Supporting Information

Close-packed nitronyl nitroxide radicals by Au-S self-assembly: Strong ferromagnetic coupling

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Figure S1. CV test data of **BS-NN** in the potential range −1V to 1V. No **calibration** sample was added.
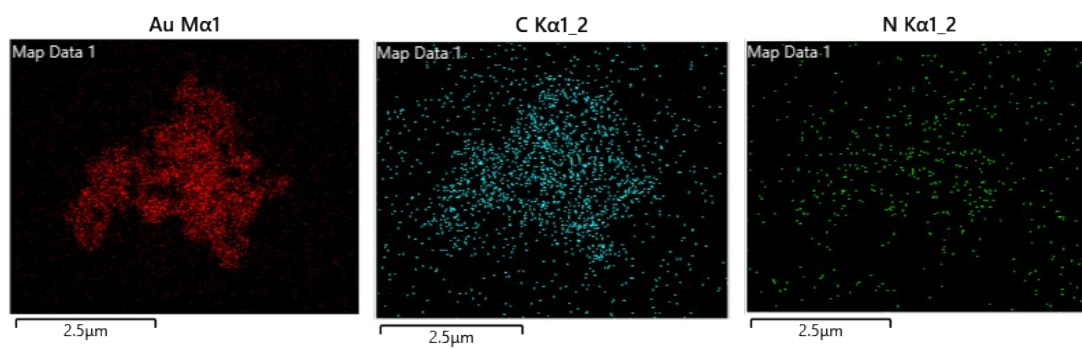
Figure S2. EDS layered image of **AuNPs**.

Electron Image 1
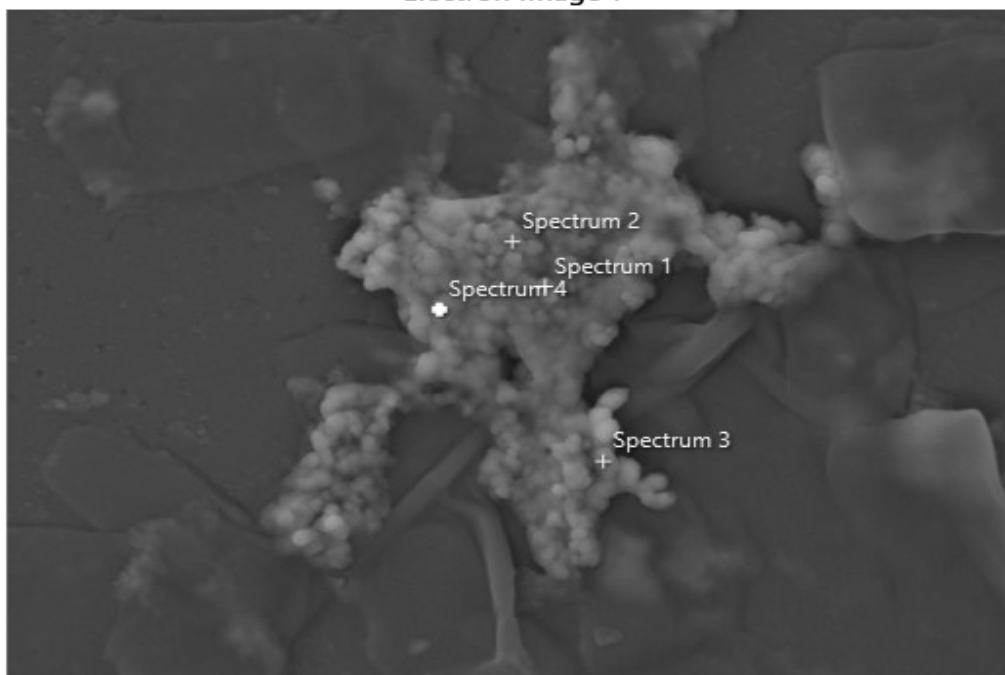
Figure S3. SEM image of EDS point sweeps used for **S-NPs**.

