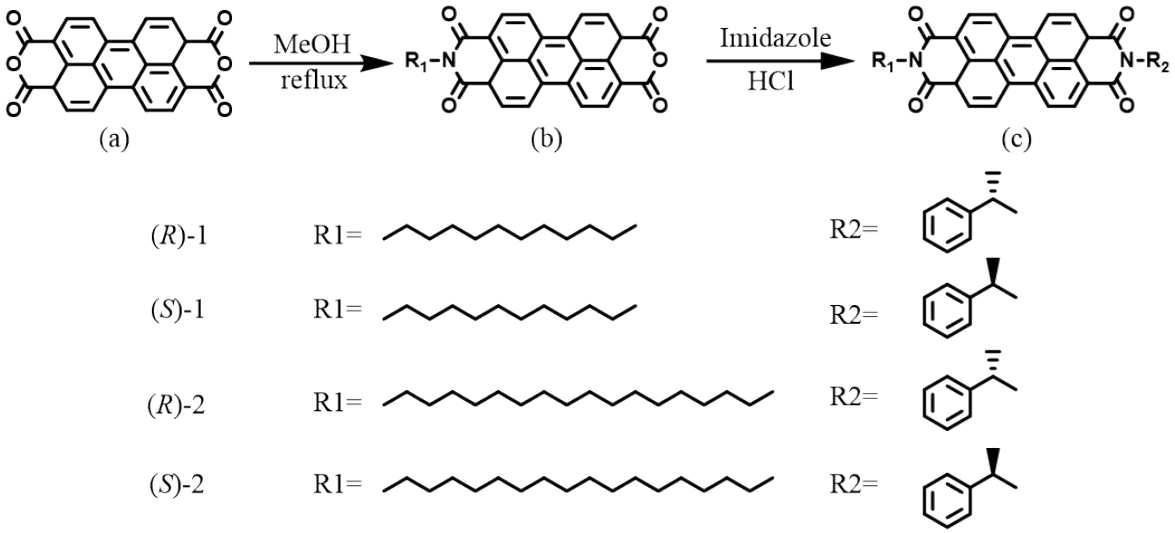
# Experimental section

## Materials

All chemicals were used as obtained without any further purification: perylene-3,4,9,10-tetracarboxylicacid dianhydride (PTCDA, Sigma-Aldrich, 97%), 1-Octad ecanamine (HEOWNS, 98%), 1-dodecylamine (TCI, 99.7%), *R*-(+)-1-Phenylethyl amine (MREDA, 99%), *S*-(-)-1-Phenylethylamine (Bidepharm, 97%), methanol ( Fuyu, 99%), hydrochloric acid (Sinophram Chemical, AR), Imidazole (Macklin, 99%), chloroform (Sinophram Chemical, AR), Petroleum ether (Sinophram Che mical, AR), Hexane (Fuyu, AR), ethanol (Sinophram Chemical, AR), *R*-(+)-Lim onene (Alfa, 96%), *S*-(-)-Limonene (TCI, 95%), *R*-(-)-Epichlorohydrin (HEOWN S, 97%), α-Pinene(Aladdin, 95%), *L*-(+)-Camphor (Macklin, AR), tetrachloroaur ate trihydrate (Adamas-beta, 99.9%+), Borane tert-butylamine (TBAB, Sigma-Al drich, 98%), 1-dodecanethiol (DDT, Sigma-Aldrich, 99%), Oleylamine (Macklin, 80%-90%), Methylcyclohexane(Macklin, 99%), hydrochloric acid (Sinophram Ch emical, AR), dodecyl trimethyl ammonium bromide (DTAB, TCI, 99%).

Synthesis steps of (*R*)/(*S*)-1 and (*R*)/(*S*)-2.




**Scheme S1**. The synthesis of molecules (*R*)/(*S*)-1 and (*R*)/(*S*)-2.

**Synthesis of molecule (b).** Perylene-3,4,9,10-tetracarboxylic acid dianhydride (a, 200 mg) and 1-dodecylamine (1 g) or 1-Octadecanamine (1.5g) were dissolvedin methanol (30 mL) and stirred for refluxfor 7 hours in a nitrogen atmosphere.A

fter the reaction is completed, the mixture is cooled to room temperature andac idified with concentrated hydrochloric acid (20 mL). The reactants turn from or ange to red and stirred overnight. The solids were collected by filtration and washed with methanol and deionized water. Then the crude product was dried at 70 °C vacuum for 8 hours. The obtained crude product does not require fur ther purification for the next step of synthesis.

**Synthesis of molecule (C).** The mixture containing compound (b, 1eq), *R*-(+)-1 -Phenylethylamine (5eq) and imidazole (6g) were heated to 145 °C under nitro gen and stirred for 5 hours. The resulting mixture was dispersed in 50 mL me thanol, followed by addition of 30 mL concentrated HCl. After stirring overnig ht, the solids were collected by filtration and washed with methanol and deioni zed water. After vacuum drying, the crude products were purified by column c hromatography (silica, chloroform: petroleum ether = 4:1) to afford compound ( *R*)-1 (*S*)-1 and (*R*)/(*S*)-2 were synthesized and purified by the same method, an d thefinal product was characterized and confirmed by $^{1}$HNMR spectroscopy as below.

(*R*)-1: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J=7.9, 5.7Hz, 1H), 8.58 (d, J= 8.1Hz, 1H), 7.56 (t, J=7.9 Hz, 1H), 7.38 (t, J=7.6Hz, 1H), 6.60 (q, J=6.9Hz, 1 H), 4.40–4.05 (m, 1H), 2.06 (d, J=7.1 Hz, 1H), 1.86–1.69 (m, 1H), 1.48–1.22 (m, 5H), 0.89 (t, J=6.8Hz, 1H).

(*S*)-1: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J=10.8, 8.0 Hz, 1H), 8.62 (dd, J=8.2, 2.7 Hz, 1H),7.53 (t, J=6.0Hz, 1H), 7.35 (t, J=7.6Hz, 1H), 6.58 (q, J=7.0 Hz, 1H), 4.25 – 4.13 (m, 1H), 2.03 (d, J=7.1Hz, 1H), 1.76 (dt, J=15.0, 7.4Hz, 1H), 1.25 (s, 5H), 0.87 (t, J =6.8Hz, 1H).

(*R*)-2: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.67 (t, J=8.6Hz, 1H), 8.60 (dd, J=8.1, 1.9Hz, 1H), 7.54 (t, J=6.6Hz, 1H), 7.35 (t, J=7.6Hz, 1H), 6.57 (q, J=7.2Hz, 1 H), 4.68–3.91 (m, 1H), 2.03 (d, J=7.1Hz, 1H), 1.91–1.63 (m, 1H), 1.46–1.08 ( m, 8H), 0.87 (t, J=6.8Hz, 1H).

(*S*)-2: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, J=7.9, 5.3Hz, 1H), 8.56 (d, J= 8.1Hz, 1H), 7.55 (d, J=7.7Hz, 1H), 7.35 (t, J=7.6Hz, 1H), 6.57 (q, J=7.2Hz, 1

H), 4.32–4.05 (m, 1H), 2.04(d, J=7.1Hz, 1H), 1.79–1.70 (m, 1H), 1.25 (s, 10H), 0.86 (d, J=7.1Hz, 2H).

## Synthesis of Au NPs.

Synthesis of chloro (triphenylphosphine) gold. Tetrachlorohydrate trihydrate and triphenylphosphine were dissolved in ethanol respectively, and then the tripheny lphosphine ethanol solution was slowly added to the tetrachlorohydrate trihydrat e ethanol solution. After the reaction was completed, the product was filtered a nd washed with ethanol.

