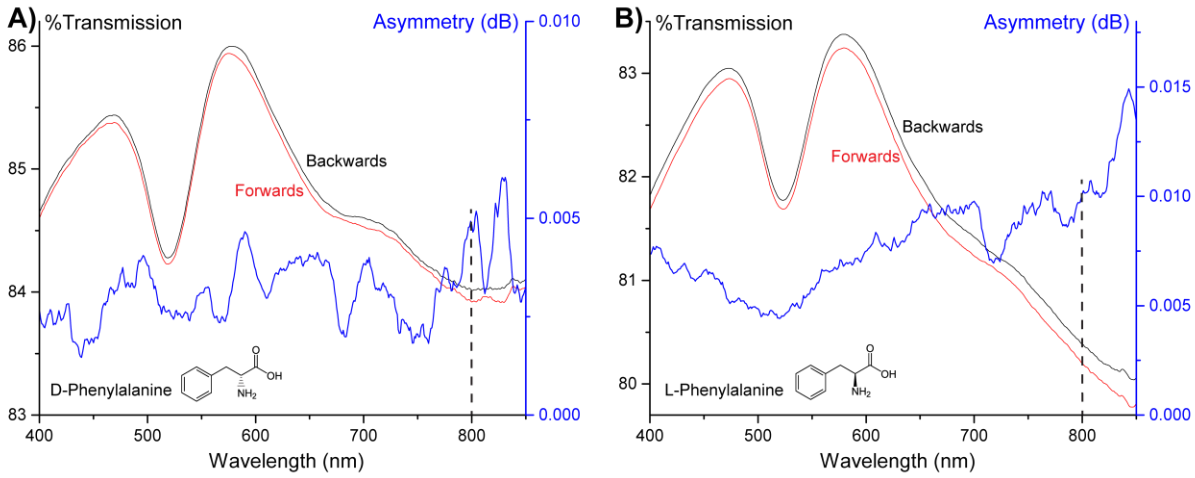

Fig. S2: Transmission and asymmetry of transmission spectra for the chiral samples. Compared to the achiral sample, the plasmon resonance is slightly red-shifted and broadened and the measured asymmetric transmission is significantly lower. These data confirm the adsorption of the chiral molecules in the plasmonic nanoparticle aggregates.

Supporting figure 3

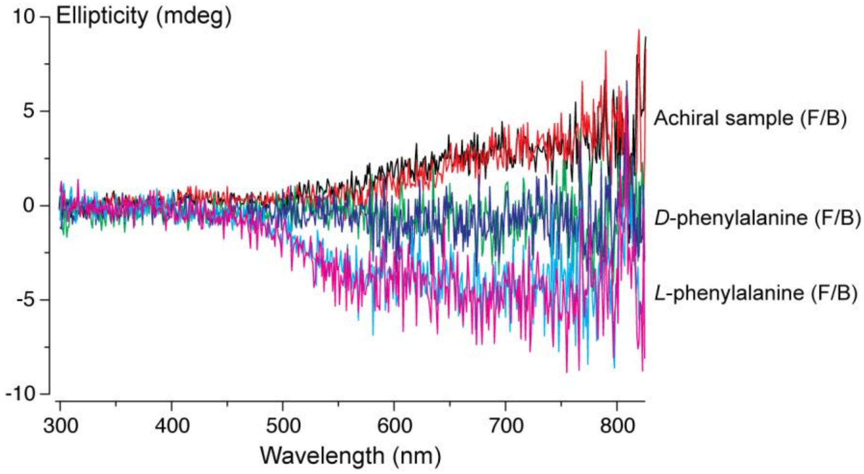

Fig. S3: CD spectra of the achiral and chiral samples in both forward and backward direction. Only noise was measured for all samples in both forward and backward direction. No difference between forward and backward direction was observed.

Supporting figure 4

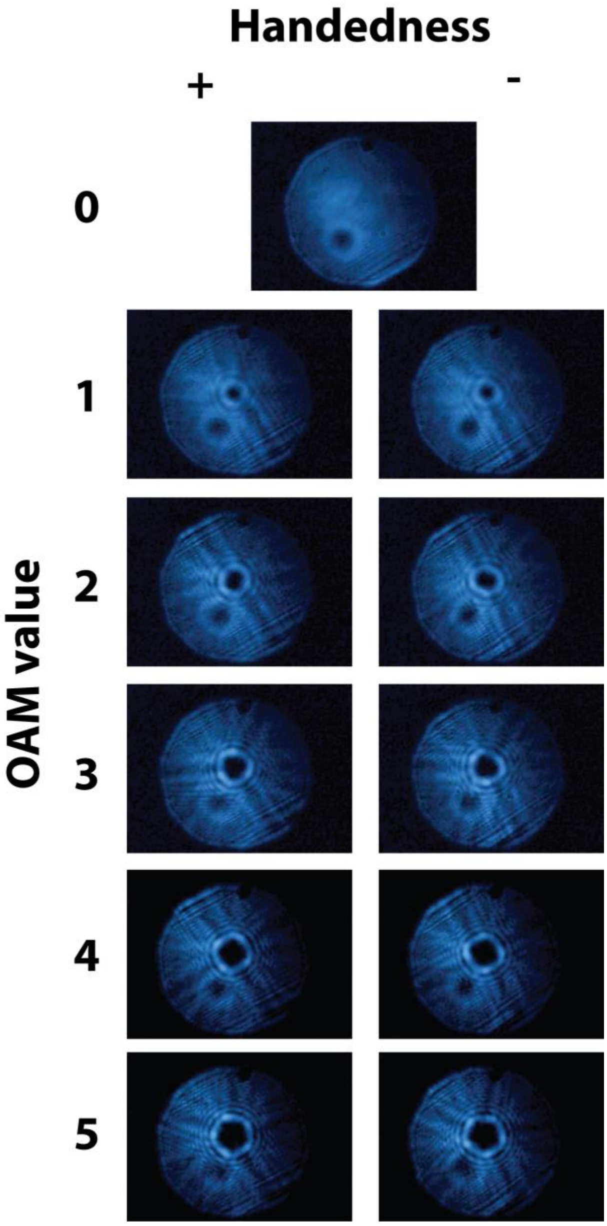

Fig. S4: Spatial intensity profiles of the produced LG beam as detected by a webcam are as expected. Note that the inhomogeneities in the beam outside of the central annulus are due to an imperfect detection system.