Electron Image 1
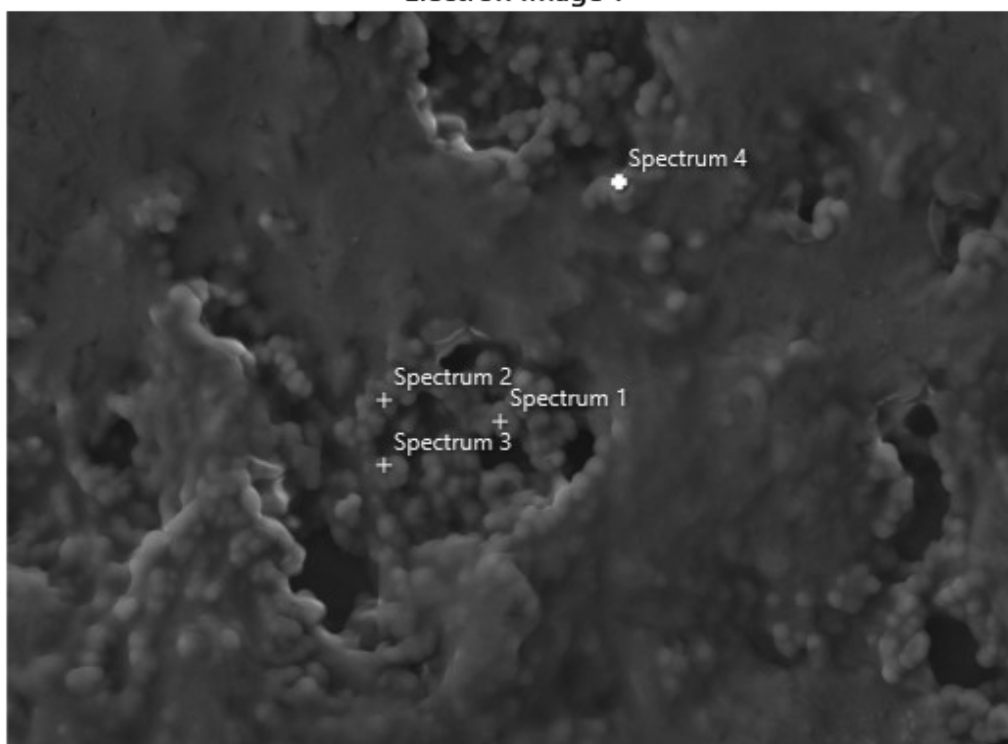
Figure S4. SEM image of EDS point sweeps used for **D-NPs**.