Synthesis of chloro (triphenylphosphine) gold. Add triphenylphosphine (124 mg) and toluene (25 mL) to a three necked flask, stir and heat to 100 ℃ under ni trogen atmosphere. Then put TBAB (200mg), toluene (3 mL) and 1-dodecyl al cohol (500 μL) in a 20 mL glass bottle for ultrasonic dissolution, add the prec ursor solution, and keep it at 100 ℃ for 5 minutes. When it is restored to ro om temperature, washing with ethanol and collecting by centrifugation at 8000 rpm for 2 minutes and the 5 nm Au nanoparticles redispersed in toluene. How ever, 10 nm Au nanoparticles were synthesized by the method of seed growth: a seed solution of toluene (2 mL), oleylamine (1 mL) and Au-5nm (0.5 mg) was prepared in a 20 mL glass. A solution containing HAuCl4•3H2O (22 mg), toluene (5 mL) and oleylamine (5 mL) was mixed at 90 °C for 5 hours. Then,e thanol (20 mL) was added to precipitate the Au NPs and collected by centrifu gation at 8000 rpm for 2 minutes and redispersed in hexane.

## Self-assembly of chiral PDI molecule by Emulsion confined meth od.

For a typical self-assembly experiment, 1 mL of (*R*)-1 or (*S*)-1 or (*R*)-2 or (*S*) -2 $CHCl_3$ solution (0.06 mg) was mixed with 2 mL of dodecyl trimethyl amm onium bromide aqueous solution (DTAB,10 mg/mL) to result in oil-in-water (O /W) emulsions after a vortex mixing (1000 rpm) for 1 min. Then the emulsion s were heated at 60 °C and kept at this temperature for 30 min to evaporate t heinner organic phase. After the suspension cooled to room temperature, the su

pernatant was removed by centrifugation. The resulting molecular assemblies was redispersed in deionized water.

**Assembly experiment method for (*R*),(*S*)-1/Limonene and (*R*),(*S*)-2/Limonene assemblies.** 940 μL of (*R*)-1 or (*S*)-1 or (*R*)-2 or (*S*)-2 $CHCl_3$ solution (0.06 mg) and 60 μL limonene were mixed with 2 mL of dodecyl trimethyl ammoni um bromide aqueous solution (DTAB, 10 mg/mL) to result in oil-in-water (O/ W) emulsions after a vortex mixing (1000 rpm) for 1 min. Then the emulsions were heated at 60 °C and kept at this temperature for 100 min to evaporate t he inner organic phase. After the suspension cooled to room temperature, the s upernatant was removed by centrifugation. The resulting molecular assemblies was redispersed in deionized water.

**Assembly experiment method for (*R*) -1/Pin assemblies.** 940 μL of (*R*)-1 or (*S*)-1 $CHCl_3$ solution (0.06 mg) and 60 μL Pinene (Pin) were mixed with 2 m L of dodecyl trimethyl ammonium bromideaqueous solution (DTAB, 10 mg/mL)t o result in oil-in-water (O/W) emulsions after a vortex mixing (1000 rpm) for 1 min. Then the emulsions were heated at 60 °C and kept at this temperature for 100 min to evaporate the inner organic phase. After the suspension cooled to room temperature the supernatant was removed by centrifugation. The resulti ng molecular assemblies was redispersed in deionized water.

**Assembly experiment method for (*R*)-1/Epichlorohydrin(ECH) assemblies.** 90 0 μL of (R)-1 $CHCl_3$ solution (0.06 mg) and 100 μL Epichlorohydrin were mi xed with 2 mL of dodecyl trimethyl ammonium bromide aqueous solution (DT AB, 10 mg/mL) to result in oil-in-water (O/W) emulsions after a vortex mixing (1000 rpm) for 1 min. Then the emulsions were heated at 60 °C and kept at t his temperature for 100 min to evaporate the inner organic phase. After the su spension cooled to room temperature, the supernatant was removed by centrifug ation. The resulting molecular assemblies was redispersed in deionized water.

**Assembly experiment method for (*R*)-1/Cam assemblies.** 900 μL of (*R*)-1 $CHCl_3$ solution (0.06 mg) and 100 μL Camphor (Cam, 20 mg/mL) were mixed with 2 mL of dodecyl trimethyl ammonium bromide aqueous solution (DTAB, 10 m

g/mL) to result in oil-in-water (O/W) emulsions after a vortex mixing (1000 rp m) for 1 min. Then the emulsions were heated at 60 °C and kept at thistemperatur e for 100 min to evaporate the inner organic phase. After the suspension coole d to room temperature, the supernatant was removed by centrifugation. The res ulting molecular assemblies was redispersed in deionized water.

**Assembly experiment method for (*R*)-1/MCH assemblies.** 900 μL of (*R*)-1 or (*S*)-1 $CHCl_3$ solution (0.06 mg) and 100 μL MCH were mixed with 2 mL of dodecyl trimethyl ammonium bromide aqueous solution (DTAB, 10 mg/mL) to result in oil-in-water (O/W) emulsions after a vortex mixing(1000 rpm) for 1 min. Then the emulsions were heated at 60 °C and kept at this temperature fo r 100min to evaporate the inner organic phase. After the suspension cooled to room temperature, the supernatant was removed by centrifugation. The resulting molecular assemblies was redispersed in deionized water.

**Co-assembly of chiral PDI molecules and Au NPs by Emulsion confined m ethod.**

Co-assembly is similarly with self-assembly. Before emulsification process, Au NPs and PDI molecules were dissolved in 1 mL of $CHCl_3$ with a mass ratio of Au NPs to (*R*)-1 (m Au/m PDI) ranging from 1 to 5. Subsequently, 2 mL of dodecyl trimethyl ammonium bromide aqueous solution (DTAB, 10 mg/mL) wa s added, and the resulting mixture was emulsified under a vortex mixing (1000 rpm) for 1 min. The emulsions were then heated to 60 °C and kept at this te mperature for 30 min to evaporate the inner organic phase. After the suspensio n cooled to room temperature, the supernatant was removed by centrifugation. The resulting molecular assemblies was redispersed in deionized water.

## Structural characterizations.

1H NMR spectrum were recorded on a 400 MHz Bruker Avance spectrometer. UV-vis absorption spectra were recorded using a UV-1900 spectrophotometer ( Shimadzu). Fluorescence spectra were recorded using a FluoroMax-4 (Horiba). CD spectra were recorded using a Jasco 1500. TEM characterization was perfo

rmed on a Hitachi HT 7700 microscope operating at 100 kV. AFM characterizatio n was performed on a Bioscope Resolve Atomic Force Microscopy (Bruker).SE M characterization of nanoparticles and assemblies was performed on a Gemini SEM 300 (Zeiss).