Phenomenological model for discrimination of molecular enantiomers by LG light

Here we develop a phenomenological model for the discrimination of molecular enantiomers by Laguerre-Gaussian (LG) light based on electric dipole, magnetic dipole and electric quadrupole contributions. We show that in polar materials, linearly polarized Laguerre-Gaussian light can discriminate molecular enantiomers based on either the observed asymmetric transmission, i.e. the difference between transmission in forward and backward transmission exhibited by polar materials (Brullot, 2015), or helical dichroism (HD), i.e. the difference in transmission for clockwise and counterclockwise rotating LG light.

Further, we show that the observed effects are due to coupling between chirality and LG light intermediated by electric quadrupole fields and that it should be possible to separate the χ^{eq} from χ^{em} contributions, which are currently indistinguishable using only CD techniques.

The presented model is an extension of a model used earlier to explain quadrupolarization-induced nonreciprocal asymmetric transmission (qAT).*(16)* Inclusion of magnetic dipole contributions to incorporate chiro-optical effects and the substitution of plane waves with LG light allow to explain the observed data.

0.1 Far-field radiation from electric and magnetic dipole and electric quadrupole sources.

First we write the radiated fields originating from electric and magnetic dipole and electric quadrupole sources. *(21)* As such, we explicitly include effects induced by quadrupolarization (electric quadrupole density) and chiro-optical effects.

- A radiating **electric dipole** generates in the far-field:

$$B_{\boldsymbol{ed}} = k^2(\boldsymbol{n} \times \boldsymbol{p})\frac{e^{ikr}}{r} \tag{1}$$

$$E_{\boldsymbol{ed}} = \boldsymbol{B} \times \boldsymbol{n} = \frac{k^2}{r}(\boldsymbol{n} \times \boldsymbol{p}) \times \boldsymbol{n} e^{ikr} \tag{2}$$

with $\boldsymbol{n}$ a unit vector.

- For a radiating **magnetic dipole** in the far field:

$$E_{\boldsymbol{md}} = -k^2(\boldsymbol{n} \times \boldsymbol{m})\frac{e^{ikr}}{r} \tag{3}$$

- For an **electric quadrupole** source, we can write the magnetic induction as

$$B_{\boldsymbol{eq}} = -\frac{ik^3}{6}\frac{e^{ikr}}{r}\boldsymbol{n} \times \boldsymbol{Q}(\boldsymbol{n}) \tag{4}$$

And since $\boldsymbol{E} = \boldsymbol{B} \times \boldsymbol{n}$:

$$E_{\boldsymbol{eq}} = -\frac{ik^3}{6}\frac{e^{ikr}}{r}(\boldsymbol{n} \times \boldsymbol{Q}(\boldsymbol{n})) \times \boldsymbol{n} \tag{5}$$

where we can define **Q(n)** as

$$\boldsymbol{Q}(\boldsymbol{n}) = \begin{bmatrix} Q_x \\ Q_y \\ Q_z \end{bmatrix} \tag{6}$$

with $Q_x = Q_{xx}n_x + Q_{xy}n_y + Q_{xz}n_z$

0.2 Calculating the total electric field in the far-field radiation zone

The total field in the far-field radiation zone is the sum of the electric fields radiated by an electric dipole (ed), a magnetic dipole (md) and an electric quadrupole (eq) term. Combining equations 2, 3 and 5 yields

$$\begin{aligned} E_{\boldsymbol{total}} &= E_{\boldsymbol{ed}} + E_{\boldsymbol{eq}} + E_{\boldsymbol{md}} \\ &= \frac{k^2}{r}e^{ikr}(\boldsymbol{n} \times \boldsymbol{p}) \times \boldsymbol{n} - \frac{ik^3}{6r}e^{ikr}(\boldsymbol{n} \times \boldsymbol{Q}(\boldsymbol{n})) \times \boldsymbol{n} - k^2(\boldsymbol{n} \times \boldsymbol{m})\frac{e^{ikr}}{r} \end{aligned} \tag{7}$$

First we calculate $\boldsymbol{n} \times \boldsymbol{p}$:

$$\boldsymbol{n} \times \boldsymbol{p} = (n_x\boldsymbol{x} + n_y\boldsymbol{y} + n_z\boldsymbol{z}) \times (p_x\boldsymbol{x} + p_y\boldsymbol{y} + p_z\boldsymbol{z}) \tag{8}$$

Using the general formula for a vector cross product

$$\boldsymbol{u} \times \boldsymbol{v} = (u_2v_3 - u_3v_2)\boldsymbol{i} + (u_3v_1 - u_1v_3)\boldsymbol{j} + (u_1v_2 - u_2v_1)\boldsymbol{k} \tag{9}$$

we can write

$$\boldsymbol{n} \times \boldsymbol{p} = (n_yp_z - n_zp_y)\boldsymbol{x} + (n_zp_x - n_xp_z)\boldsymbol{y} + (n_xp_y - n_yp_x)\boldsymbol{z} \tag{10}$$

From these equations we can obtain $(\boldsymbol{n} \times \boldsymbol{p}) \times \boldsymbol{n}$

$$\begin{aligned} (\boldsymbol{n} \times \boldsymbol{p}) \times \boldsymbol{n} = {} & [(n_zp_x - n_xp_z)n_z - (n_xp_y - n_yp_x)n_y]\boldsymbol{x} \\ & +[(n_xp_y - n_yp_x)n_x - (n_yp_z - n_zp_y)n_z]\boldsymbol{y} \\ & +[(n_yp_z - n_zp_y)n_y - (n_zp_x - n_xp_z)n_x]\boldsymbol{z} \end{aligned} \tag{11}$$

The same mathematics goes for the quadrupole contribution $(\boldsymbol{n} \times \boldsymbol{Q}(\boldsymbol{n})) \times \boldsymbol{n}$.

For the magnetic dipole contribution $(\boldsymbol{n} \times \boldsymbol{m})$ we end up with

$$(\boldsymbol{n} \times \boldsymbol{m}) = (n_x\boldsymbol{x} + n_y\boldsymbol{y} + n_z\boldsymbol{z}) \times (m_x\boldsymbol{x} + m_y\boldsymbol{y} + m_z\boldsymbol{z})$$
$$= (n_y m_z - n_z m_y)\boldsymbol{x} + (n_z m_x - n_x m_z)\boldsymbol{y} + (n_x m_y - n_y m_x)\boldsymbol{z} \quad (12)$$

0.3 Defining system geometry

To determine the relevant electric field and associated tensor components, we need to define the system's geometry (see S1). In the defined system, the incoming LG light wave propagates in the z-direction with electric field components in in all directions (x, y and z). The beam has normal incidence on the sample.

