Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Fano-like chiroptical response from plasmonic heterodimer nanostructures

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1. CD effect of the Au nanorod heterodimers under θ = 23° and θ = -23°

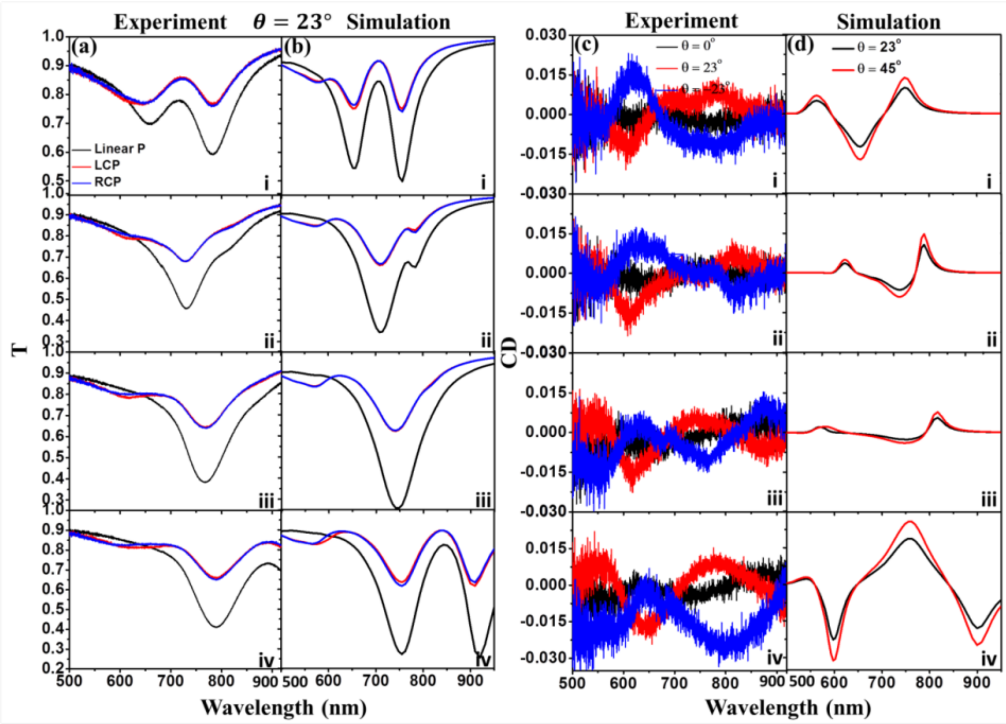

Figure S1. CD effect of the Au nanorod heterodimers under θ = 23° and θ = -23°. (a-b) Transmission spectra of structures i-iv measured experimentally (a) and by FEM simulation (b). (c) Corresponding CD spectra to (a). (d) Calculated CD spectra with an incident angle of θ = 23° (black) and θ = 45° (red).