Map Data 1
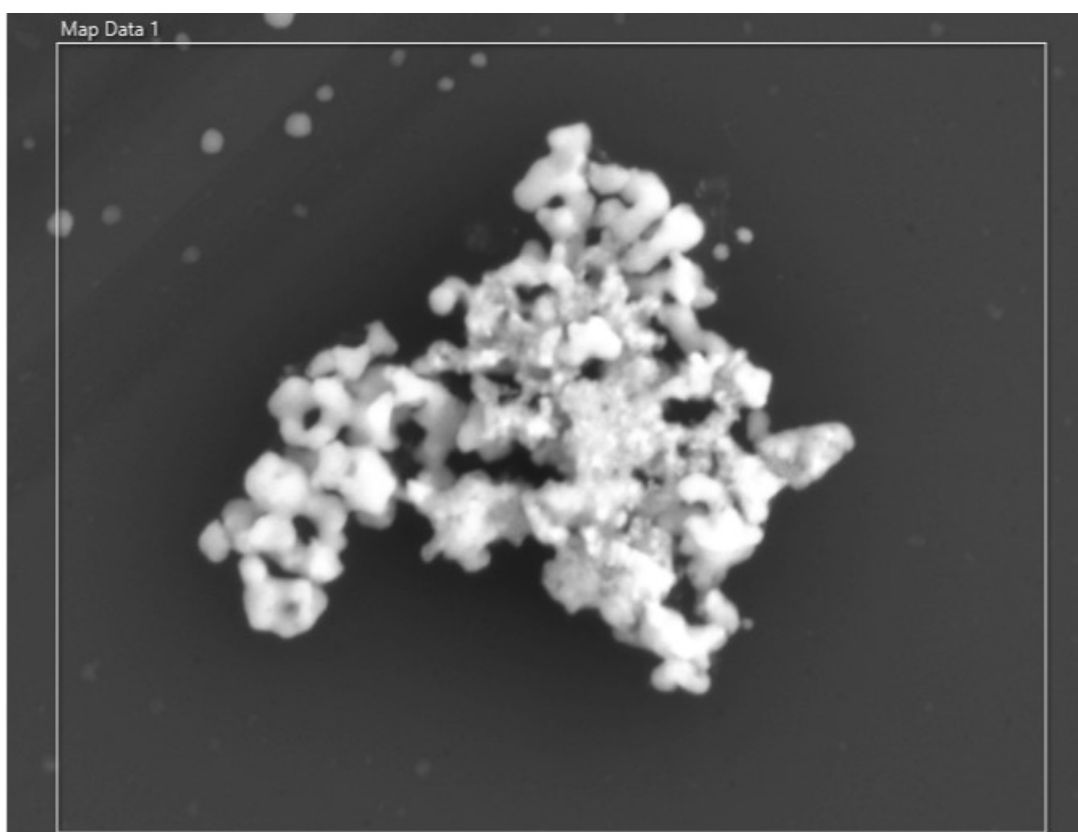
Figure S5. TEM images for EDS test analysis of **AuNPs**.

(a)

Size Distribution by Intensity

(b)