Because of the electric field components in all directions for LG light, radiation of electromagnetic fields is allowed for all directions. In terms of n, n_x, n_y and n_z are all allowed.

If we take n_x, n_y and n_z as unit vectors in the **x**, **y** and **z** directions, we can rewrite the dipolar contribution (Equation 11) to

$$(\boldsymbol{n} \times \boldsymbol{p}) \times \boldsymbol{n} = (2p_x - p_y - p_z)\boldsymbol{x} + (2p_y - p_x - p_z)\boldsymbol{y} + (2p_z - p_x - p_y)\boldsymbol{z} \quad (13)$$

As expected, radiation is possible in all directions when using LG light.

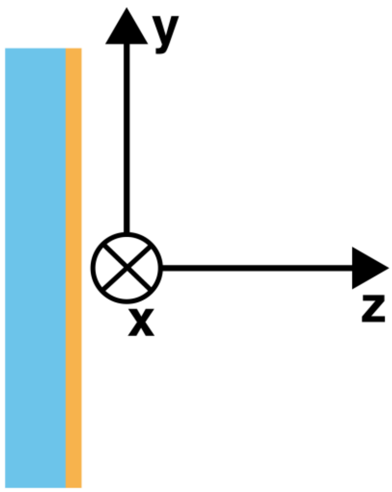

Fig. S5: Configuration of the system with visualization of the coordinate axes.

For the quadrupolar term, we then arrive at

$$(\boldsymbol{n} \times \boldsymbol{Q}(\boldsymbol{n})) \times \boldsymbol{n} = (2Q_x - Q_y - Q_z)\boldsymbol{x} + (2Q_y - Q_x - Q_z)\boldsymbol{y} + (2Q_z - Q_x - Q_y)\boldsymbol{z} \quad (14)$$

For the components of **Q(n)**, we can write

$$Q_x = Q_{xx}n_x + Q_{xy}n_y + Q_{xz}n_z = Q_{xx} + Q_{xy} + Q_{xz}$$

$$Q_y = Q_{yx}n_x + Q_{yy}n_y + Q_{yz}n_z = Q_{yx} + Q_{yy} + Q_{yz} \tag{15}$$

$$Q_z = Q_{zx}n_x + Q_{zy}n_y + Q_{zz}n_z = Q_{zx} + Q_{zy} + Q_{zz}$$

Finally, for the magnetic dipole term, we get

$$(\boldsymbol{n} \times \boldsymbol{m}) = (m_z - m_y)\boldsymbol{x} + (m_x - m_z)\boldsymbol{y} + (m_y - m_x)\boldsymbol{z} \tag{16}$$

We can then write the total field components from Equation 7 as

$$E_{total,x} = [\frac{k^2}{r}e^{ikr}(2p_x - p_y - p_z) - \frac{ik^3}{6r}e^{ikr}(2Q_x - Q_y - Q_z)$$

$$+\frac{k^2}{r}e^{ikr}(m_z - m_y)]\boldsymbol{x}$$

$$\sim \left[2p_x - p_y - p_z - \frac{ik}{3}Q_x + \frac{ik}{6}Q_y + \frac{ik}{6}Q_z + m_z - m_y\right]\boldsymbol{x}$$

$$E_{total,y} = [\frac{k^2}{r}e^{ikr}(2p_y - p_x - p_z) - \frac{ik^3}{6r}e^{ikr}(2Q_y - Q_x - Q_z)$$

$$+\frac{k^2}{r}e^{ikr}(m_x - m_z)]\boldsymbol{y} \tag{17}$$

$$\sim \left[2p_y - p_x - p_z - \frac{ik}{3}Q_y + \frac{ik}{6}Q_x + \frac{ik}{6}Q_z + m_x - m_z\right]\boldsymbol{y}$$

$$E_{total,z} = [\frac{k^2}{r}e^{ikr}(2p_z - p_x - p_y) - \frac{ik^3}{6r}e^{ikr}(2Q_z - Q_x - Q_y)$$

$$+\frac{k^2}{r}e^{ikr}(m_y - m_x)]\boldsymbol{z}$$

$$\sim [2p_z - p_x - p_y - \frac{ik}{3}Q_z + \frac{ik}{6}Q_x + \frac{ik}{6}Q_y + m_y - m_x]\boldsymbol{z}$$

0.4 The total radiated electric field as a function of tensor components

0.4.1 Electric field components of LG light

Laguerre-Guassian light, LG_p^l with p the radial and l the azimuthal indices of the LG mode, has a quantized orbital angular momentum l in the paraxial limit, when the beam is not or only weakly focused.

In the paraxial limit and using LG beams that have a large beam waist radius ($\omega_0 >>> \lambda$), the electric field components of an LG beam propagating in the $+z$ direction can be written as: *(22)*

$$E_x(x,y,z) = \alpha_z E_0 e^{ikz} e^{i|l|\phi} \left(\frac{\sqrt{2}\rho}{\omega_0}\right)^{|l|} e^{\left[-\frac{\rho^2}{\omega_0^2}\right]} L_p^{|l|}\left(\frac{2\rho^2}{\omega_0^2}\right)$$

$$E_y(x,y,z) = \beta_z E_0 e^{ikz} e^{i|l|\phi} \left(\frac{\sqrt{2}\rho}{\omega_0}\right)^{|l|} e^{\left[-\frac{\rho^2}{\omega_0^2}\right]} L_p^{|l|}\left(\frac{2\rho^2}{\omega_0^2}\right) \quad (18)$$

$$E_z(x,y,z) = if\left[(\alpha_z + i\beta_z)\frac{l\omega_0(x-iy)}{\rho^2} E_0 e^{ikz} e^{i|l|\phi} \left(\frac{\sqrt{2}\rho}{\omega_0}\right)^{|l|} e^{\left[-\frac{\rho^2}{\omega_0^2}\right]} L_p^{|l|}\left(\frac{2\rho^2}{\omega_0^2}\right)\right]$$

In these equations, L_p^l is the associated Laguerre polynomial, $\rho = \sqrt{x^2+y^2}$, $\phi = \arctan(y/x)$, E_0 is the initial field amplitude, ω_0 is the beam waist radius, $f = 1/(k\omega_0) = \lambda/(2\pi\omega_0)$ is the natural expansion factor and α_z and β_z are normalized phase factors, such that $|\alpha_z|^2 + |\beta_z|^2 = 1$.

