Helical nanoparticle-induced enantiospecific adsorption of N3 dyes

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It is of fundamental demand for heterogeneous asymmetric catalysis on generating intrinsically chiral metal catalysts without modification of chiral ligands on which molecular substrates can be enantiospecifically adsorbed, which is lack of investigation. Herein, we demonstrate that the anchoring of N3 dyes on plasmonic helical nanoparticles (PhNPs) made of silver through the formation of NCS–Ag contacts leads to enantiospecific adsorption of N3 dyes. The enantiospecific configuration of the immobilized N3 dyes is primarily determined by the helical handedness, and the maximization of the adsorption enantiospecificity occurs at a nominal helical pitch of ~15 nm, probably ascribed to the formation of supramolecular chiral complexes and/or the helical handedness-induced break of mirror symmetry of adsorption configuration. This study may pave the way for developing of PhNPs to function as intrinsically chiral catalysts and devising an alternative method to operate heterogeneous asymmetric catalysis with high enantioselectivity, which is practically desired for the manufacture of prominent single-enantiomer chemicals.

Homochirality, a general phenomenon in nature where chiral biomolecules preferentially exist in a stereoisomeric configuration over its mirror counterpart, leads to the primary demand of obtaining optically pure chemicals such as pharmaceuticals, agrochemicals, flavors and fragrances. Asymmetric catalysis fundamentally stems from enantiospecific adsorption of molecular substrates on chiral catalysts, which can be made of naturally chiral solids (such as quartz), chiral kinks at high Miller index metallic surfaces, and achiral metallic surfaces modified with chiral ligands. In terms of the last catalysts, it has been proposed that enantioselectivity can be ascribed to direct modifier–substrate interactions on the catalyst surfaces and enantiospecific adsorption of molecular substrates at the chiral empty sites of achiral catalytic surfaces that are covered with supramolecular chiral assemblies and at chiral ligand-induced restructuring sites of metallic single-crystal surfaces.

Intrinsically chiral metal catalysts without chiral ligands are highly demanded. The existing candidate is the chiral kinks created by cutting metal single crystals, but their catalytic application is severely prohibited by low population and limited stability of ideal chiral kink sites with asymmetrically catalytic activity. Recently, metals can be chirally sculptured in the helix with a helical pitch that is not shorter than 20 nm. Compared to the molecular scale, the characteristic P appears to be too large to make molecular substrates effectively perceive the helical chirality. Hence, metallic micro/nano-helices do not seem suitable to effectively function as intrinsically chiral catalysts. Currently, we reported the employment of glancing angle deposition (GLAD) with fast substrate rotation to reliably generate plasmonic helical nanoparticles (PhNPs) with a sub-10 nm nominal pitch, which was comparable to the molecular scale. The sub-10 nm-pitch PhNPs can promisingly function as intrinsically chiral catalysts with a prerequisite of the enantiospecific adsorption of molecular substrates on PhNPs; however, this lacks proper investigation.

In this study, we demonstrate the enantiospecific adsorption of cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) (i.e., N3 dyes, inset in Fig. 1a) on silver PhNPs (i.e., AgPhNPs). Their enantiospecific adsorption configuration have been widely applied, heterogeneous chiral catalysts tend to offer practically superior features, including catalysis stability, process scalability, as well as ease of catalyst separation and regeneration, for chemical manufacture.

Heterogeneous asymmetric catalysis has been overwhelmingly employed to enantioselectively produce single-enantiomer chemicals. Although homogeneous asymmetric catalysts made from transition metals coordinated to chiral ligands...
CD