## Result and discussion.

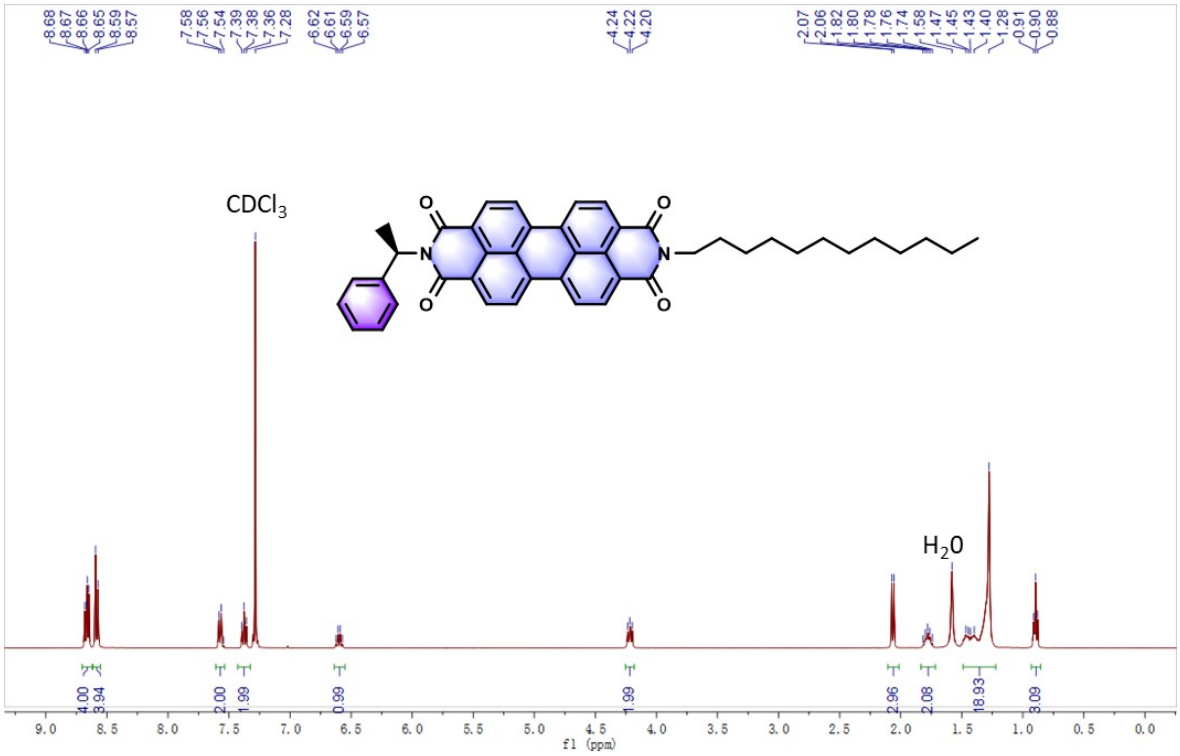



**Fig S1**.[1]H-NMR spectrum of (*R*)-1.

**Fig S2.** [1]H-NMR spectrum of (*S*)-1.

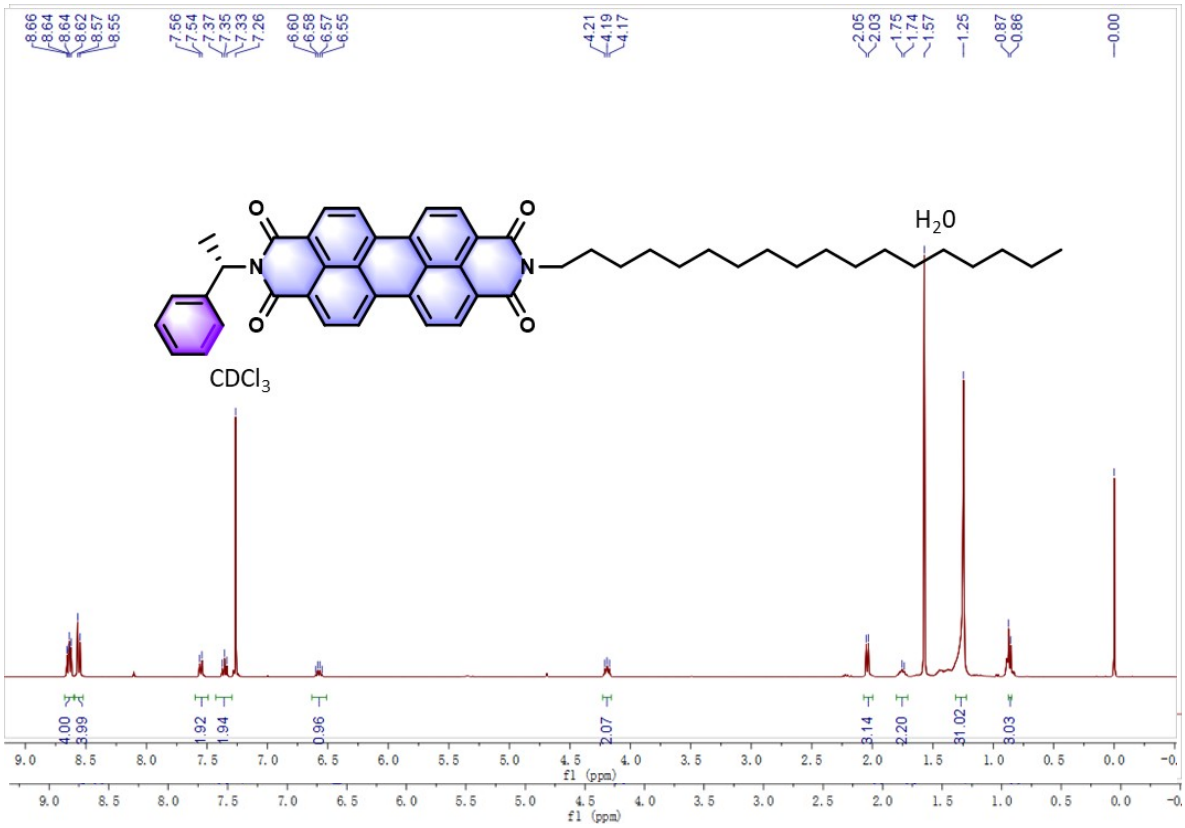



**Fig S3.**[1]H-NMR spectrum of (*R*)-2.

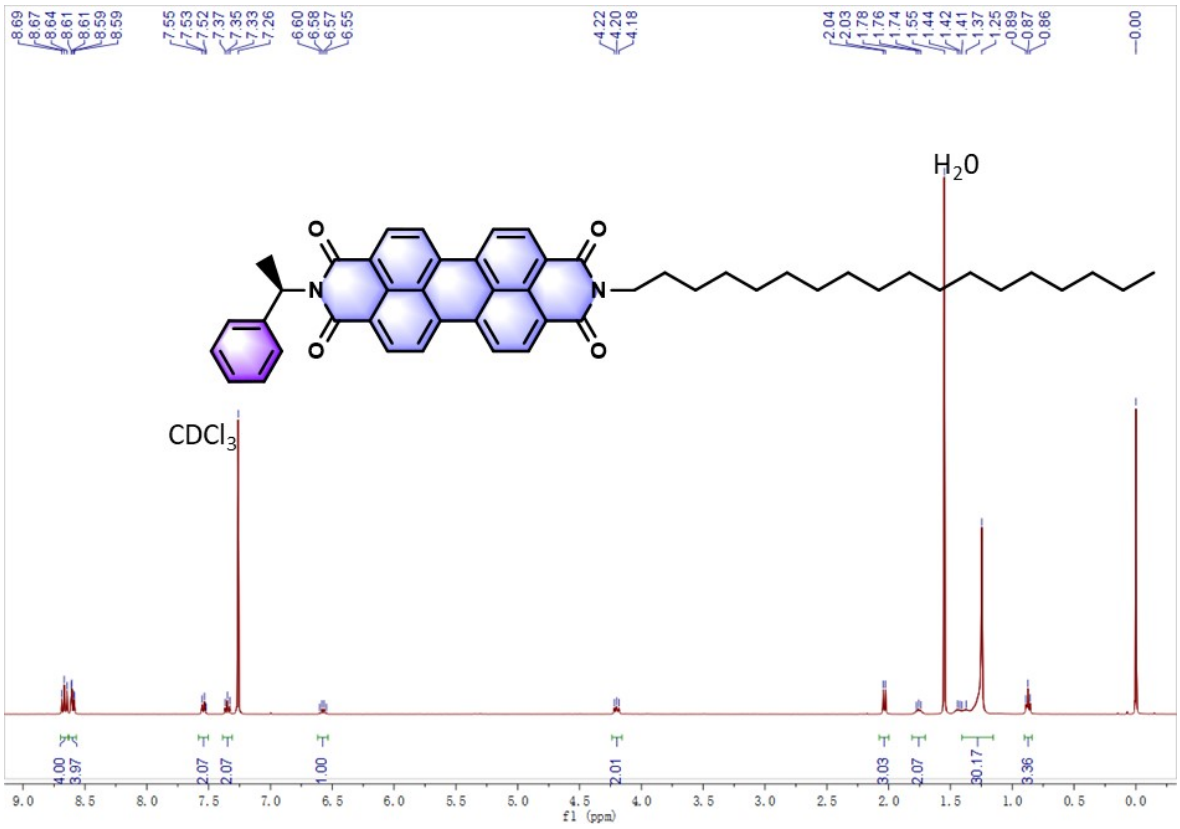