Size Distribution by Intensity
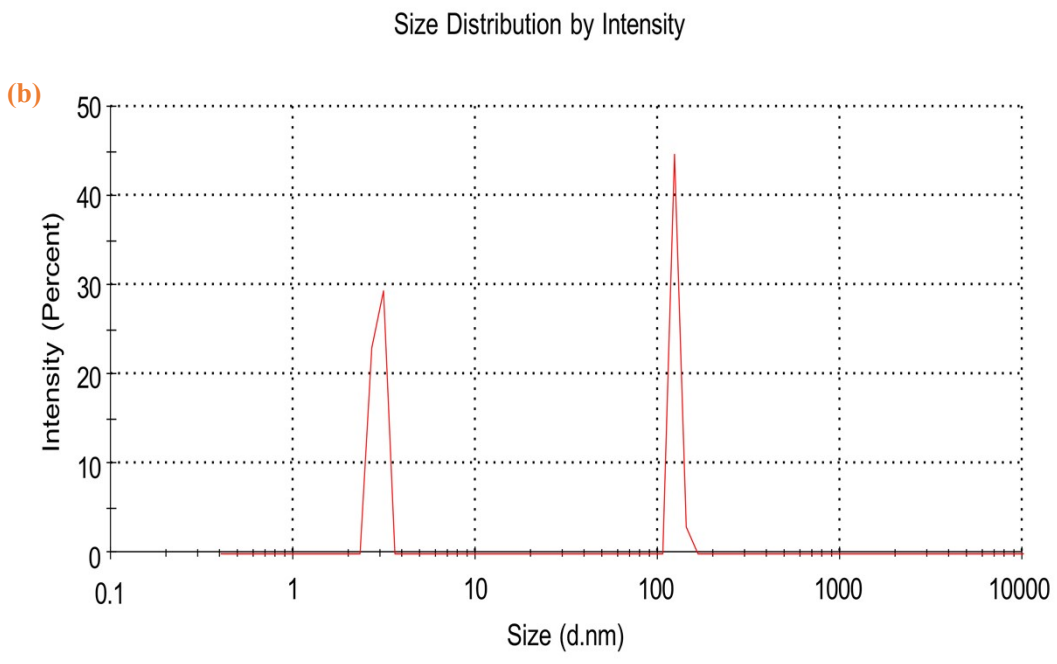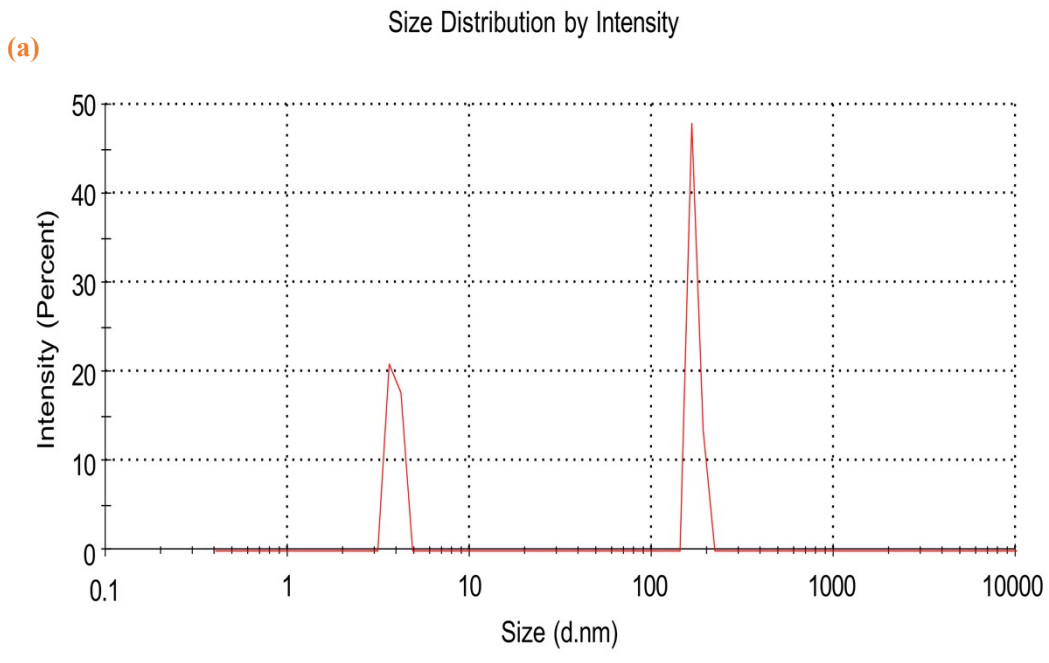
Figure S6. ζ particle size test data.
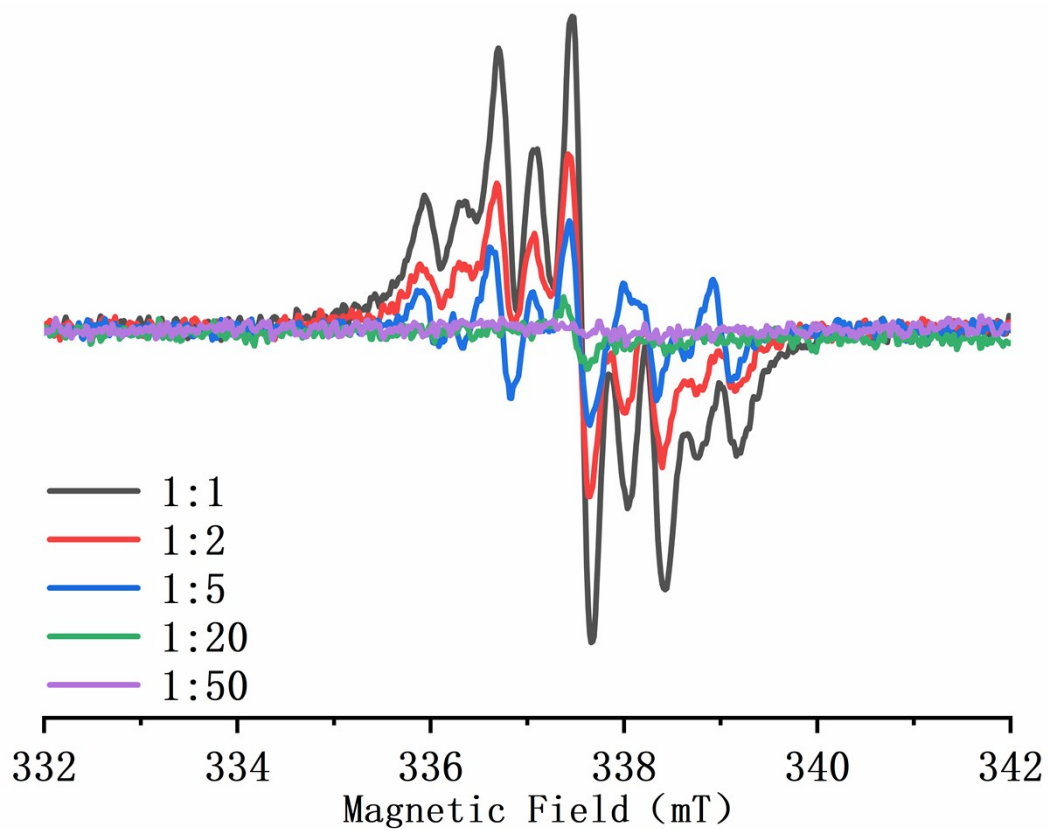
Figure S7. EPR test plots of different molar ratios of **BS-NN** (n_{BS-NN} : n_{HAuCl4}) self-assembled into **S-NPs** samples.