Important to note is that all but one dependences of E_x and E_y on l are on the absolute value of l ($|l|$). The exception can be found for E_z where the pre-exponential factor depends on just l. This will be important later on in the analysis when dealing with the differences between $+l$ and $-l$ LG light.

In terms of gradients, ∇_z is the same for LG light as for plane wave light ($E_x = E_{0x}e^{i(kz-\omega t)}$): $\nabla_z E_j = ikE_j$ with $j = x, y$ or z. Contrary to plane waves propagating in the z direction, where the field gradients ∇_x or ∇_y become 0, this is not the case for LG beams. As the exact form of these gradients is of no importance for the following analysis, we will suffice with explicitly including all components that depend on ∇_x or ∇_y.

0.4.2 Polarizations, quadrupolarizations and magnetizations

Generally, for a system with electric dipole, electric quadrupole and magnetic dipole contributions, we can write the polarization, quadrupolarization and magnetization in vector format as follows.

$$P = \chi^{ee}E + \chi^{eq}\nabla E + \chi^{em}B$$

$$Q = \chi^{qe}E \quad (19)$$

$$M = \chi^{me}E$$

Important: for the following analysis, we start from LG light that is linearly polarized in the x direction. This allows to simplify the equations and only include the E_x, E_z, B_y and B_z fields.

Starting from linearly polarized LG light, we can write the full polarizations, quadrupolarizations and magnetizations as

$$p_x = \chi^{ee}_{xx} E_x + \chi^{eq}_{xzx} \nabla_z E_x + \chi^{eq}_{xxz} \nabla_x E_z + \chi^{eq}_{xyz} \nabla_y E_z + \chi^{em}_{xy} B_y$$

$$p_y = \chi^{eq}_{yzx} \nabla_z E_x + \chi^{eq}_{yxz} \nabla_x E_z + \chi^{eq}_{yyz} \nabla_y E_z + \chi^{em}_{yy} B_y$$

$$p_z = \chi^{ee}_{zz} E_z + \chi^{eq}_{zzz} \nabla_z E_z + \chi^{eq}_{zxx} \nabla_x E_x + \chi^{eq}_{zyx} \nabla_y E_x$$

$$Q_{xx} = \chi^{qe}_{xxz} E_z$$

$$Q_{xy} = \chi^{qe}_{xyz} E_z$$

$$Q_{xz} = \chi^{qe}_{xzx} E_x$$

$$Q_{yy} = \chi^{qe}_{yyz} E_z$$

$$Q_{yx} = \chi^{qe}_{yxz} E_z \quad (20)$$

$$Q_{yz} = \chi^{qe}_{yzx} E_x$$

$$Q_{zz} = \chi^{qe}_{zzz} E_z$$

$$Q_{zx} = \chi^{qe}_{zxx} E_x$$

$$Q_{zy} = \chi^{qe}_{zyx} E_x$$

$$m_x = \chi^{me}_{xx} E_x$$

$$m_y = \chi^{me}_{yx} E_x$$

$$m_z = \chi^{me}_{zz} E_z$$

Note that in the expression for p_z, a term $+\chi^{em}_{zz} B_z$ could be expected. However, we chose to group the diagonal χ^{ee} and χ^{em} components because they cannot be separated in a straightforward manner and are experimentally indistinguishable. Further, we neglect the $\chi^{ee}_{yx} E_x$ term because it is irrelevant in the analysis.

Next we want to eliminate the B_x and B_y terms in the equation by transposing them to electric field terms. According to Cerjan and Cerjan,*(22)* the following relations are valid for LG beams:

$$B_x = -\frac{k}{\omega} E_y$$

$$B_y = \frac{k}{\omega} E_x \quad (21)$$

With these relations we can now rewrite Equation 20 to

$$p_x = \chi^{ee}_{xx} E_x + \chi^{eq}_{xzx} \nabla_z E_x + \chi^{eq}_{xxz} \nabla_x E_z + \chi^{eq}_{xyz} \nabla_y E_z + \frac{k}{\omega} \chi^{em}_{xy} E_x$$

$$p_y = \chi^{eq}_{yzx} \nabla_z E_x + \chi^{eq}_{yxz} \nabla_x E_z + \chi^{eq}_{yyz} \nabla_y E_z + \frac{k}{\omega} \chi^{em}_{yy} E_x$$

$$p_z = \chi^{ee}_{zz} E_z + \chi^{eq}_{zzz} \nabla_z E_z + \chi^{eq}_{zxx} \nabla_x E_x + \chi^{eq}_{zyx} \nabla_y E_x$$

$$Q_{xx} = \chi^{qe}_{xxz} E_z$$

$$Q_{xy} = \chi^{qe}_{xyz} E_z$$

$$Q_{xz} = \chi^{qe}_{xzx} E_x$$

$$Q_{yy} = \chi^{qe}_{yyz} E_z \qquad (22)$$

$$Q_{yx} = \chi^{qe}_{yxz} E_z$$

$$Q_{yz} = \chi^{qe}_{yzx} E_x$$

$$Q_{zz} = \chi^{qe}_{zzz} E_z$$

$$Q_{zx} = \chi^{qe}_{zxx} E_x$$

$$Q_{zy} = \chi^{qe}_{zyx} E_x$$

$$m_x = \chi^{me}_{xx} E_x$$

$$m_y = \chi^{me}_{yx} E_x$$

$$m_z = \chi^{me}_{zz} E_z$$

0.4.3 Total radiated fields in tensor components

Filling in these formulas in Equations 17 yields the full radiated field equations

$$\begin{aligned} E_{total,x} &= \left[2p_x - p_y - p_z - \frac{ik}{3} Q_x + \frac{ik}{6} Q_y + \frac{ik}{6} Q_z + m_z - m_y\right] \boldsymbol{x} \\ &= 2\chi^{ee}_{xx} E_x + 2\chi^{eq}_{xzx} \nabla_z E_x + 2\chi^{eq}_{xxz} \nabla_x E_z + 2\chi^{eq}_{xyz} \nabla_y E_z + \frac{2k}{\omega} \chi^{em}_{xy} E_x \\ &\quad - \chi^{eq}_{yzx} \nabla_z E_x - \chi^{eq}_{yxz} \nabla_x E_z - \chi^{eq}_{yyz} \nabla_y E_z - \frac{k}{\omega} \chi^{em}_{yy} E_x \\ &\quad - \chi^{ee}_{zz} E_z - \chi^{eq}_{zzz} \nabla_z E_z - \chi^{eq}_{zxx} \nabla_x E_x - \chi^{eq}_{zyx} \nabla_y E_x \end{aligned} \qquad (23)$$