Enantiospecific adsorption of N3 dyes on AgPhNPs. N3 dyes are (a) dissolved in ethanol at a concentration of 1.0 mmol L⁻¹, and adsorbed on (b) AgPhNPs (with a nominal helical pitch (P) of ~4.5 nm) and (c) achiral AgNPs. UV-Visible spectra of (I) CD, (a-II) absorbance (i.e., A), (b-II and c-II) extinction (i.e., Ext), and (III) anisotropic g-factor. (a-I) CD spectra were monitored as a function of time: 0 min (black), 5 min (orange), 10 min (yellow), 15 min (green), 20 min (navy), 25 min (violet), and 30 min (red). (b) LH-AgPhNPs (red lines), RH-AgPhNPs (blue lines), pristine AgPhNPs (dotted lines), and N3-grafted AgPhNPs (solid lines). The anchoring of N3 dyes causes the LSPR transverse-mode (T-mode) of the AgPhNPs to redshift (represented by the black arrow in (b-II)), and makes the transverse/longitudinal chiroptical modes of the AgPhNPs simultaneously have a red shift (represented by red and blue arrows in (b-III)). (c) Pristine (black lines) and N3-grafted (green lines) achiral AgNPs. Insets: (a) Molecular structure of N3 dye; SEM cross-sectional images of (b-I) LH-AgPhNPs (with red dotted border) and RH-AgPhNPs (with blue dotted border), and (c-I) achiral AgNPs. UV-Visible spectra of (I) CD, (a-II) absorbance (i.e., A), (b-II and c-II) extinction (i.e., Ext), and (III) anisotropic g-factor (Fig. 1(b-III) and Fig. S4-III, ESI†). Substrate rotation rate was controlled to sculpt the LSPR transverse mode (T-mode) of the AgPhNPs at the wavelength of 320 nm and longitudinal mode (L-mode) in the broad visible region (dotted spectra, Fig. 1(b-II), ~10 nm (insets in Fig. S4a-I, ESI†), ~15 nm (insets in Fig. S4b-I, ESI†), and ~32 nm (insets in Fig. S4c-I, ESI†) (refer to ESI-S1,† Experimental methods). The deposited AgPhNPs are polycrystalline and appear to be achiral NPs having undifferentiable nanostructures at different nominal P (Fig. S1, ESI†) due to P < d (wire diameter of nanohelices).19 The AgPhNPs with diverse P generally exhibit the transverse mode (T-mode) of local surface plasmon resonance (LSPR) at the wavelength of ~370 nm and longitudinal mode (L-mode) in the broad visible region (dotted spectra, Fig. 1(b-II) and Fig. S4-II, ESI†).19 Resonantly, the AgPhNPs exhibit bisignate T-modes and broad monosignate L-mode of optical activity characterized by CD spectroscopy, and the CD spectra appear to flip around the zero-CD axis upon switching the helical handedness (dotted spectra, Fig. 1(b-I) and Fig. S4-I, ESI†). Optical activity of individual AgPhNPs can be evaluated by calculating the anisotropic g-factor (Fig. 1(b-III) and Fig. S4-III, ESI†) given by

\[ g = \frac{CD}{16500 \text{Ext}} \]  

where CD is the ellipticity (units: millidegree, or mdeg), and Ext is the extinction. Achiral AgNPs, deposited by GLAD without is substantially determined by their helical handedness. The enantiospecific adsorption of N3 dyes as a function of P has been monitored by circular dichroism (CD), which is widely used to characterize the optical activity of chiral molecules. Here are the reasons to select AgPhNPs and N3 dyes in this study. On the one hand, as an important catalyst, silver is cheaper than other noble metals (such as platinum and gold), and chiroptical activity of AgPhNPs has been systematically studied as a function of P.19 On the other hand, N3 dyes can be covalently immobilized on Ag via spontaneously creating NCS–Ag contacts. They exhibit broad-band absorption in the UV-visible region (Fig. 1(a-II)), resulting in high possibility to monitor the absorption-resonant CD signals of the enantiospecifically grafted N3 dyes that don’t spectrally overlap with those of AgPhNPs.

N3 dyes dispersed in ethanol mainly absorb light roughly centered at a wavelength of 320 nm, 400 nm and 540 nm (Fig. 1(a-II) and Fig. S3-II, ESI†), assigned to the bipyridine (bpy)-centered π–π* transition and two metal-to-ligand charge transfer (MLCT) bands, respectively.21 Although the intramolecular stereo-arrangement of the two bpy ligands could impose chirality on N3 dyes, it was generally observed at a concentration range of 0.1–1.5 mmol L⁻¹ that dispersed N3 dyes exhibited optical activity fluctuating in CD magnitude and sign (Fig. 1(a-I) and Fig. S3-I, ESI†). It is indicated that N3 dyes exhibit unstable absolute configuration probably due to the thermally activated change of the intra-molecular two-bpy stereo-arrangement of dispersed N3 dyes.