2. Transmission spectra measured experimentally

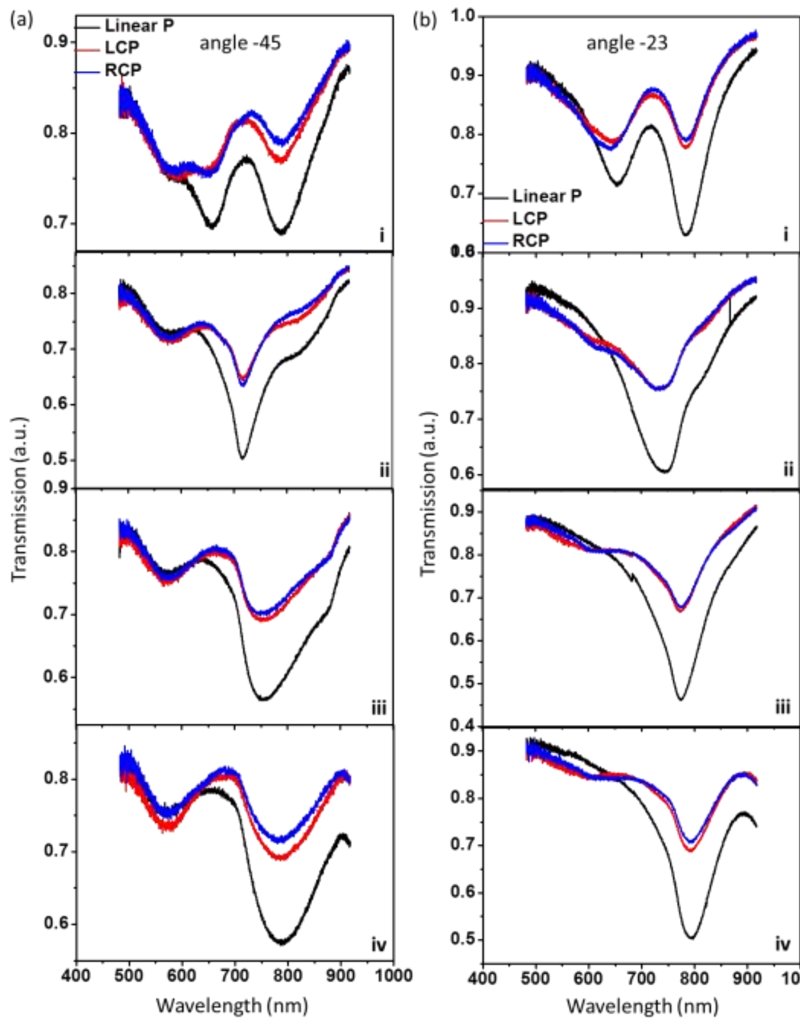

Figure S2. Transmission spectra measured experimentally under the linearly polarized (black), left (red) and right (blue) circularly polarized (LCP and RCP) light excitation, with an oblique incident angle of θ = -45° (a) and θ = -23° (b).

3. Fano-like CD spectra induced by electric-magnetic dipole interaction

I. The derivation of G''

Taking into account the fact that the radiation of an electric (magnetic) dipole has a Lorentz profile, the electric and magnetic Lorentz polarization amplitudes are calculated based on equations 1-2.

$$\mathrm{p} = \frac{A_1\gamma_{10}}{\omega_{10}-\omega-i\gamma_{10}} \qquad (1)$$

$$\mathrm{m} = \frac{A_2\gamma_{20}}{\omega_{20}-\omega-i\gamma_{20}} \qquad (2)$$

Then G'' can be derived based on equation 3 in the text.

$$\begin{aligned}
G'' = \mathrm{Im}(\mathrm{p}^* * \mathrm{m}) &= \frac{A_1A_2\gamma_{10}\gamma_{20}[(\omega_{10}-\omega)\gamma_{20}-(\omega_{20}-\omega)\gamma_{10}]}{[(\omega_{10}-\omega)^2+{\gamma_{10}}^2][(\omega_{20}-\omega)^2+{\gamma_{20}}^2]} \\
&= A_1A_2\gamma_{10}\gamma_{20}\frac{(\omega_{10}\gamma_{20}-\omega_{20}\gamma_{10})+(\gamma_{10}-\gamma_{20})\omega}{[(\omega_{10}-\omega)^2+{\gamma_{10}}^2][(\omega_{20}-\omega)^2+{\gamma_{20}}^2]} \\
&= A_1A_2{\gamma_{10}}^2{\gamma_{20}}^2\frac{\frac{(\omega_{10}\gamma_{20}-\omega_{20}\gamma_{10})}{\gamma_{10}\gamma_{20}}+\frac{(\gamma_{10}-\gamma_{20})}{\gamma_{10}\gamma_{20}}\omega}{[(\omega_{10}-\omega)^2+{\gamma_{10}}^2][(\omega_{20}-\omega)^2+{\gamma_{20}}^2]} \\
&= A_1A_2{\gamma_{10}}^2{\gamma_{20}}^2\frac{\left(\frac{\omega}{\gamma}+\mathrm{q}'\right)}{[(\omega_{10}-\omega)^2+{\gamma_{10}}^2][(\omega_{20}-\omega)^2+{\gamma_{20}}^2]} \\
&= A_1A_2\gamma_{10}\gamma_{20}(\gamma_{10}-\gamma_{20})\frac{(\omega+\mathrm{q}'\gamma)}{[(\omega_{10}-\omega)^2+{\gamma_{10}}^2][(\omega_{20}-\omega)^2+{\gamma_{20}}^2]} \qquad (3)
\end{aligned}$$

where $\gamma = \frac{\gamma_{10}\gamma_{20}}{\gamma_{10}-\gamma_{20}}$, $\mathrm{q}' = \frac{\omega_{10}\gamma_{20}-\omega_{20}\gamma_{10}}{\gamma_{10}\gamma_{20}}$.