$$-\frac{ik}{3}\chi^{qe}_{xxz}E_z-\frac{ik}{3}\chi^{qe}_{xyz}E_z-\frac{ik}{3}\chi^{qe}_{xzx}E_x$$

$$+\frac{ik}{6}\chi^{qe}_{yyz}E_z+\frac{ik}{6}\chi^{qe}_{yxz}E_z+\frac{ik}{6}\chi^{qe}_{yzx}E_x$$

$$+\frac{ik}{6}\chi^{qe}_{zzz}E_z+\frac{ik}{6}\chi^{qe}_{zxx}E_x+\frac{ik}{6}\chi^{qe}_{zyx}E_x$$

$$+\chi^{me}_{zz}E_z-\chi^{me}_{yx}E_x$$

$$E_{total,y}=\left[2p_y-p_x-p_z-\frac{ik}{3}Q_y+\frac{ik}{6}Q_x+\frac{ik}{6}Q_z+m_x-m_z\right]\boldsymbol{y}$$

$$=+2\chi^{eq}_{yzx}\nabla_zE_x+2\chi^{eq}_{yxz}\nabla_xE_z+2\chi^{eq}_{yyz}\nabla_yE_z+\frac{2k}{\omega}\chi^{em}_{yy}E_x$$

$$-\chi^{ee}_{xx}E_x-\chi^{eq}_{xzx}\nabla_zE_x-\chi^{eq}_{xxz}\nabla_xE_z-\chi^{eq}_{xyz}\nabla_yE_z-\frac{k}{\omega}\chi^{em}_{xy}E_x$$

$$-\chi^{ee}_{zz}E_z-\chi^{eq}_{zzz}\nabla_zE_z-\chi^{eq}_{zxx}\nabla_xE_x-\chi^{eq}_{zyx}\nabla_yE_x \tag{24}$$

$$-\frac{ik}{3}\chi^{qe}_{yyz}E_z-\frac{ik}{3}\chi^{qe}_{yxz}E_z-\frac{ik}{3}\chi^{qe}_{yzx}E_x$$

$$+\frac{ik}{6}\chi^{qe}_{xxz}E_z+\frac{ik}{6}\chi^{qe}_{xyz}E_z+\frac{ik}{6}\chi^{qe}_{xzx}E_x$$

$$+\frac{ik}{6}\chi^{qe}_{zzz}E_z+\frac{ik}{6}\chi^{qe}_{zxx}E_x+\frac{ik}{6}\chi^{qe}_{zyx}E_x$$

$$+\chi^{me}_{xx}E_x-\chi^{me}_{zz}E_z$$

$$E_{total,z}=\left[2p_z-p_x-p_y-\frac{ik}{3}Q_z+\frac{ik}{6}Q_x+\frac{ik}{6}Q_y+m_y-m_x\right]\boldsymbol{z}$$

$$=2\chi^{ee}_{zz}E_z+2\chi^{eq}_{zzz}\nabla_zE_z+2\chi^{eq}_{zxx}\nabla_xE_x+2\chi^{eq}_{zyx}\nabla_yE_x$$

$$-\chi^{ee}_{xx}E_x-\chi^{eq}_{xzx}\nabla_zE_x-\chi^{eq}_{xxz}\nabla_xE_z-\chi^{eq}_{xyz}\nabla_yE_z-\frac{k}{\omega}\chi^{em}_{xy}E_x$$

$$-\chi^{eq}_{yzx}\nabla_zE_x-\chi^{eq}_{yxz}\nabla_xE_z-\chi^{eq}_{yyz}\nabla_yE_z-\frac{k}{\omega}\chi^{em}_{yy}E_x \tag{25}$$

$$-\frac{ik}{3}\chi^{qe}_{zzz}E_z-\frac{ik}{3}\chi^{qe}_{zxx}E_x-\frac{ik}{3}\chi^{qe}_{zyx}E_x$$

$$+\frac{ik}{6}\chi^{qe}_{xxz}E_z+\frac{ik}{6}\chi^{qe}_{xyz}E_z+\frac{ik}{6}\chi^{qe}_{xzx}E_x$$

$$+\frac{ik}{6}\chi^{qe}_{yyz}E_z+\frac{ik}{6}\chi^{qe}_{yxz}E_z+\frac{ik}{6}\chi^{qe}_{yzx}E_x$$

$$+\chi^{me}_{yx}E_x-\chi^{me}_{xx}E_x$$

A first simplification we introduce is the same as used before, we group the diagonal χ^{ee} and χ^{em} components because they cannot be separated in a straightforward manner and are experimentally indistinguishable. This means that the terms $-\chi^{em}_{yy}E_x$ and $+\chi^{me}_{zz}E_z$ in $E_{total,x}$; $+2\chi^{em}_{yy}E_x$, $+\chi^{me}_{xx}E_x$ and $-\chi^{me}_{zz}E_z$ in $E_{total,y}$; and $-\chi^{em}_{yy}E_x$ and $-\chi^{me}_{xx}E_x$ in $E_{total,z}$ can be regrouped. Further, for the readers' convenience, we group the tensor components by the corresponding electric field component (E_x or E_z).

