Supplemental Material for "Diverse axial chiral assemblies of J-aggregates in plexcitonic nanoparticles"

Jiaqi Guo , Fan Wu ,Gang Song ,Yuming Huang, Rongzhen Jiao and Li Yu

S1. The length-diameter ratio histograms of three different samples are shown in Fig.S1, and the average lengths, diameters and the aspect ratios of twelve samples are shown in Table S1. The Au NRs were purchased from Nanoseedz (HongKong).

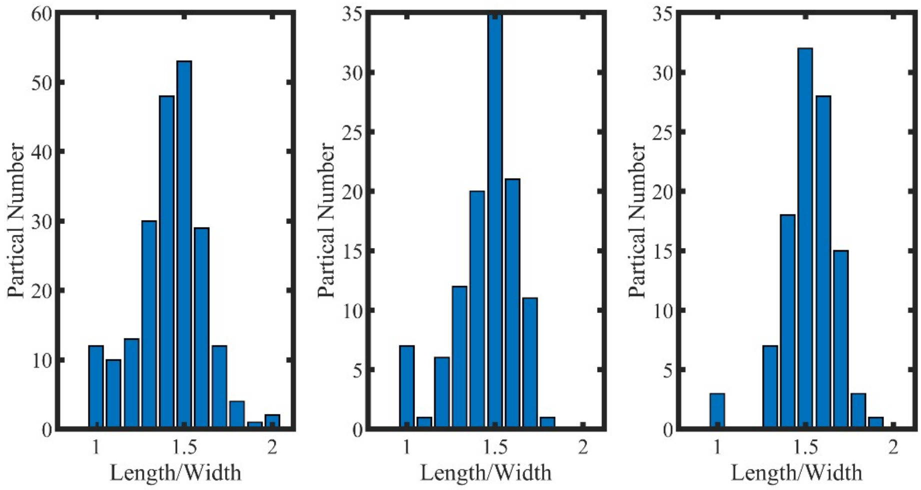

Figure S1. The length-diameter ratio histograms of three different samples. (1,5 and 8)

No. of NRs	1	2	3	4	5	6	7	8	9	10	11	12
Length	85.7	86.2	69.4	80.5	92.3	86.0	111.4	111.7	104.9	110.5	124.5	110.9
Diameter	60.2	59.3	46.4	50.5	57.5	52.9	67.4	67.0	61.7	65.2	72.0	54.6
Aspect Ratio	1.43	1.45	1.51	1.60	1.61	1.63	1.66	1.69	1.70	1.72	1.74	2.05

Table S1. The average lengths, diameters and the aspect ratios of the twelve samples.

S2. We calculated the extinction cross sections and the CD cross sections in ellipsoid coordinates (ξ,η,ζ). The plexcitonic hybrid is treated as an ellipsoid and the half-axis length of the ellipsoid is a, b and c. $(a \ge b \ge c)$ The Laplace's equation of the hybrid is:

$$\nabla^2\varphi = w[(\eta-\zeta)R_\xi\frac{\partial}{\partial\xi}\left(R_\xi\frac{\partial\varphi}{\partial\xi}\right) + (\zeta-\xi)R_\eta\frac{\partial}{\partial\eta}\left(R_\eta\frac{\partial\varphi}{\partial\eta}\right) + (\xi-\eta)R_\zeta\frac{\partial}{\partial\zeta}\left(R_\zeta\frac{\partial\varphi}{\partial\zeta}\right)] \tag{S2-1}$$

where, $w = \frac{4}{(\xi-\eta)(\eta-\zeta)(\zeta-\xi)}$ and $R_\mu = \sqrt{(\mu+a^2)(\mu+b^2)(\mu+c^2)},(\mu=\xi,\eta,\zeta)$. By solving Laplace's equation, the electric and magnetic polarizabilities under left/right circularly polarized incident light are given as:

$$\alpha^{L(R)}_u = \frac{4\pi abc}{3}\frac{(\varepsilon_m-\varepsilon_j) \pm \sqrt{\varepsilon_j}\kappa + (1-V_u)\kappa^2}{\varepsilon_m V_u + (1-V_u)\varepsilon_j - (1-V_u)^2\kappa^2}$$

$$\beta_u^{L(R)} = \frac{4\pi abc}{3} \frac{(1-V_u)\kappa^2 \pm \varepsilon_m \varepsilon_j^{-1/2}\kappa}{\varepsilon_m V_u + (1-V_u)\varepsilon_j - (1-V_u)^2\kappa^2}$$

(S2-2)

$$V_u = \frac{abc}{2}\int_0^\infty \frac{ds}{\sqrt{(s+a^2)(s+b^2)(s+c^2)(u^2+s)}}, u = a,b,c$$