GLAD with fast substrate rotation in clockwise/counterclockwise directions was employed to deposit AgPhNPs sculptured in the right/left-handed (RH/LH) forms that exhibited homogeneous helical nanostructures on the substrates over an area of 1.5 × 1.5 cm² (Table S1, ESI†). Substrate rotation rate was controlled to sculpt a P of ~4.5 nm (insets in Fig. 1(b-I)), ~10 nm (insets in Fig. S4a-I, ESI†), ~15 nm (insets in Fig. S4b-I, ESI†), and ~32 nm (insets in Fig. S4c-I, ESI†) (refer to ESI-S1,† Experimental methods). The deposited AgPhNPs are polycrystalline and appear to be achiral NPs having undifferentiable nanostructures at different nominal P (Fig. S1, ESI†) due to P < d (wire diameter of nanohelices). The AgPhNPs with diverse P generally exhibit the transverse mode (T-mode) of local surface plasmon resonance (LSPR) at the wavelength of ~370 nm and longitudinal mode (L-mode) in the broad visible region (dotted spectra, Fig. 1(b-II) and Fig. S4-II, ESI†). Resonantly, the AgPhNPs exhibit bisignate T-modes and broad monosignate L-mode of optical activity characterized by CD spectroscopy, and the CD spectra appear to flip around the zero-CD axis upon switching the helical handedness (dotted spectra, Fig. 1(b-I) and Fig. S4-I, ESI†). Optical activity of individual AgPhNPs can be evaluated by calculating the anisotropic g-factor (Fig. 1(b-III) and Fig. S4-III, ESI†) given by

\[ g = \frac{CD}{16500 \text{Ext}} \]
substrate rotation, exhibit LSPR centered at a wavelength of ~460 nm but not detectable optical activity (black spectra, Fig. 1(c-I–III)). It is illustrated that the AgPhNPs have optical response intrinsically stemming from the structural helicity induced by substrate rotation during GLAD.

N3 dyes were covalently grafted on the AgPhNPs through the spontaneous formation of NCS-Ag contacts (ESI-S2†). The AgPhNPs were spontaneously oxidized under ambient conditions and covered by amorphous silver oxides with a thickness of a few nm (Fig. S1, ESI†). Ambient aging of the AgPhNPs tends to deteriorate the surface grafting of N3 dyes, such that the surface modification was operated on the freshly deposited AgPhNPs. The grafting of N3 dyes has a negligible effect on the optical response axis upon switching the helical surface and the grafted N3 enantiomers (Fig. S2, ESI†) owing to the T-mode of the N3-grafted AgPhNPs (centered at the wavelength of ~540 nm). The grafting of N3 dyes has a negligible effect on the optical response axis upon switching the helical surface and the grafted N3 enantiomers (Fig. S3, ESI†) owing to the T-mode of the N3-grafted AgPhNPs (centered at the wavelength of ~540 nm). The grafting of N3 dyes has a negligible effect on the optical response axis upon switching the helical surface and the grafted N3 enantiomers (Fig. S4, ESI†) owing to the T-mode of the N3-grafted AgPhNPs (centered at the wavelength of ~540 nm).

Quantitative evaluation of the enantiospecific adsorption of N3 dyes on AgPhNPs, as a function of helical handedness and P (in a range of 4–35 nm). (a) Visible spectra of anisotropic g-factor of the N3-anchored LH-AgPhNPs (dotted lines) and RH-AgPhNPs (solid lines), as a function of P of ~4.5 nm (orange lines), ~10 nm (olive lines), ~15 nm (blue lines), and ~32 nm (magenta lines). It is partially shown the monosignate spectra in the visible region for clarity, and the full UV-visible spectra are shown in Fig. 1b-III and Fig. S4-III (ESI†). (a–c) White and blue backgrounds are used to highlight the T-mode of the N3-grafted AgPhNPs and the MLCT mode (centered at the wavelength of ~520 nm) of the enantiospecifically adsorbed N3 dyes, respectively. The spectra shown in (a) are fitted by Gaussian function (Fig. S9, ESI†), to statistically evaluate (b) \( \lambda_{\text{max}} \) (peak position, marked in (a)) and (c) \( g_{\text{max}} \) (peak maximum amplitude, marked in (a)) of the two g-factor peaks in terms of algebraic average value and standard deviation, as a function of P (b and c) LH-AgPhNPs (red squares), RH-AgPhNPs (blue squares). (c) Plot of surface grafting density of N3 dyes (\( S_{N3} \)) anchored on the LH-AgPhNPs as a function of P (olive squares).
Due to the covalent grafting of N3 dyes on the AgPhNPs via the formation of NCS–Ag contacts, chiral footprints of the helical topography can be transferred to the supramolecular adsorbents,\textsuperscript{25} this leads to the enantiospecific adsorption of N3 dyes. It has been characterized by Fourier-transform infrared spectroscopy that the inter-carboxyl hydrogen bonds can hardly be created at $P > 10$ nm (ESI-S2 and Fig. S6a, ESI†); this illustrates that the inter-carboxyl hydrogen bonds don’t play a significant role in the formation of supramolecular chiral complexes. High-vacuum STM has been widely used to characterize the role in the formation of supramolecular chiral complexes. It has been characterized by Fourier-transform infrared spectroscopy that the inter-carboxyl hydrogen bonds can hardly be created at $P > 10$ nm (ESI-S2 and Fig. S6a, ESI†); this illustrates that the inter-carboxyl hydrogen bonds don’t play a significant role in the formation of supramolecular chiral complexes.