**Fig S4.**[1]H-NMR spectrum of (*S*)-2.

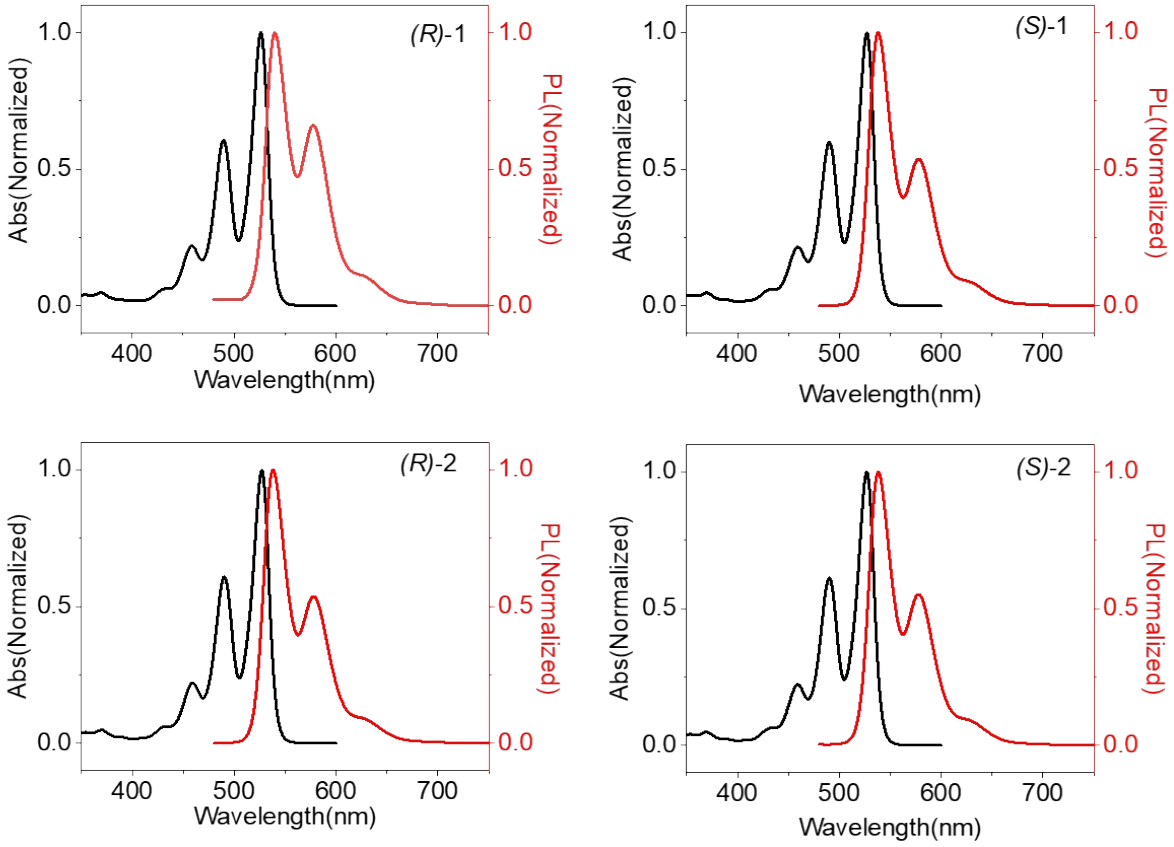



**Fig S5.** The UV-Vis absorption spectra (black color) and fluorescence spectra (red color) of monomer (*R*)-1 (a), (*S*)-1 (b), (*R*)-2 (c) and (*S*)-2 (d).