According to Figure S7, the optimum packing molar ratio ($HAuCl_4$: NN=5:1) was selected for the synthesis of S-NPs, and the same ratio was used for D-NPs for comparison.
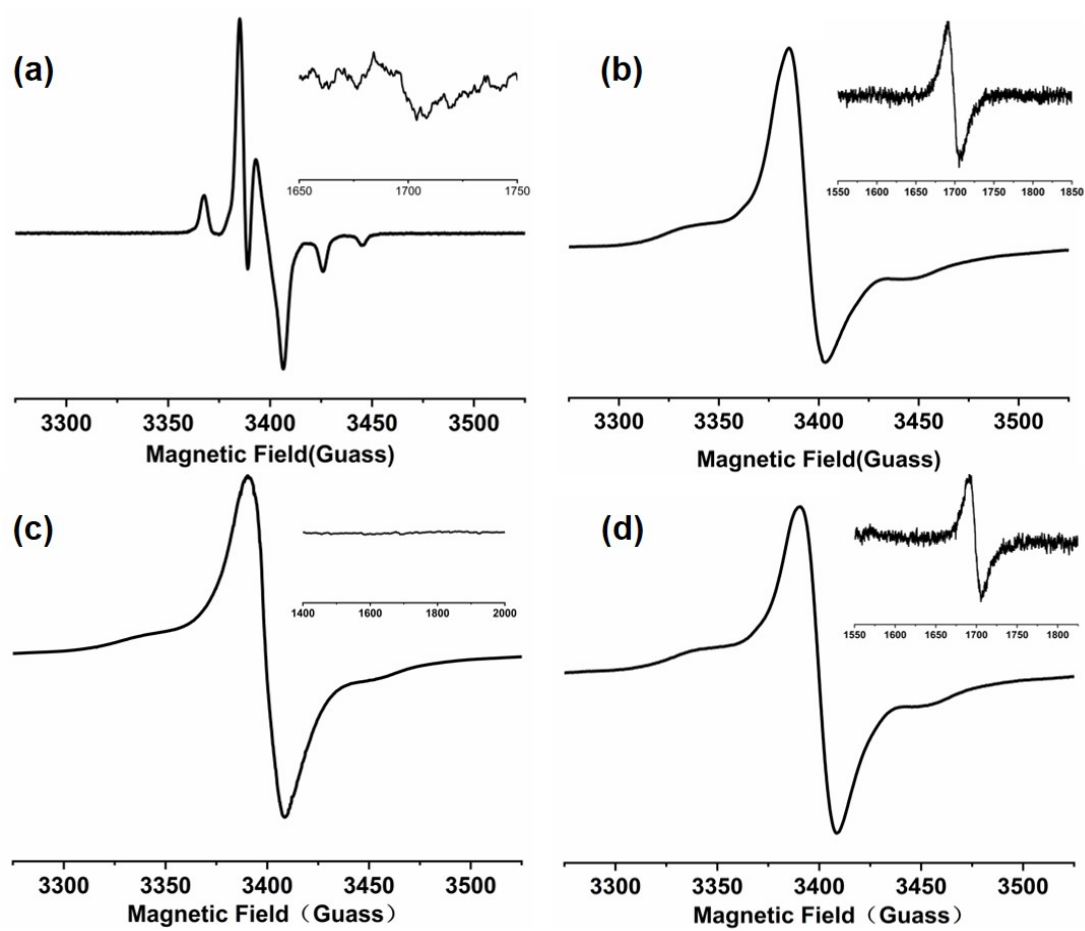
Figure S8. Spectra of EPR tests performed in DCM solution at 100 K: (a) **BS-NN**; (b) **BD-NN**; (c) **S-NPs**; (d) **D-NPs**.
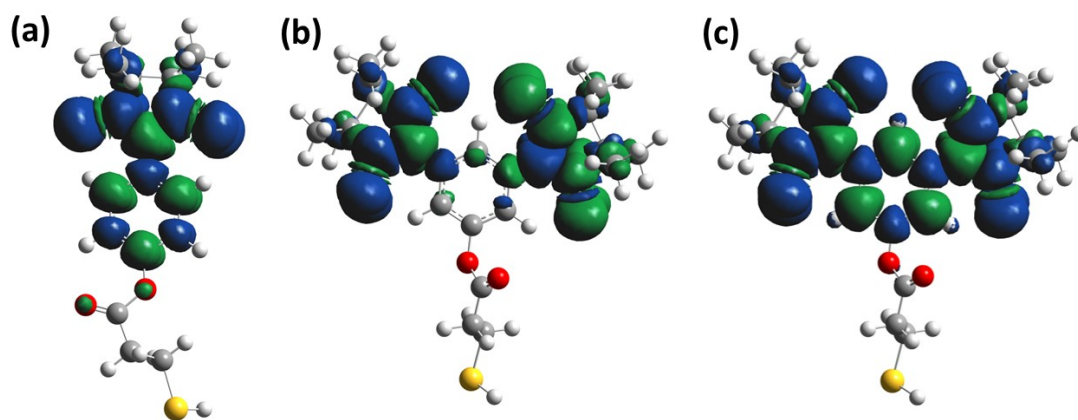
Figure S9. (a) Spin density calculations of doublet **BS-NN** fractions self-assembled on gold surfaces; (b) Spin density calculations