To investigate the relation between the asymmetry factor and the asymmetry degree like in Fano formula, we define $\mathrm{q}_0 = \frac{\boldsymbol{\omega_{resonant}}}{\boldsymbol{\gamma}}$, and G'' can be expressed as equation 4.

$$G'' = A_1A_2\gamma_{10}\gamma_{20}(\gamma_{10}-\gamma_{20})\frac{(\omega+(\mathrm{q}-\mathrm{q}_0)\gamma)}{[(\omega_{10}-\omega)^2+{\gamma_{10}}^2][(\omega_{20}-\omega)^2+{\gamma_{20}}^2]} \qquad (4)$$

where $\mathrm{q}' = \mathrm{q}-\mathrm{q}_0$, and $\mathrm{q} = \mathrm{q}'+\mathrm{q}_0$. Based on this definition, $\mathrm{q} = 0$ is the most asymmetric profile. As the value of $|\mathrm{q}|$ increases, the profile becomes more symmetric (Figure S3). We define q as the asymmetry factor. As shown in Figure S4, when $\omega_{10} = \omega_{20}$ (blue curve), the profile is totally asymmetric.

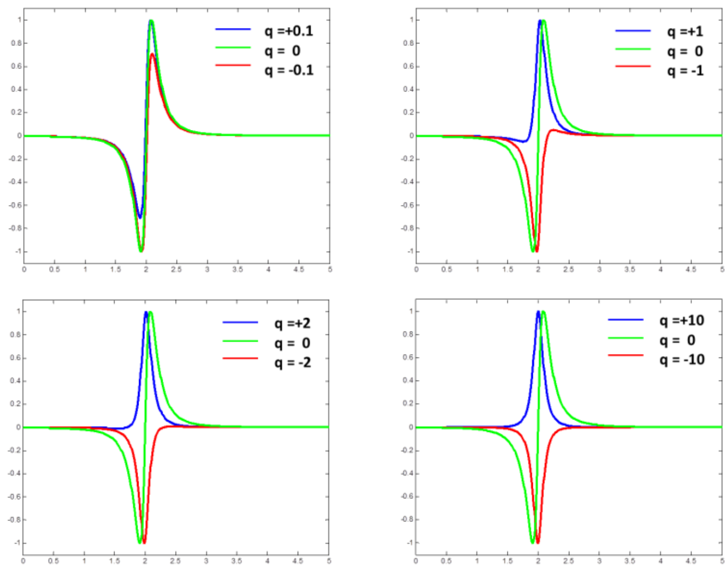

Figure S3. Fano-like profile with different q according to equation 4, with $\omega_{10} = 2.5\ eV$, $\gamma_{10} = 1\ eV$, $A_1 = 1$, $\omega_{20} = 2.3\ eV$, $\gamma_{20} = 0.2\ eV$, $A_2 = 1$. The curves show that as $|q|$ becomes larger, the profile becomes more symmetric. When $|q| = 0$, the profile is the most asymmetric.

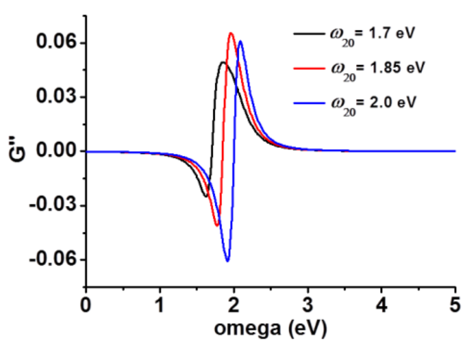

Figure S4. When $\omega_{10} = \omega_{20}$, G'' profile is totally asymmetric. $\omega_{10} = 2.0\ eV$, $\gamma_{10} = 0.3\ eV$, $\gamma_{20} = 0.1\ eV$, $A_1 = 1$, $A_2 = 0.2$, $q = 0$.