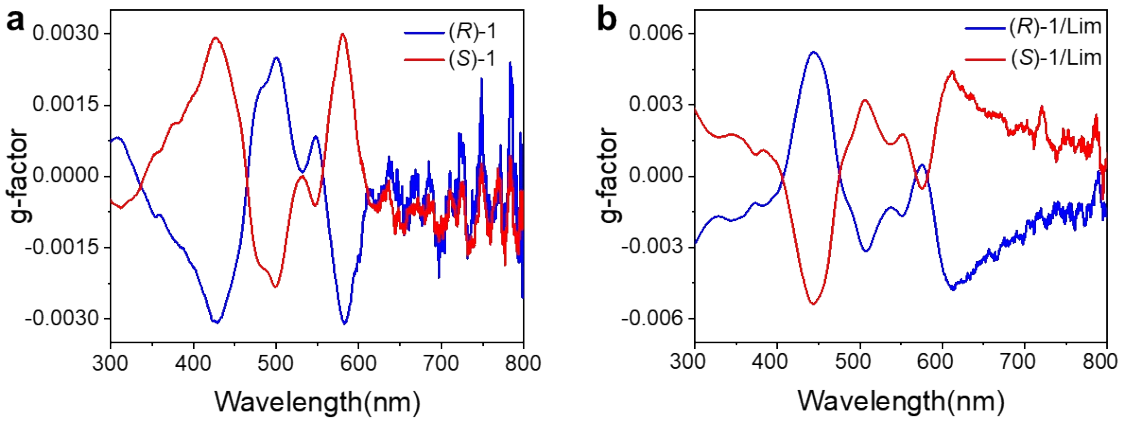



**Fig S6.** g-factor spectra of (*R*)-1, (*S*)-1 assemblies (a) and (*R*)-1/Lim, (*S*)-1/Lim assemblies (b).

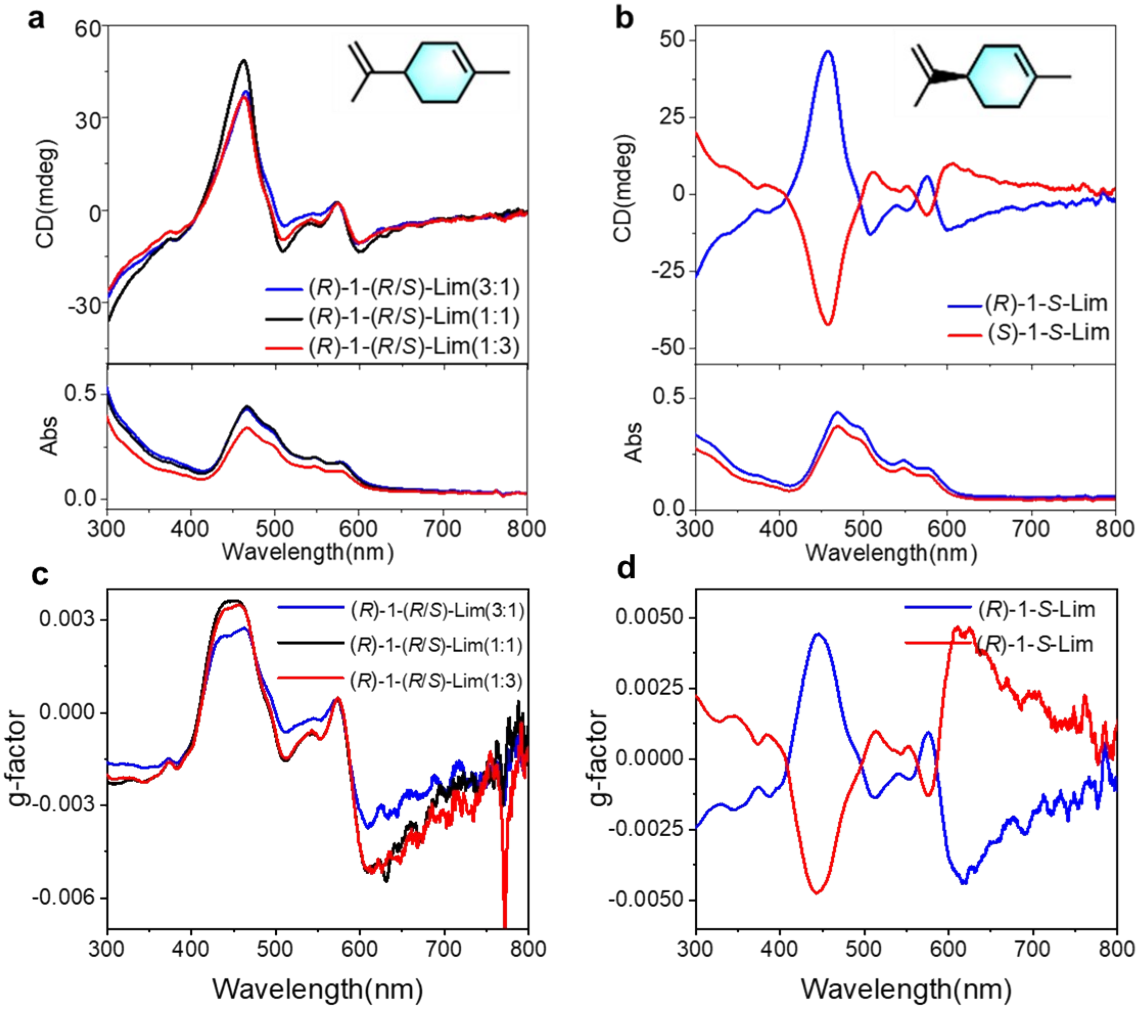



**Fig S7.** (a) CD and UV-vis absorption spectra of (*R*)-1 assemblies prepared in the presence of different ratio of *R*/*S*-limonene. (b) CD and UV-vis absorption spectra of (*R*)-1 assemblies prepared in the presence of *S*-limonene. (c) g-factor spectra of (*R*)-1 assemblies prepared in the presence of different ratio of *R*/*S*-li monene. (d) g-factor spectra of (*R*)-1 assemblies prepared in the presence of *S*-limonene.