of singlet **BD-NN** fractions self-assembled on gold surfaces; (c) Spin density calculations of triplet **BD-NN** fractions self-assembled on gold surfaces. All data are calculated at the UB3LYP/6-31G(d) level of theory. (Blue and green surfaces represent α and β spin densities, respectively.)
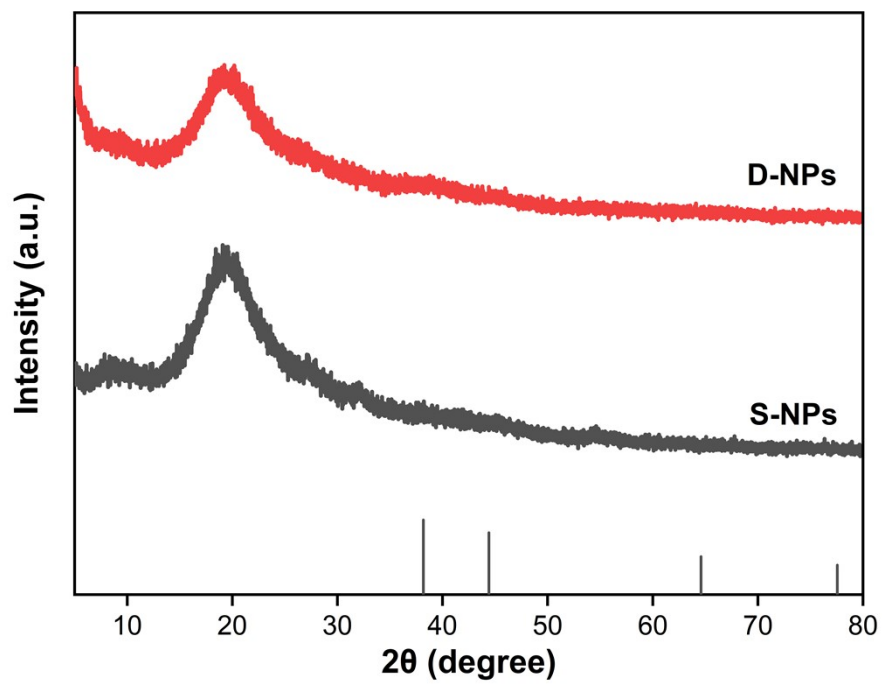
Figure S10. XRD spectrum of **S-NPs**, **D-NPs** and Au standard card. Polystyrene was used to fix the sample, and NPs accounted for 5% of the weight of the test sample.