However, large surface curvature of the AgPhNPs will introduce a severe difficulty in obtaining stable STM images with atomic resolution. It is shown in this study that far-field CD spectroscopy can enable us to facilely characterize the enantiospecific adsorption of N3 dyes on non-flat helical surfaces.

In summary, although N3 dyes dispersed in ethanol exhibit unstable absolute configuration and optical activity, the anchoring of N3 dyes on the AgPhNPs through the formation of NCS–Ag contacts leads to the enantiospecific adsorption of N3 dyes. The enantiospecific configuration of the adsorbed N3 dyes is primarily determined by the helical handedness of the AgPhNPs, and the adsorption enantiospecificity tends to be maximum at the nominal helical pitch of $\sim 15$ nm. The enantiospecific adsorption may be ascribed to the formation of supramolecular chiral complexes and/or the helical handedness-induced break of mirror symmetry of adsorption configuration. This study may pave the way for developing PhNPs to function as intrinsically chiral catalysts. It would contribute to devising an alternative methodology to operate heterogeneous asymmetric catalysis with high enantioselectivity, and enriching the fundamental understanding of asymmetric catalysis. This method will enable us to not to use chiral ligands for triggering heterogeneous asymmetric catalysis, which will be practically desired to reduce environmental pollution in the manufacture of single-enantiomer pharmaceuticals, agrochemicals, flavors and fragrances.

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Conflicts of interest

The authors declare no competing financial interest.

References

Electronic Supplementary Information (ESI)

Helical Nanoparticle-Induced Enantiospecific Adsorption of N3 Dyes

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S1. Experimental Methods

**GLAD:** In a custom-built physical vapor deposition system (JunSun Tech Co. Ltd., Taiwan) with a high vacuum $(10^{-7}$-$10^{-6}$ Torr), Ag pellets (99.99%, Kurt J. Lesker) were evaporated at a rate of 0.3 nm/s monitored by a quartz crystal microbalance (QCM) with electron-beam accelerating voltage of 8.0 kV and emission current of 15 – 22 mA. At a deposition angle of 86° with respect to the substrate normal, Ag was deposited on sapphire (MTL Hong Kong) and Si wafer (Semiconductor Wafer, Inc.) over an area of $1.5 \times 1.5 \ cm^2$. During deposition, an ethanol cooling system was used to control substrate temperature at roughly -60 °C. Clockwise/counterclockwise substrate rotation led to producing RH/LH-AgPhNPs. Helical pitch ($P$, units: nm) of AgPhNPs was engineered according to

$$P = 360 \frac{R_d}{R_r} \quad (S1)$$

where $R_d$ is the deposition rate at the substrate surface calibrated as 0.045 nm/s, and $R_r$ (units: degree per second, or °/s) is the substrate rotation rate. To produce AgPhNPs with a nominal $P$ in a range of 4.5 – 35 nm, $R_r$ was controlled to decrease from 3.6 to 0.5 °/s. $P$ was experimentally evaluated by