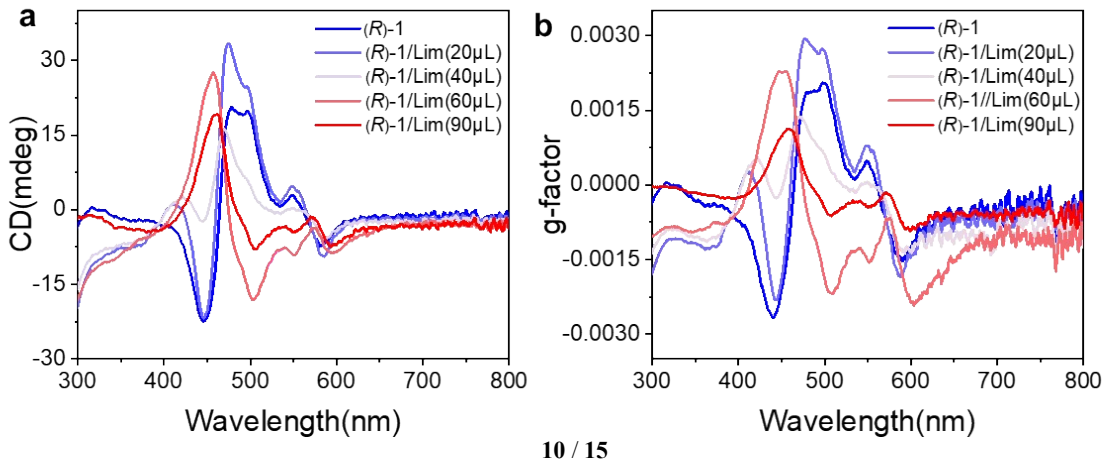


**Fig S8.** (a) CD and (b) g-factor spectra of (*R*)-1 assemblies prepared in the different volume of Limonene.

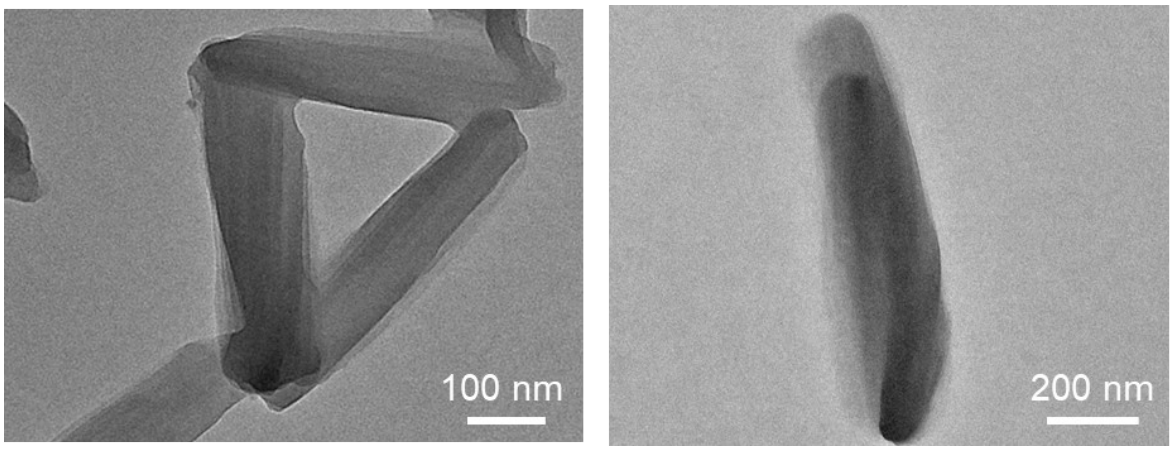



**Fig S9.** TEM images of (*S*)-1/Lim assemblies.

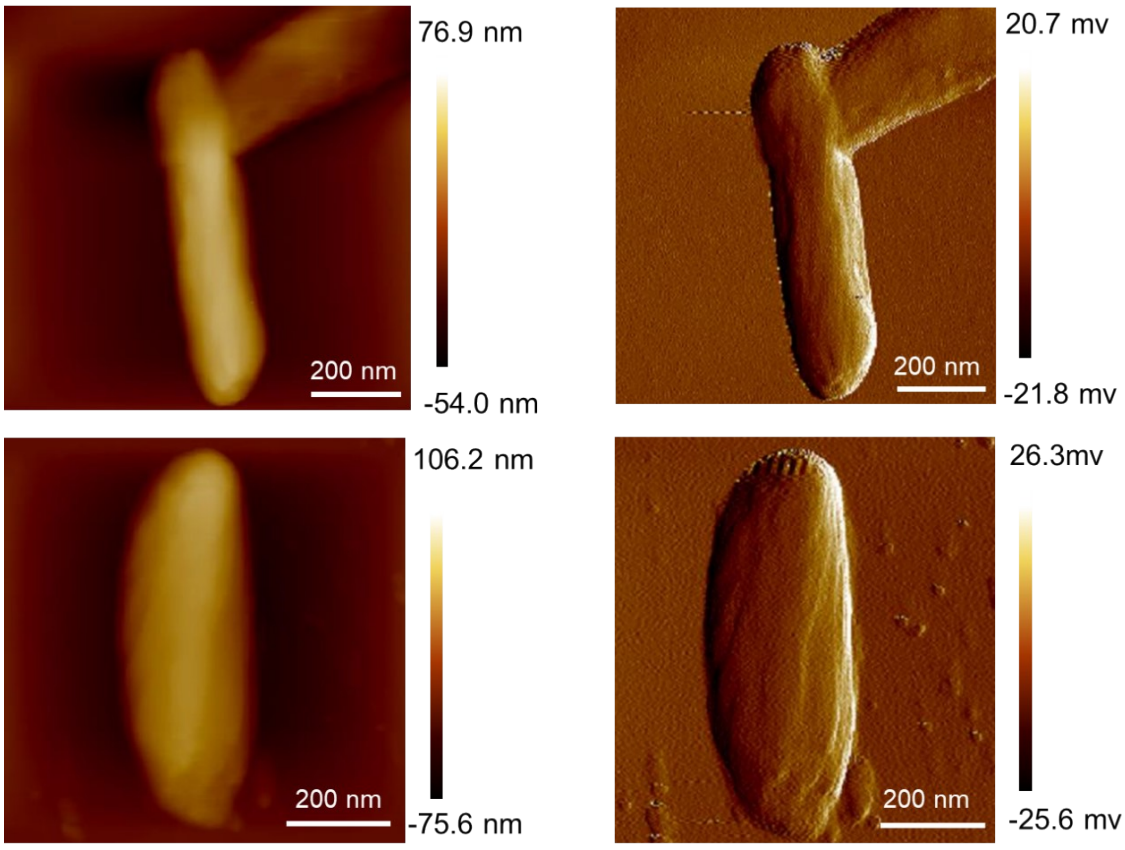



**Fig S10.** AFM images of (*S*)-1 /Limonene assemblies.



**Fig S7.** TEM images of (*S*)-1/Lim assemblies.

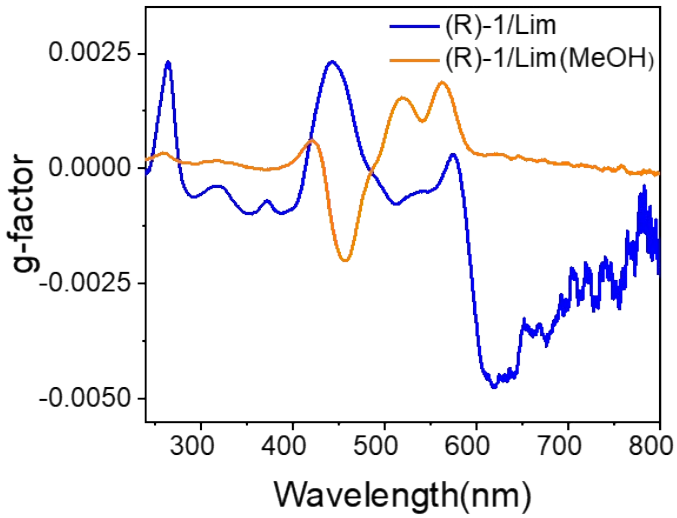



**Fig S11.** g-factor spectra of (*R*)-1/Lim and (*R*)-1/Lim (MeOH) assemblies.

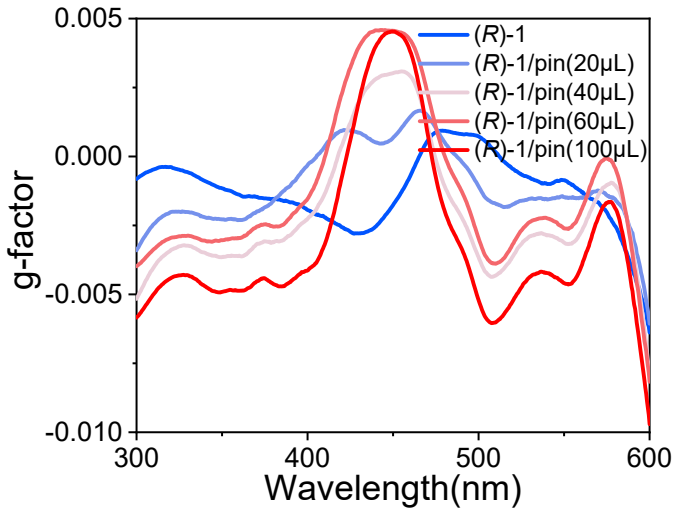