II. Zero point of the asymmetry factor: $\mathbf{q_0} = \frac{\boldsymbol{\omega_{resonant}}}{\boldsymbol{\gamma}} \approx \frac{\boldsymbol{\omega_{narrower\_gamma}}}{\boldsymbol{\gamma}}$

For the spectrum profile of G'', when $\mathrm{q} = 0$, it is the most asymmetric (Figure S3). We used Mathematica to calculate the extremal points ω_{min} and ω_{max}. Because the maximum and the minimum peaks are symmetric to the resonant position in the profile, $\omega_{resonant} = \frac{\omega_{min}+\omega_{max}}{2}$ and $\omega_{resonant} \approx \omega_{narrower\_gamma}$ (Table S1). When $\omega_{10} = \omega_{20}$, $\omega_{resonant} = \omega_{narrower\_gamma}$. We calculated q to investigate the asymmetry of the profile, with $\mathrm{q}_0 = \frac{\boldsymbol{\omega_{resonant}}}{\boldsymbol{\gamma}} \approx \frac{\boldsymbol{\omega_{narrower\_gamma}}}{\boldsymbol{\gamma}}$.

Table S1. Comparison of the approximate resonance position $\omega_{resonant} = \omega_{narrower\_gamma}$ and calculated resonance position $(\omega_{min} + \omega_{max})/2$, with a asymmetry factor of $q = 0$.

ω_{10}	ω_{20}	γ_{10}	γ_{20}	ω_{min}	ω_{max}	2γ	γ_{cal}	$(\omega_{min} + \omega_{max})/2$	$\omega_{res,narrow}$
3.0	2.0	2.0	0.1	1.84171	2.06309	0.210526	0.221381	1.9524	2.0
2.5	2.0	2.0	0.1	1.87391	2.07874	0.210526	0.20483	1.976325	2.0
2.5	2.0	1.0	0.1	1.88057	2.08328	0.22222	0.202704	1.981925	2.0
2.5	2.0	1.5	0.1	1.86466	2.0732	0.214286	0.208538	1.96893	2.0
2.5	2.0	0.5	0.1	1.76459	2.04776	0.25	0.283177	1.906175	2.0
2.5	2.0	0.1	2.0	2.42126	2.62609	0.210526	0.20483	2.523675	2.5
2.5	2.0	0.1	1.0	2.43587	2.65537	0.22222	0.219492	2.54562	2.5
2.5	2.0	0.1	1.5	2.4268	2.63534	0.214286	0.208538	2.53107	2.5
2.5	2.0	0.1	0.5	2.45224	2.73541	0.25	0.283177	2.593825	2.5
2.7	2.0	2.0	0.1	1.86166	2.07192	0.210526	0.210264	1.96679	2.0
2.3	2.0	2.0	0.1	1.88525	2.08638	0.210526	0.201127	1.985815	2.0

Table S2. Zero point q_0 and the asymmetry factor q.

ω_{10}	ω_{20}	γ_{10}	γ_{20}	$\omega_{res,narrow}$	γ	$q_0 = \frac{\omega_{narrower\_gamma}}{\gamma}$	$q' = \frac{\omega_{10}\gamma_{20} - \omega_{20}\gamma_{10}}{\gamma_{10}\gamma_{20}}$	$q = q' + q_0$
3.0	2.0	2.0	0.1	2.0	0.1053	19.0000	-18.5000	0.5000
2.5	2.0	2.0	0.1	2.0	0.1053	19.0000	-18.7500	0.2500
2.5	2.0	1.0	0.1	2.0	0.1111	18.0000	-17.5000	0.5000
2.5	2.0	1.5	0.1	2.0	0.1071	18.6667	-18.3333	0.3333
2.5	2.0	0.5	0.1	2.0	0.1250	16.0000	-15.0000	1.0000
2.5	2.0	0.1	2.0	2.5	-0.1053	-23.7500	24.0000	0.2500
2.5	2.0	0.1	1.0	2.5	-0.1111	-22.5000	23.0000	0.5000
2.5	2.0	0.1	1.5	2.5	-0.1071	-23.3333	23.6667	0.3333
2.5	2.0	0.1	0.5	2.5	-0.1250	-20.0000	21.0000	1.0000
2.7	2.0	2.0	0.1	2.0	0.1053	19.0000	-18.6500	0.3500
2.3	2.0	2.0	0.1	2.0	0.1053	19.0000	-18.8500	0.1500
2.0	2.0	1.0	0.1	2.0	0.1111	18.0000	-18.0000	0.0000