$$\begin{aligned}E_{total,x} = {} & [2\chi^{ee}_{xx}+\frac{2k}{\omega}\chi^{em}_{xy}-\chi^{me}_{yx}+2\chi^{eq}_{xzx}\nabla_z-\frac{ik}{3}\chi^{qe}_{xzx}-\chi^{eq}_{zxx}\nabla_x+\frac{ik}{6}\chi^{qe}_{zxx} \\ & +\frac{ik}{6}\chi^{qe}_{zyx}-\chi^{eq}_{zyx}\nabla_y+\frac{ik}{6}\chi^{qe}_{yzx}-\chi^{eq}_{yzx}\nabla_z]E_x \\ & +[-\chi^{ee}_{zz}-\chi^{eq}_{yyz}\nabla_y+\frac{ik}{6}\chi^{qe}_{yyz}+2\chi^{eq}_{xxz}\nabla_x-\frac{ik}{3}\chi^{qe}_{xxz}+\frac{ik}{6}\chi^{qe}_{zzz}-\chi^{eq}_{zzz}\nabla_z \\ & -\frac{ik}{3}\chi^{qe}_{xyz}+2\chi^{eq}_{xyz}\nabla_y-\chi^{eq}_{yxz}\nabla_x+\frac{ik}{6}\chi^{qe}_{yxz}]E_z\end{aligned} \tag{26}$$

$$\begin{aligned}E_{total,y} = {} & [-\chi^{ee}_{xx}-\frac{k}{\omega}\chi^{em}_{xy}-\chi^{eq}_{xzx}\nabla_z+\frac{ik}{6}\chi^{qe}_{xzx}-\chi^{eq}_{zxx}\nabla_x+\frac{ik}{6}\chi^{qe}_{zxx} \\ & +2\chi^{eq}_{yzx}\nabla_z-\chi^{eq}_{zyx}\nabla_y-\frac{ik}{3}\chi^{qe}_{yzx}+\frac{ik}{6}\chi^{qe}_{zyx}]E_x \\ & +[-\chi^{ee}_{zz}-\chi^{eq}_{xxz}\nabla_x+2\chi^{eq}_{yyz}\nabla_y-\frac{ik}{3}\chi^{qe}_{yyz}+\frac{ik}{6}\chi^{qe}_{xxz}-\chi^{eq}_{zzz}\nabla_z+\frac{ik}{6}\chi^{qe}_{zzz} \\ & +2\chi^{eq}_{yxz}\nabla_x-\chi^{eq}_{xyz}\nabla_y-\frac{ik}{3}\chi^{qe}_{yxz}+\frac{ik}{6}\chi^{qe}_{xyz}]E_z\end{aligned} \tag{27}$$

$$\begin{aligned}E_{total,z} = {} & [-\chi^{ee}_{xx}-\frac{k}{\omega}\chi^{em}_{xy}+\chi^{me}_{yx}-\chi^{eq}_{xzx}\nabla_z+\frac{ik}{6}\chi^{qe}_{xzx}+2\chi^{eq}_{zxx}\nabla_x-\frac{ik}{3}\chi^{qe}_{zxx} \\ & +2\chi^{eq}_{zyx}\nabla_y-\chi^{eq}_{yzx}\nabla_z-\frac{ik}{3}\chi^{qe}_{zyx}+\frac{ik}{6}\chi^{qe}_{yzx}]E_x \\ & +[2\chi^{ee}_{zz}-\chi^{eq}_{xxz}\nabla_x-\chi^{eq}_{yyz}\nabla_y+\frac{ik}{6}\chi^{qe}_{yyz}+\frac{ik}{6}\chi^{qe}_{xxz}+2\chi^{eq}_{zzz}\nabla_z-\frac{ik}{3}\chi^{qe}_{zzz} \\ & -\chi^{eq}_{xyz}\nabla_y-\chi^{eq}_{yxz}\nabla_x+\frac{ik}{6}\chi^{qe}_{xyz}+\frac{ik}{6}\chi^{qe}_{yxz}]E_z\end{aligned} \tag{28}$$

0.4.4 Applicable tensor relations

By using applicable tensor relations, it is possible to drastically reduce the number of tensor components in the equations.*(23, 24)* Relations are categorized based on the field component they belong to.

Electric dipole

$$\chi_{xx}^{ee} = \chi_{yy}^{ee}$$
$$\chi_{xy}^{ee} = -\chi_{yx}^{ee} \quad (29)$$
$$\chi_{zz}^{ee}$$

Magnetic dipole

$$\chi^{em} = -\chi^{me}$$
$$\chi_{xx}^{em} = \chi_{yy}^{em} \quad (30)$$
$$\chi_{xy}^{em} = -\chi_{yx}^{em}$$
$$\chi_{zz}^{em}$$

Electric quadrupole
In general:

$$\chi_{ijk}^{eq} = \chi_{ikj}^{eq}$$
$$\chi_{ijk}^{qe} = \chi_{jik}^{qe} \quad (31)$$
$$\chi_{ijk}^{eq} = \chi_{kji}^{qe}$$

For χ^{eq}:

$$\chi_{zzz}^{eq}$$
$$\chi_{zxx}^{eq} = \chi_{zyy}^{eq}$$
$$\chi_{xxz}^{eq} = \chi_{xzx}^{eq} = \chi_{yyz}^{eq} = \chi_{yzy}^{eq} \quad (32)$$
$$\chi_{xyz}^{eq} = \chi_{xzy}^{eq} = -\chi_{yxz}^{eq} = -\chi_{yzx}^{eq}$$

For χ^{qe}:

$$\chi_{zzz}^{qe}$$
$$\chi_{zxx}^{qe} = \chi_{zyy}^{qe} = \chi_{xzx}^{qe} = \chi_{yzy}^{qe} \quad (33)$$

$\chi^{qe}_{xxz} = \chi^{qe}_{yyz}$

$\chi^{qe}_{zxy} = \chi^{qe}_{xzy} = -\chi^{qe}_{zyx} = -\chi^{qe}_{yzx}$

Using the relations described above, we can write the following summarizing equations:

$$\begin{aligned}
&\chi^{eq}_{zzz} = \chi^{qe}_{zzz} \\
&\chi^{eq}_{zxx} = \chi^{eq}_{zyy} = \chi^{qe}_{xxz} = \chi^{qe}_{yyz} \\
&\chi^{eq}_{xxz} = \chi^{eq}_{xzx} = \chi^{eq}_{yyz} = \chi^{eq}_{yzy} = \chi^{qe}_{zxx} = \chi^{qe}_{zyy} = \chi^{qe}_{xzx} = \chi^{qe}_{yzy} \\
&\chi^{eq}_{xyz} = \chi^{eq}_{xzy} = -\chi^{eq}_{yxz} = -\chi^{eq}_{yzx} = -\chi^{qe}_{zxy} = -\chi^{qe}_{xzy} = \chi^{qe}_{zyx} = \chi^{qe}_{yzx} \\
&\chi^{eq}_{zyx} = \chi^{eq}_{zxy} = \chi^{qe}_{yxz} = \chi^{qe}_{xyz} = 0
\end{aligned} \tag{34}$$

0.4.5 Simplified equations

Using the tensor relations described above and knowing that $\nabla_z E_j = ikE_j$ with $j = x, y$ or , we can rewrite and simplify Equations 26, 27 and 28.