**Fig S12.** g-factor spectra of (*R*)-1/pin assemblies prepared in the different volume of Pinene.

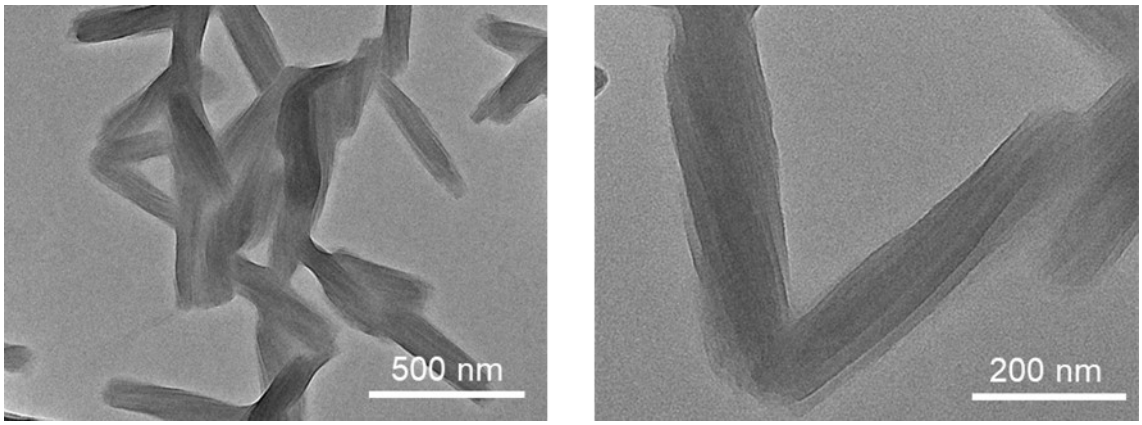



**Fig S13.** TEM images of (*R*)-1/Pin assemblies.

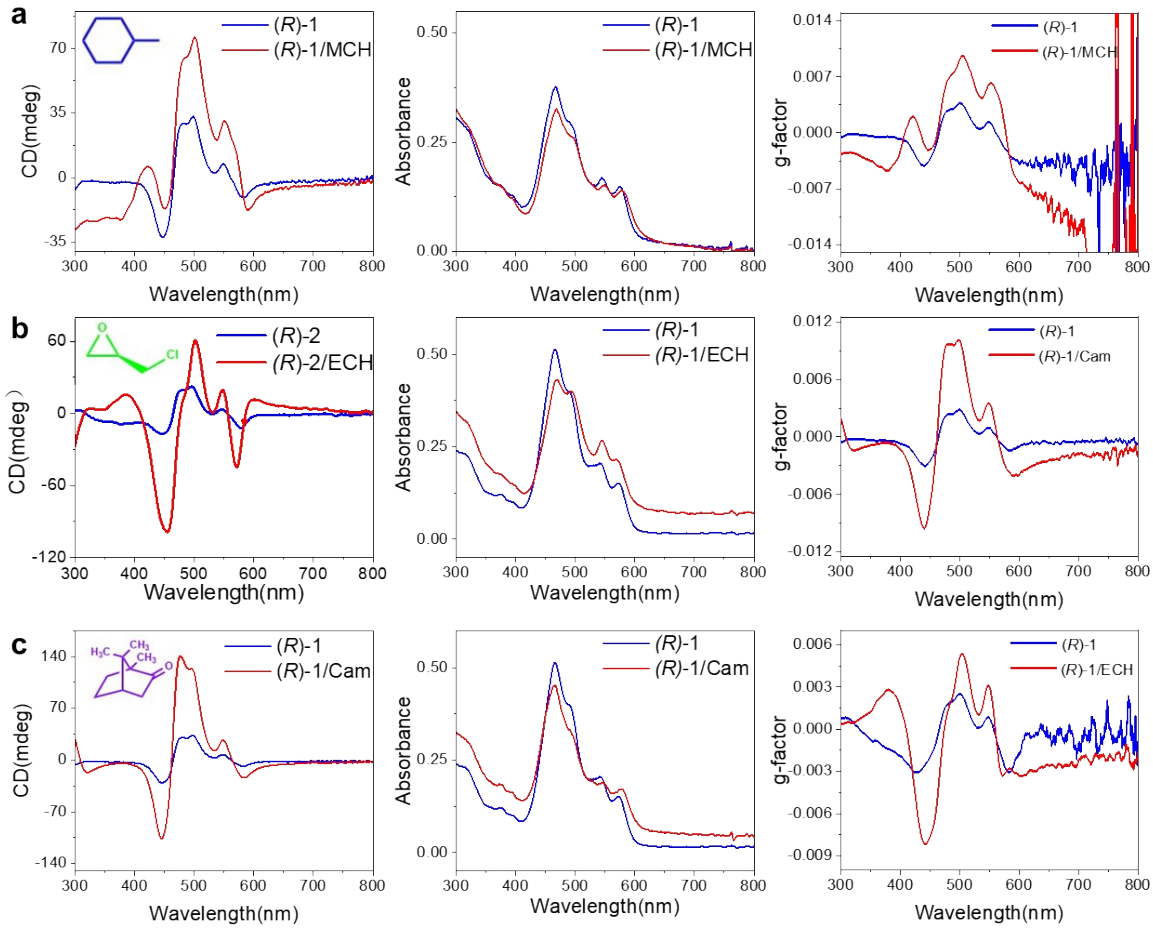



**Fig S14.** (a) CD and UV-vis absorption spectra of (*R*)-1 and (*R*)-1/MCH asse mblies. (b) CD spectra and UV-vis absorption spectra of (*R*)-1 and (*R*)-1/ECH assemblies. (c) CD spectra and UV-vis absorption spectra of (*R*)-1 and (*R*)-1/C amassemblies.