$$P = \frac{H}{n} \quad (S2)$$

where $H$ is the helix height controlled to be roughly 100 nm, and $n$ is the number of $P$ equal to that of circles a substrate was rotated in. The structural parameters of LH/RH-AgPhNPs are summarized in Table S1, illustrating that the deposited helical nanostructures are homogeneous on the substrates over an area of $1.5 \times 1.5 \ cm^2$. At the deposition angle of 86° and substrate temperature of roughly -60 °C, Ag were deposited on a non-rotating substrate with the nominal thickness of 30 nm monitored by QCM, followed by rotating the substrate in 180° and the subsequent non-substrate-rotation deposition of Ag with the nominal thickness of 30 nm. Such the deposition led to generating achiral AgNPs with no detectable optical activity.
Table S1. Summary of helical structures of AgPhNPs, including helical handedness (left-handed: LH; right-handed: RH), diameter ($D$), height ($H$), number of pitch ($n$), and nominal helical pitch ($P = H/n$). For each sample, multiple (not less than 10) measurements were operated to evaluate algebraic average value ± standard deviation. The ratios of standard deviation and average value are added in parentheses to the measured values of $D$, $H$ and $P$. The evaluated ratios are generally smaller than 15%, indicating that the deposited helical nanostructures are homogeneous on the substrates over an area of $1.5 \times 1.5 \text{ cm}^2$.

<table>
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<tr>
<th>Helical handedness</th>
<th>LH (nm)</th>
<th>RH (nm)</th>
<th>LH (nm)</th>
<th>RH (nm)</th>
<th>LH (nm)</th>
<th>RH (nm)</th>
<th>LH (nm)</th>
<th>RH (nm)</th>
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<td></td>
<td>$65 \pm 7$ (11%)</td>
<td>$67 \pm 9$ (13%)</td>
<td>$68 \pm 8$ (12%)</td>
<td>$67 \pm 8$ (12%)</td>
<td>$64 \pm 6$ (9%)</td>
<td>$64 \pm 6$ (9%)</td>
<td>$60 \pm 6$ (10%)</td>
<td>$61 \pm 7$ (11%)</td>
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<tr>
<td>$H$ (nm)</td>
<td>$85 \pm 5$ (6%)</td>
<td>$83 \pm 6$ (7%)</td>
<td>$87 \pm 7$ (8%)</td>
<td>$89 \pm 6$ (7%)</td>
<td>$94 \pm 6$ (6%)</td>
<td>$92 \pm 5$ (5%)</td>
<td>$103 \pm 8$ (8%)</td>
<td>$99 \pm 7$ (7%)</td>
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<td>18.5</td>
<td>8.8</td>
<td>8.8</td>
<td>6.1</td>
<td>6.1</td>
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<td>$P$ (nm)</td>
<td>$4.6 \pm 0.3$ (7%)</td>
<td>$4.5 \pm 0.3$ (7%)</td>
<td>$9.9 \pm 0.8$ (8%)</td>
<td>$10.1 \pm 0.7$ (7%)</td>
<td>$15.4 \pm 1.0$ (6%)</td>
<td>$15.1 \pm 0.8$ (5%)</td>
<td>$33.2 \pm 2.6$ (8%)</td>
<td>$31.9 \pm 2.3$ (7%)</td>
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Figure S1. High-resolution TEM images of (a) LH- and (b) RH-AgPhNPs, having a $P$ of (I) $\sim 4.5$ nm, (II) $\sim 10$ nm, (III) $\sim 15$ nm, and (IV) $\sim 32$ nm. Insets: low resolution TEM images; (b-I) XRD spectrum of the sample (b-I), illustrating that the deposited AgPhNPs have polycrystalline nanostructures; the regions highlighted by two dashed black lines represent the spontaneously formed amorphous silver oxides.
**Grafting of N3 dyes:** The AgPhNPs freshly deposited on sapphire were soaked in ethanol dissolved with 1 mmol/L N3 dyes for 12 hours, with no exposure to sunlight. Then the treated samples were sufficiently rinsed with ethanol and dried with N\textsubscript{2} gas, to remove N3 dyes physically adsorbed on the samples. To study the solvent effect on chiroptical activity of the AgPhNPs, the samples were immersed in ethanol for 12 hours without exposure to sunlight, followed by drying the samples with N\textsubscript{2} gas.

*Figure S2.* SEM images of AgPhNPs (having a \(P\) of \(\sim 4.5\) nm) without (a) and with (b) the surface grafting of N3 dyes.