$$\begin{aligned}
E_{total,x} = &\left[2\chi^{ee}_{xx} + \left(\frac{2k}{\omega} - 1\right)\chi^{em}_{xy} + \chi^{eq}_{xzx}\left(\frac{11}{6}ik\right) - \chi^{eq}_{zxx}\nabla_x + \chi^{eq}_{xyz}\left(-\frac{4}{3}ik\right)\right]E_x \\
&+[-\chi^{ee}_{zz} + \chi^{eq}_{xzx}(2\nabla_x - \nabla_y) + \chi^{eq}_{zxx}(-\frac{ik}{6}) + \chi^{eq}_{zzz}(-\frac{5}{6}ik) + \chi^{eq}_{xyz}(\nabla_x + 2\nabla_y)]E_z
\end{aligned} \tag{35}$$

$$\begin{aligned}
E_{total,y} = &\left[-\chi^{ee}_{xx} - \frac{k}{\omega}\chi^{em}_{xy} + \chi^{eq}_{xzx}\left(-\frac{2}{3}ik\right) - \chi^{eq}_{zxx}\nabla_x + \chi^{eq}_{xyz}\left(-\frac{13}{6}ik\right)\right]E_x \\
&+[-\chi^{ee}_{zz} - \chi^{eq}_{xzx}(\nabla_x + 2\nabla_y) + \chi^{eq}_{zxx}(-\frac{ik}{6}) + \chi^{eq}_{zzz}(-\frac{5}{6}ik) + \chi^{eq}_{xyz}(-2\nabla_x - \nabla_y)]E_z
\end{aligned} \tag{36}$$

$$\begin{aligned}
E_{total,z} = &\left[-\chi^{ee}_{xx} + \chi^{eq}_{xzx}\left(-\frac{5}{6}ik\right) + \chi^{eq}_{zxx}2\nabla_x + \chi^{eq}_{xyz}\left(\frac{5}{6}ik\right)\right]E_x \\
&+[2\chi^{ee}_{zz} - \chi^{eq}_{xzx}(\nabla_x - \nabla_y) + \chi^{eq}_{zxx}(\frac{ik}{3}) + \chi^{eq}_{zzz}(\frac{5}{3}ik) + \chi^{eq}_{xyz}(\nabla_x - \nabla_y)]E_z
\end{aligned} \tag{38}$$

These equations include all electric and magnetic dipole and electric quadrupole contributions applicable in the defined system geometry.

0.5 Influence of enantiomers and propagation direction

0.5.1 Influence of enantiomers on tensor components

Changing enantiomers (e.g. D to L) has an influence on chiral tensor components. These chiral components change sign with changing enantiomers. In the simplified Equations 35, 36 and 37,the chiral tensor components are of the χ^{em}_{xy} and χ^{eq}_{xyz} types.

For clarity, tensor components of the χ_{xy}^{em} and χ_{xyz}^{eq} types are not allowed for achiral samples.

0.5.2 Influence of propagation direction on tensor components

The results shown in the article are based on asymmetric transmission. Samples were first measured in the forward and then in the backward direction and the data was subtracted and divided by the average to obtain a % asymmetry.

For the theoretical side, it is important to know what happens to the tensor components when the direction of light is reversed. Electric (χ^{ee}) and magnetic ($\chi^{em}; \chi^{me}$) dipole components are not influenced by the direction of light. Some electric quadrupole ($\chi^{eq}; \chi^{qe}$) components, however, are sensitive to the direction of light travel.

If we look at the quadrupolar tensor components that remain in Equations 35, 36 and 37, we can categorize them in polar ($\chi_{xzx}^{eq}; \chi_{zxx}^{eq}; \chi_{zzz}^{eq}$) and chiral ($\chi_{xyz}^{eq}$) tensor components. While there are multiple ways of dealing with the directional sensitivity of quadrupolar tensor components, e.g. based on $\nabla_z E_x$, we base our analysis on the appropriate tensor sign changes under the influence of a two-fold rotation, which corresponds to the experimental protocol. *In concreto*, when applying a two-fold rotation to the sample $+z \rightarrow -z$ and $+x \rightarrow -x$ (see Figure S5). For chiral quadrupolar components $\chi_{xyz}^{eq} \rightarrow \chi_{-xy-z}^{eq}$, implying invariance under two-fold rotation. Polar quadrupolar components, however, do change sign and are thus sensitive to the propagation direction ($\chi_{xzx}^{eq}; \chi_{zxx}^{eq}; \chi_{zzz}^{eq} \rightarrow -\chi_{-x-z-x}^{eq}; -\chi_{-z-x-x}^{eq}; -\chi_{-z-z-z}^{eq}$).

0.6 Asymmetric transmission and helical dichroism

The presented experimental results for asymmetric transmission and helical dichroism were acquired by measuring light intensities. To pinpoint the origin of the observed effects, we resort to expressing the expected intensities as a function of tensor components.
In general, intensities can be calculated from electric field components as follows

$$I_{\mathrm{fw}} \sim |E_x|^2 + |E_y|^2 + |E_z|^2 \tag{38}$$

with the absolute square of a complex number z being

$$|z|^2 \equiv zz^* \tag{39}$$

with z^* denoting the complex conjugate of z. If the complex number is written as $z = x + iy$, with x and y real, then the absolute square can be written as

$$|x + iy|^2 = x^2 + y^2 \tag{40}$$

Fully calculating these absolute squares directly from Equations 35, 36 and 37 is very cumbersome due to the large number of tensor components and the different field dependencies and will result in a very large number of terms, rendering the solution unclear. However, for a correct analysis of the equations to find the origin of the observed effects, full calculations are not required.

When calculating the intensity from the absolute squares of the electric field components, multiplication pairs of tensor components in the electric field components are formed (real or imaginary). Examples of such tensor component pairs are $\chi_{xx}^{ee}\chi_{xzx}^{eq}$, $\chi_{xx}^{ee}\chi_{xyz}^{eq}$ or $\chi_{xzx}^{eq}\chi_{xyz}^{eq}$.

Based on tensor component properties under certain circumstances, we can now analyze the origin of the observed effects.

0.6.1 Asymmetric transmission

As detailed earlier in Section 0.5.2, changing the propagation direction has an influence on particular tensor components ($+z \rightarrow -z$, $\chi_{xzx}^{eq}; \chi_{zxx}^{eq}; \chi_{zzz}^{eq} \rightarrow -\chi_{xzx}^{eq}; -\chi_{zxx}^{eq}; -\chi_{zzz}^{eq}$).