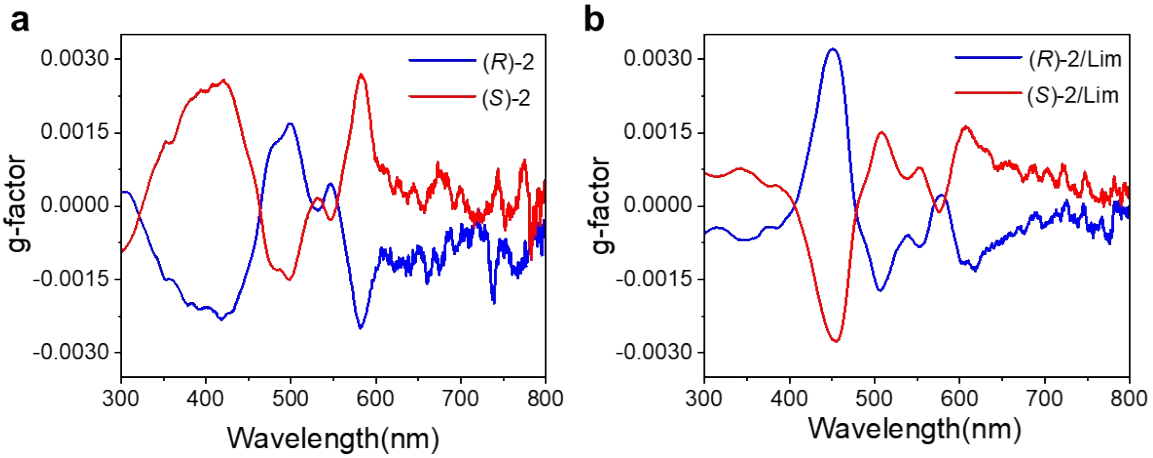



**Fig S15.** g-factor spectra of (*R*)-2, (*S*)-2 assemblies (a) and (*R*)-2/Lim, (*S*)-2/Li m assemblies (b).

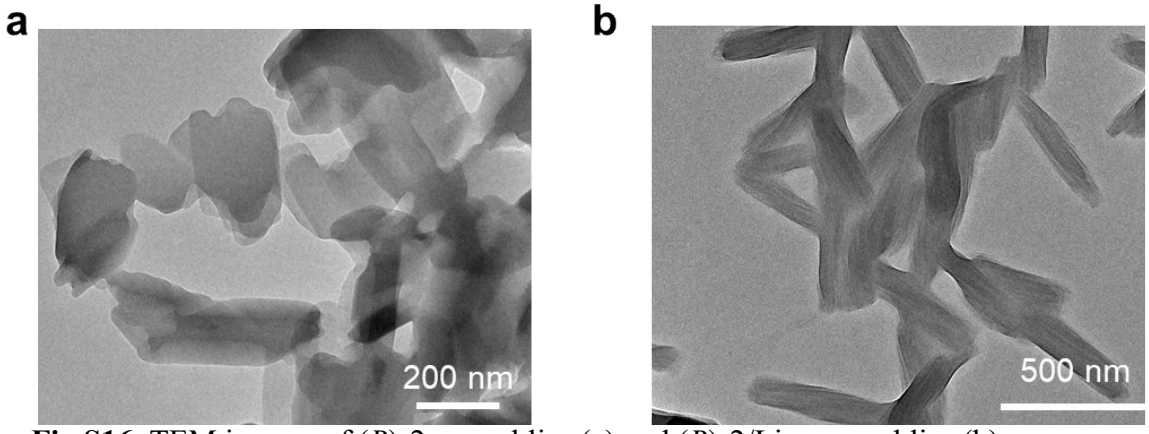



**Fig S16.** TEM images of (*R*)-2 assemblies (a) and (*R*)-2/Lim assemblies (b).

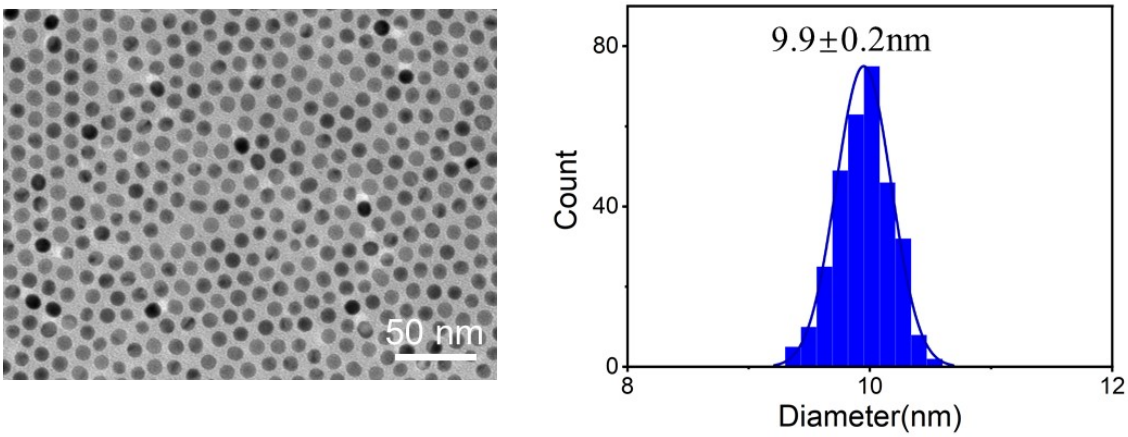



**Fig S17.** TEM image and size histograms of $Au_{10}$@12SH/OAm.

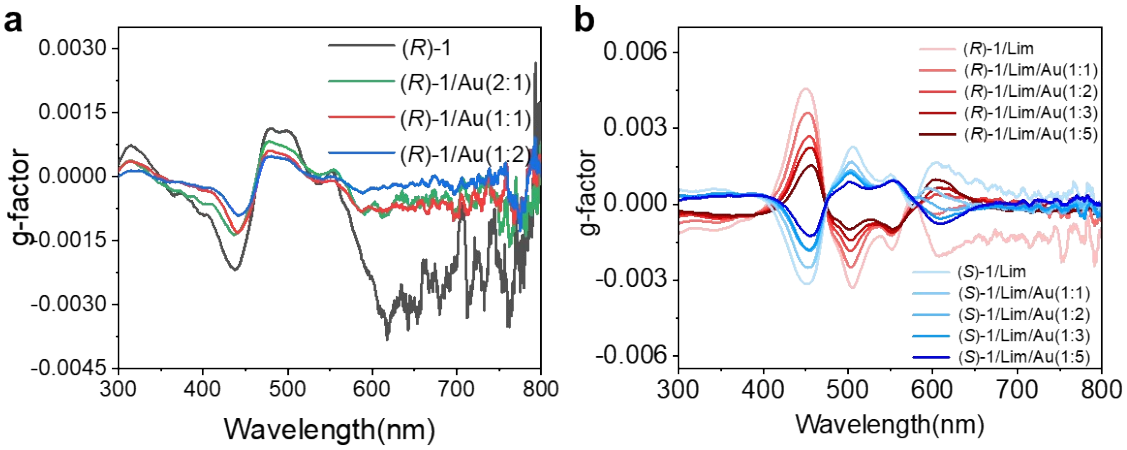



**Fig S18.** g-factor spectra of (*R*)-1/Au assemblies (a) and (*R*)-1/Lim/Au assembli es (b)

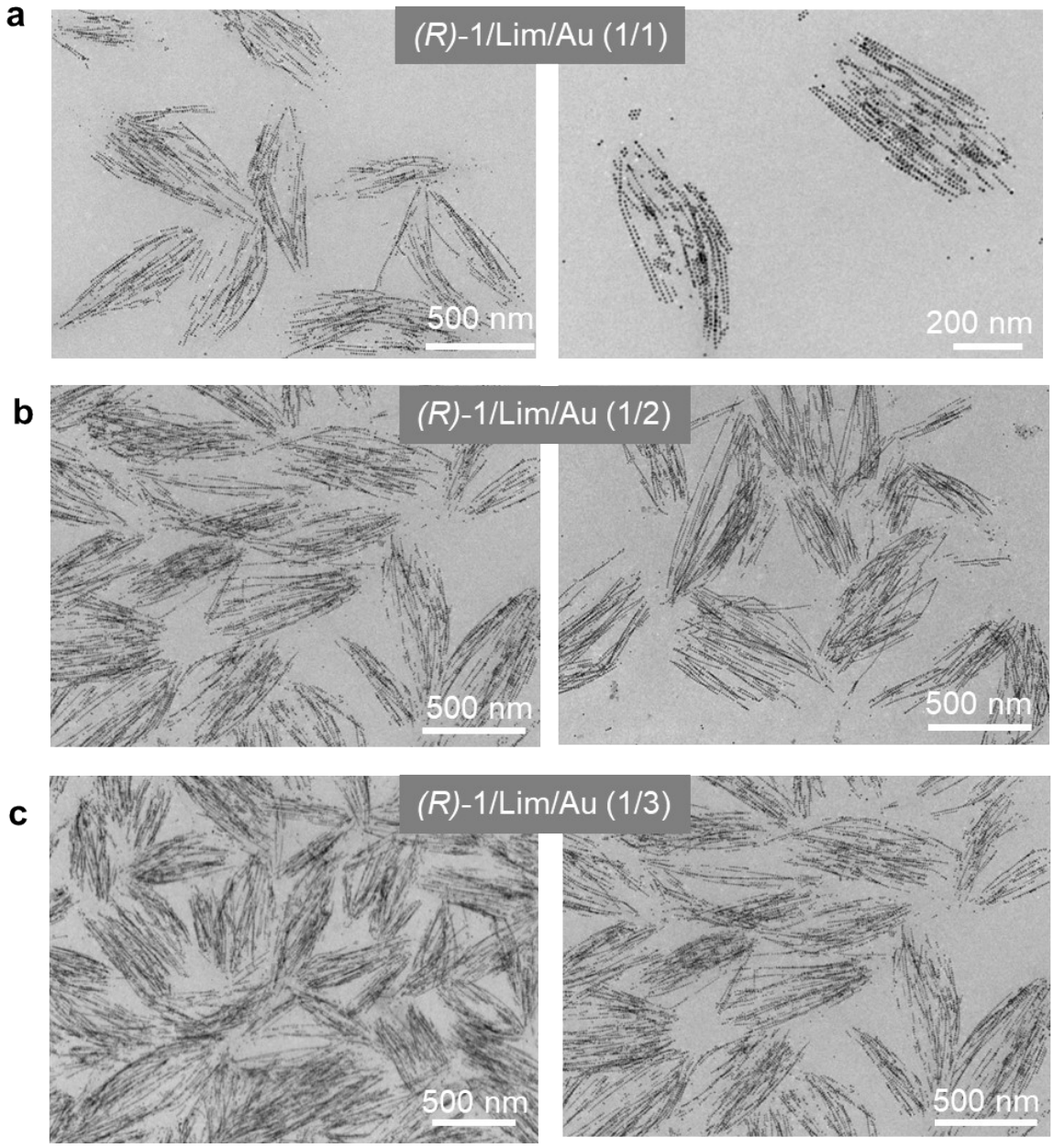



**Fig S19**. (a) TEM images of (*R*)-1/Lim/Au (1/1) assemblies. (b) TEM images of (*R*)-1/Lim/Au (1/2) assemblies. (c) TEM images of (*R*)-1/Lim/Au (1/3) assemblies.