**Measurement of CD and UV-visible absorption/extinction spectroscopies:** Bio-Logic CD (MOS 500) was used to monitor CD and UV-visible extinction spectra of the samples deposited on sapphire, under an incidence of circularly polarized light along the substrate normal. The measurement was ambiently operated. To eliminate linear birefringence, at 0.2 rpm a sample was rotated clockwise in 270° to monitor a CD spectrum in the wavelength range of 200 – 800 nm. Four CD spectra were subsequently recorded and algebraically averaged to obtain a CD spectrum of the sample. Quartz cuvette (Guanglianggaoke, Jiangsu), with an optic path length of 1 mm and volume of \(\sim 0.45\) mL, was used to monitor UV-visible absorption spectra of ethanol dissolved with N3 dyes at diverse concentrations. To study the CD stability, CD signals of a given sample were repeatedly monitored as a function of time in a range of 0 – 30 min, at an interval of 5 min. To further investigate the CD fluctuation of the N3 dye solutions, multiple solutions at a given N3 concentration were monitored by CD spectroscopy, as shown in *Figure S3.*
Figure S3. UV-visible spectra of (I) CD and (II) absorbance (A) of ethanol dissolved with N3 dyes at a concentration of (a) 1.5 mmol/L, (b) 1.0 mmol/L, (c) 0.5 mmol/L, and (d) 0.1 mmol/L. (I) Diverse colors represent CD spectra of multiple solutions at a given concentration. Blue background highlights the MLCT band of N3 dyes centered at ~540 nm.

Figure S4. Enantiospecific adsorption of N3 dyes on AgPhNPs, as a function of P: (a) ~10 nm, (b) ~15 nm, and (c) ~32 nm. UV-visible spectra of (I) CD, (II) extinction (i.e., Ext), and (III) anisotropic g-factor: LH-AgPhNPs (red lines), RH-AgPhNPs (blue lines), pristine AgPhNPs (dotted lines), and N3-grafted AgPhNPs (solid lines). The anchoring of N3 dyes causes the LSPR T-mode of the AgPhNPs to redshift (represented by the black arrow in II), and makes the transverse/longitudinal chiroptical modes of the AgPhNPs simultaneously have a red shift (represented by red and blue arrows in III). Insets: (I) SEM cross-sectional images of LH-AgPhNPs (with red dotted border) and RH-AgPhNPs (with blue dotted border), scale bar: 50 nm. (a-c) Blue background highlights the MLCT band of N3 dyes centered at ~540 nm.
**Figure S5.** CD spectra of N3 dyes anchored on LH-AgPhNPs (red spectra) and RH-AgPhNPs (blue spectra) with a $P$ of ~4.5 nm, monitored as a function of time: 0 (solid lines), 0.5 (dashed lines) and 1 hour (dash-dot lines). Variation of the CD spectra as a function of monitoring time is negligible, illustrating that the grafted N3 dyes exhibit stable optical activity.

**Material characterization:** The as-deposited substrates were mechanically split, leaving the freshly exposed surfaces for SEM characterization (Oxford, LEO 1530). Without any post-GLAD treatment, the samples deposited on sapphire were characterized by FTIR spectroscopy (PerkinElmer Spectrum Two), X-ray photoelectron spectroscopy (XPS, Sengyang SKL-12, non-monochromatic Mg Kα radiation of 1253.6 eV, with a current of 15 mA, voltage of 10 kV, takeoff angle of 90° and vacuum of $\sim 2\times 10^{-9}$ mbar), and X-ray diffraction (XRD, Bruker, nonmonochromated Cu Kα x-ray with wavelength of 0.15418 nm, Advance D8 multipurpose x-ray diffractometer).
S2. Characterization of the grafting of N3 Dyes on AgPhNPs