Asymmetric transmission (AT) is calculated by subtracting the intensity measured in the backward from the one in the forward direction.

$$\mathrm{AT} \sim I_{\mathrm{fw}} - I_{\mathrm{bw}} \tag{41}$$

Origin of AT - interaction of OAM with electric quadrupole fields

Since the polar quadrupolar χ_{xzx}^{eq}, χ_{zxx}^{eq} and χ_{zzz}^{eq} tensor components are the only ones that remain in the equation after forward minus backward subtraction, all terms in the AT intensity expression are of the type $\chi_{xzx}^{eq}\chi_{**}^{**}$ with χ_{**}^{**} being one of the other allowed tensor components in the electric field component equation. The polar quadrupolar tensor components are the origin of the observed asymmetric transmission.

Because the polar electric quadrupole tensor components are the only ones remaining in the AT equation, changes in AT as a function of the orbital angular momentum of the LG beam can only be due to these specific tensor components.

While our analysis does uncover the origin of the observed AT and confirms the interaction of OAM with electric quadrupole fields, it is not possible to straightforwardly explain the measured dependence of the AT on the value of l of the incoming LG beam based on these equations. This is because all electric field components of the incoming LG light beam (Equations 18) depend on the value of l, which makes that all terms in Equations 35, 36 and 37 depend on l.

Chiral samples - enantiomers

The difference between achiral and chiral samples is the existence of additional terms in the expression for AT in the latter case. *In concreto*, terms of the type $\chi_{xzx}^{eq}\chi_{xyz}^{eq}$, $\chi_{zxx}^{eq}\chi_{xyz}^{eq}$, $\chi_{zzz}^{eq}\chi_{xyz}^{eq}$ or $\chi_{xzx}^{eq}\chi_{xy}^{em}$, $\chi_{zxx}^{eq}\chi_{xy}^{em}$, $\chi_{zzz}^{eq}\chi_{xy}^{em}$ are only possible for chiral samples. When changing the molecular enantiomer, tensor components of the χ_{xyz}^{eq} and χ_{xy}^{em} types change sign as explained earlier in Section 0.5.1. This means that the difference in observed asymmetric transmission for both enantiomers is related to the following expression.

$$\mathrm{AT_D} - \mathrm{AT_L} \sim 2[\chi_{xzx}^{eq}\chi_{xyz}^{eq} + \chi_{zxx}^{eq}\chi_{xyz}^{eq} + \chi_{zzz}^{eq}\chi_{xyz}^{eq} + \chi_{xzx}^{eq}\chi_{xy}^{em} + \chi_{zxx}^{eq}\chi_{xy}^{em} + \chi_{zzz}^{eq}\chi_{xy}^{em}] \tag{42}$$

Or, more simplified,

$$\mathrm{AT_D} - \mathrm{AT_L} \sim \chi^{eq}_{polar}\chi^{em}_{chiral} + \chi^{eq}_{polar}\chi^{eq}_{chiral} \quad (43)$$

So the origin of the observed difference in asymmetric transmission for both enantiomers is the combination of polar electric quadrupolar and chiral electric quadrupolar or chiral magnetic dipolar tensor components.

Note that for regular linearly polarized Gaussian light beams ($l_z = 0$), the difference $\mathrm{AT_D} - \mathrm{AT_L}$ will become 0. This because linearly polarized plane wave light incident normal on the sample (for reference see Figure S5) cannot address the chiral χ^{em}_{xy} (χ^{em}_{chiral}) or χ^{eq}_{xyz} (χ^{eq}_{chiral}) tensor components.

0.6.2 Helical dichroism

Helical dichroism (HD) is defined as the difference in transmittivity or absorption of right- (l_+) and left- (l_-) handed helical light.

$$\mathrm{HD} \sim I_{l_+} - I_{l_-} \quad (44)$$

Only a prefactor in the E_z electric field component of the incoming LG light is directly dependent on the value of l. In all other cases, the electric field components relate to the absolute value of l (see Equations 18). This implies that only terms in Equations 35, 36 and 37 that depend on E_z need to be considered for HD.

Only chiral tensor components of the χ^{eq}_{xyz} (and not χ^{em}_{xy}) type depend on E_z, so whatever HD difference measured between different enantiomers in chiral samples is due to this type of component. For chiral samples the following tensor component pairs are relevant in the HD intensity expressions: $\chi^{ee}_{zz}\chi^{eq}_{xyz}$, $\chi^{eq}_{xzx}\chi^{eq}_{xyz}$, $\chi^{eq}_{zxx}\chi^{eq}_{xyz}$ and $\chi^{eq}_{zzz}\chi^{eq}_{xyz}$. This means that the difference observed for both enantiomers is related to the following expression.

$$\mathrm{HD_D} - \mathrm{HD_L} \sim 2[\chi^{ee}_{zz}\chi^{eq}_{xyz} + \chi^{eq}_{xzx}\chi^{eq}_{xyz} + \chi^{eq}_{zxx}\chi^{eq}_{xyz} + \chi^{eq}_{zzz}\chi^{eq}_{xyz}] \quad (45)$$

Or, more simplified,

$$\mathrm{HD_D} - \mathrm{HD_L} \sim \chi^{ee}_{isotropic}\chi^{eq}_{chiral} + \chi^{eq}_{polar}\chi^{eq}_{chiral} \quad (46)$$

So the origin of the observed difference in HD, which in itself is a difference in transmittivity for (l_+) and (l_-) helical light, for different enantiomers is the combination of polar and chiral electric quadrupole tensor components. Although considered a hallmark of molecular chirality, no magnetic dipole contributions are required to measure the chiral response using differential HD measurements. In future experiments with spectral resolution, it should be possible to separate the χ^{eq} from χ^{em} contributions, which are currently indistinguishable using only CD techniques.

Resolving enantiomers based on the difference in HD signal ($\mathrm{HD_D} - \mathrm{HD_L}$) is not possible with plane wave Gaussian light ($l_z = 0$), simply because measuring the absorption/transmittivity difference between (l_+) and (l_-) helical light requires $l_z \neq 0$.

From the above analysis it is also clear that assignment of enantiomers based on HD measurements is possible, since different enantiomers will yield different HD values.

As was the case for the shape of the AT curve, the fundamental origin of the shape of the HD curve as a function of OAM value remains to be elucidated.