4. Spectra fitting

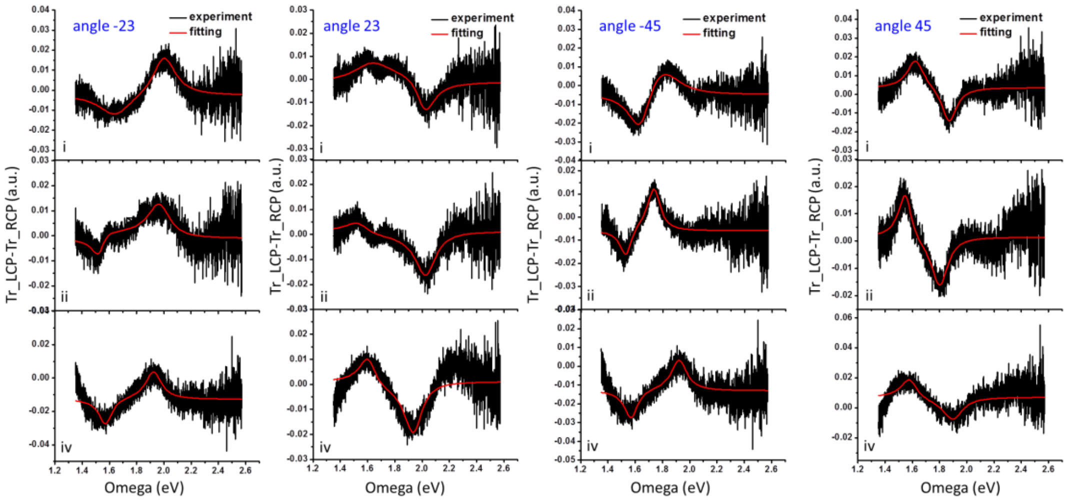

Figure S5. Fitting results of experimental transmission spectra according to equation 6 in the main text.

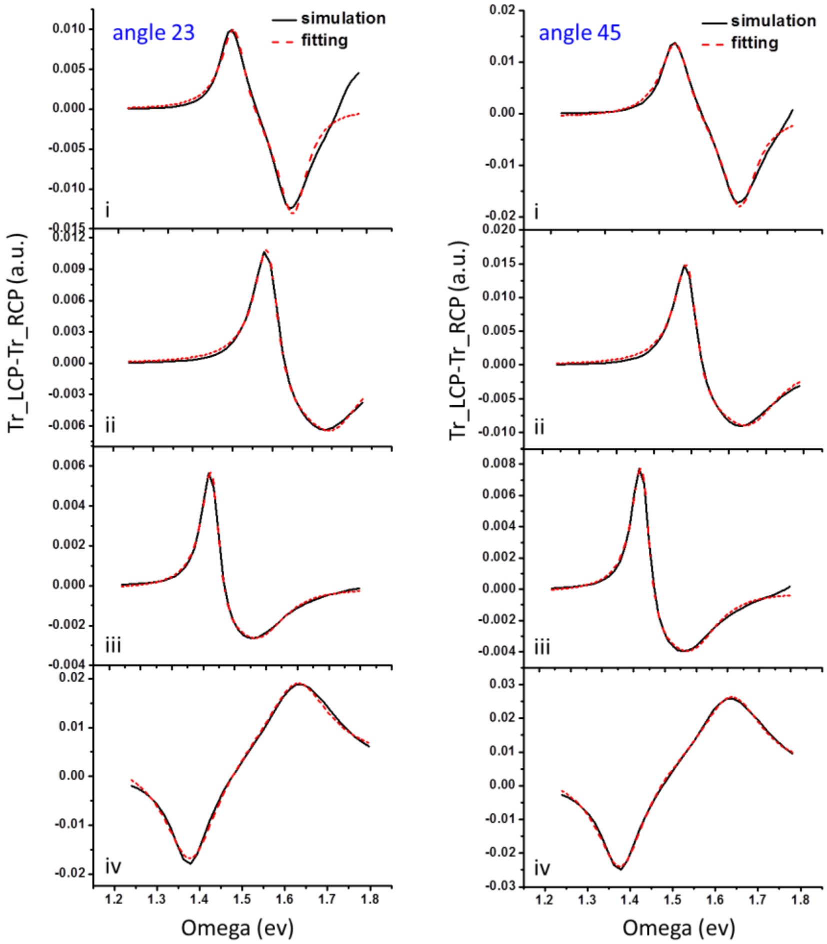

Figure S6. Fitting results of simulation transmission spectra according to equation 6 in the main text.