(S2-3)

and the extinction cross section and the CD cross section of different axes under left/right circularly polarized incident light are:

$$EX_u^{L(R)} = \frac{4\pi abc}{3} KIm\left[\frac{(\varepsilon_m - \varepsilon_j) \pm \sqrt{\varepsilon_j}\kappa \pm \varepsilon_m \varepsilon_j^{-1/2}\kappa + 2(1-V_u)\kappa^2}{\varepsilon_m V_u + (1-V_u)\varepsilon_j - (1-V_u)^2\kappa^2}\right]$$

$$CD_u = \frac{8\pi abc}{3} KIm\left[\frac{\sqrt{\varepsilon_j}\kappa + \varepsilon_m \varepsilon_j^{-1/2}\kappa}{\varepsilon_m V_u + (1-V_u)\varepsilon_j - (1-V_u)^2\kappa^2}\right]$$

(S2-4)

and for chiral J-aggregates, $\kappa \ll \varepsilon_j$, the above equation can be simplified as:

$$EX_u^L \approx EX_u^R = \frac{4\pi abc}{3} KIm\left[\frac{\varepsilon_m - \varepsilon_j}{\varepsilon_m V_u + (1-V_u)\varepsilon_j}\right]$$

$$CD_u \approx \frac{8\pi abc}{3} KIm\left[\frac{\kappa(\varepsilon_m + \varepsilon_j)}{\sqrt{\varepsilon_j}(\varepsilon_m V_u + (1-V_u)\varepsilon_j)}\right]$$

(S2-5)

The theoretical calculations can also be found in our previous work. [1]

S3. Measured extinctions and calculated extinctions of Au NRs with different sizes are shown in Fig.S2. When we calculated the extinctions of Au NRs, the permittivity of the metal was modified to fit the spectral broadening in experimental results because of the size distributions of Au NRs shown in Fig.S1.

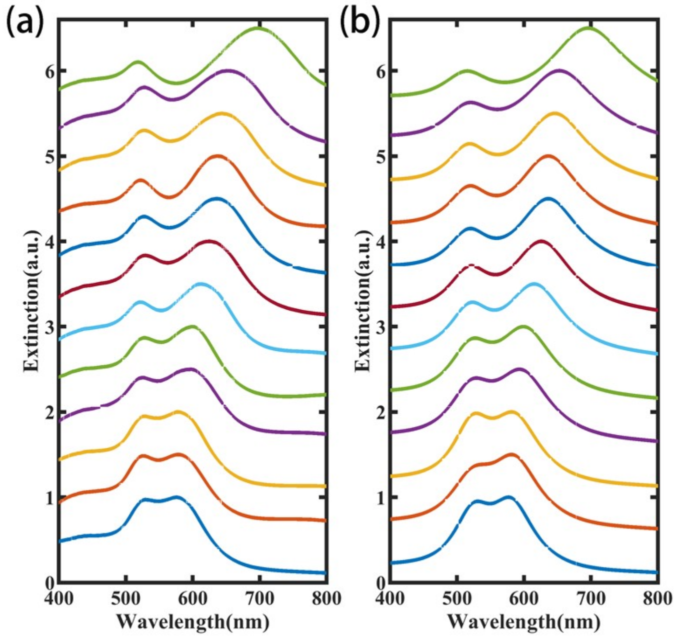

Figure S2. (a)Measured extinctions of Au NRs with different sizes. (b)Calculated extinctions of Au NRs with different sizes.

S4. Calculated extinctions and CD spectra of Au NRs@TDBC with different sizes are shown in Fig.S3(a,b). Peak positions of calculated extinctions and CD spectra of Au NRs@TDBC with different sizes are shown in Fig.S3(c).

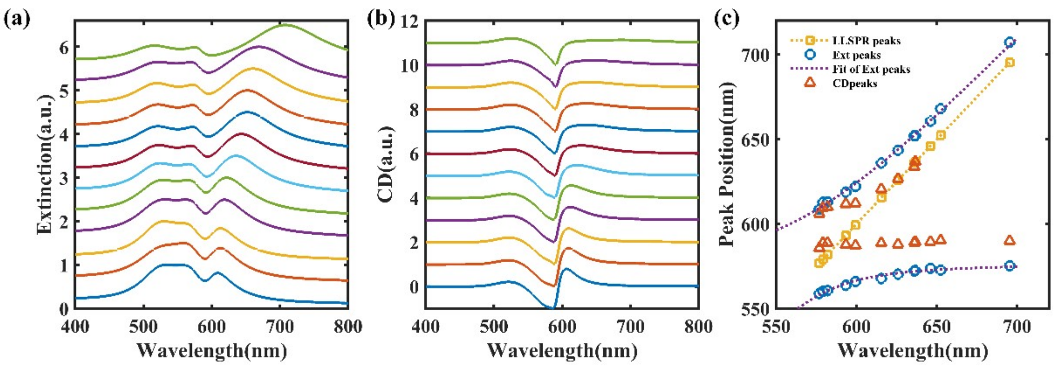

Figure S3. (a)Calculated extinctions of Au NRs@TDBC with different sizes. (b)Calculated CD spectra of Au NRs@TDBC with different sizes. (c)Peak positions of calculated extinctions and CD spectra of Au NRs@TDBC with different sizes.

Reference

1. F. Wu, J. Guo, Y. Huang, K. Liang, L. Jin, J. Li, X. Deng, R. Jiao,Y. Liu, J. Zhang, W. Zhang and L. Yu, ACS Nano, 2021, 15,2292–2300.