N3 dyes were covalently grafted on the AgPhNPs, which can be verified by diverse spectroscopic techniques. First, characterized by UV-visible extinction spectroscopy, it was shown that the N3 anchoring causes the AgPhNPs to exhibit the characteristic peaks of N3 dyes located at the wavelength of ~320 nm, ~400 nm (shoulder peak) and ~540 nm (solid spectra, Figure 1b-II and Figures S4-II). Second, the surface immobilization with N3 dyes was verified by Fourier-transform infrared spectroscopy (FTIR, Figure S6a). Pristine AgPhNPs nearly show no detectable FTIR signal in a wavenumber range of 2200 – 1200 cm\(^{-1}\), and exhibit characteristic molecular vibrations of N3 dyes after the molecular grafting. The N3 anchoring causes the C=\(N\) stretching to markedly shift from 2117 cm\(^{-1}\) of the pristine N3 powders to 2131 cm\(^{-1}\), indicating the formation of NCS-Ag contacts. The bpy-associated vibrations at 1640 – 1450 cm\(^{-1}\) appear to have a negligible shift after the N3 grafting, indicating that the bpy ligands do not directly interact with the helical surfaces. For the carboxyl groups, the N3 grafting causes the C=O and C-O stretching to have a slight shift, and the shift becomes slightly more marked when \(P\) is reduced from ~10 nm to ~4.5 nm. The N3 grafting-induced shift is probably attributed to the formation of inter-carboxyl hydrogen bonds, which is favored when N3 dyes are attached to the sub-10-nm-pitch helical surfaces, owing to the dimensional comparability of the sub-10-nm pitch to N3 dyes. Third, XPS shows that compared to the pristine AgPhNPs (Figure S7), the peaks of N1s, Ru3d and S2p emerge after the N3 grafting (Figure S6d). Compared to the XPS signals of N3 powders (Figure S6b), the N3 anchoring makes the Ru3d (3/2 and 5/2) peaks (at binding energy (BE) of 284.8 and 280.5 eV, respectively) and the bpy-associated peaks of N1S-C (at 399.7 eV), N1s-Ru (at 397.9 eV) and C1S (at 284.9 eV) have a negligible shift; but evidently causes the NCS-associated peaks of N1s=C=S to have an upward shift of 0.64 eV, N=C1s=S to have a downward shift of 1.06 eV, S2p (1/2) to have an upward shift of 1.92 eV, and S2p (3/2) to have an upward shift of 1.47 eV (Figure S6b versus S6d), having a well agreement with the previous report.\(^{S1}\) Furthermore, the N3 grafting causes Ag3d (3/2 and 5/2) to exhibit emerging peaks at 375.1 and 369.1 eV, respectively (Figure S6c versus S6d), assigned to NCS-Ag3d. It is illuminated that N3 dyes are grafted on AgPhNPs through forming the NCS-Ag contacts, consistent with the FTIR results.
Figure S6. Characterization of the anchoring of N3 dyes on LH-AgPhNPs by (a) FTIR and (b, c) XPS. (a) N3 dye powders (green solid line); pristine LH-AgPhNPs with a P of ~4.5 nm (red dotted line); and N3-grafted LH-AgPhNPs with a P of ~4.5 nm (red solid line), ~10 nm (orange solid line), ~15 nm (violet solid line) and ~32 nm (blue solid line). (b) N3 dye powders, (c) pristine and (d) the N3-grafted LH-AgPhNPs with a P of ~4.5 nm, in terms of N1s, C1s, Ru3d, S2p, and Ag3d.

Figure S7. XPS characterization of pristine LH-AgPhNPs with a P of ~4.5 nm: (a) N1s, (b) C1s, and (c) S2p.
Figure S8. Solvent (ethanol) effect on the UV-visible spectra of (I) CD, (II) extinction (i.e., Ext), and (III) anisotropic $g$-factor, of LH-AgPhNPs (red lines) and RH-AgPhNPs (blue lines) with a $P$ of (a) ~4.5 nm, (b) ~10 nm, (c) ~15 nm and (d) ~32 nm. Pristine AgPhNPs (dotted lines), and the AgPhNPs immersed in ethanol (solid lines).
S3. Quantitative evaluation of the enantiospecific adsorption of N3 dyes

Optical activity of the LSPR T-mode of the AgPhNPs (centered at the wavelength of ~450 nm) partially overlaps with that of the MLCT mode of the grafted N3 dyes (centered at the wavelength of ~520 nm), so that Gaussian fitting was operated to quantitatively evaluate the anisotropic \( g \)-factor of the enantiospecific MLCT mode (marked by blue background, Figure S9), i.e., the adsorption enantiospecificity. In Figures S9b-d, the peaks marked by pink background, assigned to the L-mode of the AgPhNPs, were not analyzed.

Figure S9. Gaussian fitting (black and green lines) of the visible spectra of anisotropic \( g \)-factor of the N3-grafted LH-AgPhNPs (red lines) and RH-AgPhNPs (blue lines), with a \( P \) of (a) ~4.5 nm, (b) ~10 nm, (c) ~15 nm and (d) ~32 nm. (b-d) The enantiospecific MLCT mode of the grafted N3 dyes is highlighted by blue background, and L-mode of the AgPhNPs was highlighted by pink background.
Figure S10. Plot of $g_{\text{max}}$ of the plasmonic T-mode of the N3-grafted LH-AgPhNPs (red squares) and RH-AgPhNPs (blue squares) as a function of $P$, in terms of algebraic average value and standard deviation.

**S4. Evaluation of surface grafting density of N3 dyes adsorbed on LH-AgPhNPs**

Surface grafting density of N3 dyes adsorbed on the AgPhNPs ($S_{N3}$) can be evaluated by calculating the number of adsorbed N3 dyes ($N_{N3,\text{ad}}$) and surface area of the AgPhNPs ($A_{NP}$) where N3 dyes are grafted, given by

$$S_{N3} = \frac{N_{N3,\text{ad}}}{A_{NP}} \quad (S3)$$

UV-visible absorption spectrum of ethanol dissolved with N3 dyes at an initial concentration ($C_0$) of 1 mmol/L was monitored before and after the grafting of N3 dyes on LH-AgPhNPs with a geometric area of 1.5×1.5 cm$^2$. After the molecular grafting, the grafted sample was removed and the residual solution was monitored with UV-visible absorption spectroscopy, as shown in Figure S11.

Figure S11. UV-visible absorption spectra of the initial (black line) and residual N3 solution after the N3 grafting on LH-AgPhNPs with a $P$ of ~4.5 nm (orange line), ~10 nm (olive line), ~15 nm (blue line) and ~32 nm (magenta line).
According to the Beer-Lambert Law, the N3 concentration \((C')\) of the residual solution can be calculated by

\[
\frac{C'}{C_0} = \frac{A'}{A_0} \quad (S4)
\]

where \(A_0\) and \(A'\) are the absorbance of the initial and residual N3 solution at the maximum absorption wavelength of \(\sim 540\) nm, respectively (inset in Figure S11). \(N_{N3,ad}\) can be calculated by

\[
N_{N3, ad} = (C_0 - C)V_NA \quad (S5)
\]

where \(N_A\) is the Avogadro’s constant, and \(V\) is the volume of the N3 solution in which the samples were soaked, which is 1 ml in this work. It was found that the AgPhNPs appear to have a cylindrical profile (insets in Figures 1b-I and S4-I) with a height of \(H\) and diameter of \(D\). \(A_{NP}\) can be calculated by

\[
A_{NP} = N_{NP} \left[\pi DH + \frac{\pi (D/2)^2}{2}\right] \quad (S6)
\]

where \(N_{NP}\) is the number of AgPhNPs deposited on a sapphire over an area of \(1.5\times1.5\) cm\(^2\). The measurement of diverse parameters and evaluation of \(S_{N3}\) on the LH-AgPhNPs are summarized in Table S2.

**Table S2.** Evaluation of surface grafting density of N3 dyes \((S_{N3})\) adsorbed on LH-AgPhNPs as a function of \(P\).

<table>
<thead>
<tr>
<th>Helical pitch (nm) of LH-AgPhNPs</th>
<th>(A' \times 539) nm</th>
<th>(C') (mmol/L)</th>
<th>(N_{N3, ad})</th>
<th>(H) (nm)</th>
<th>(D) (nm)</th>
<th>(N_{NP})</th>
<th>(A_{NP}) (m(^2))</th>
<th>(S_{N3}) (m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>~4.5</td>
<td>1.018</td>
<td>0.885</td>
<td>7.15×10(^{16})</td>
<td>85 ± 5</td>
<td>65 ± 7</td>
<td>3.38×10(^{10})</td>
<td>6.98×10(^{-4})</td>
<td>1.02×10(^{18})</td>
</tr>
<tr>
<td>~10</td>
<td>0.996</td>
<td>0.866</td>
<td>8.33×10(^{16})</td>
<td>87 ± 7</td>
<td>68 ± 8</td>
<td>2.64×10(^{10})</td>
<td>5.87×10(^{-4})</td>
<td>1.42×10(^{18})</td>
</tr>
<tr>
<td>~15</td>
<td>0.977</td>
<td>0.850</td>
<td>9.33×10(^{16})</td>
<td>94 ± 6</td>
<td>64 ± 6</td>
<td>2.95×10(^{10})</td>
<td>6.41×10(^{-4})</td>
<td>1.46×10(^{18})</td>
</tr>
<tr>
<td>~32</td>
<td>1.031</td>
<td>0.900</td>
<td>6.22×10(^{16})</td>
<td>103 ± 8</td>
<td>60 ± 6</td>
<td>3.18×10(^{10})</td>
<td>7.07×10(^{-4})</td>
<td>0.88×10(^{18})</td>
</tr>
</tbody>
</table>
References