Experimental synthesis steps and Mass
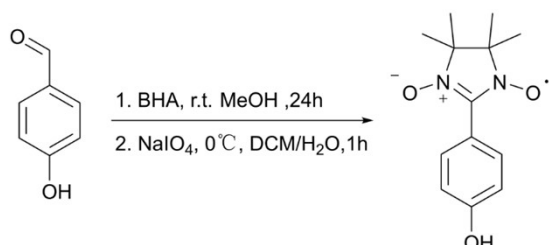
2-(4'-Hydroxylphenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl(S-NN):

According to the method reported in the previous literature[1], 244 mg (2 eq) of 4-hydroxybenzaldehyde and 296 mg (2 eq) of 2,3-dimethyl-2,3-dihydroxyaminobutane were added into a 50 ml two-necked flask. Subsequently, 4 ml of methanol was added into the flask, which was then purged with N_2 and stirred at room temperature for 24h. After the reaction, transfer it to a flask, and dry it using a rotary evaporator to obtain the crude 2-(4-hydroxyphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol. Add the 2-(4-hydroxyphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol made above into a 250 mL round bottom flask. Then, pour in 50 mL of DCM and 50 mL of deionized water into the flask. Mix the contents in a water bath at 0°C. Prepare the sodium periodate solution by dissolving 428mg in 20ml of deionized water, then add it slowly into the flask. TLC detection reaction should continue until the newly generated colored radicals are stable in color. After extracting it with DCM (20 mL * 3), drying with anhydrous sodium sulfate, filtration, spin-drying, and column chromatography (DCM: EAC = 1:1), a blue crystalline powder product was obtained with a yield of 55%.
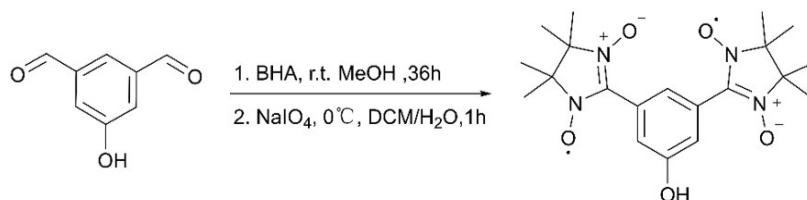
2,2'-(5-hydroxy-1,3-phenylene)-bis(4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl) (D-NN):

Take 5-hydroxyisophthalaldehyde (300 mg, 2 eq) and 2,3-dimethyl-2,3-dihydroxyaminobutane (651.2 mg, 4.4 eq) into a 100 mL two-necked flask. Add 20 mL of methanol, protect with N_2, and stir at room temperature for 36h. After the reaction, transfer the mixture to a flask, and dry it using a rotary evaporator to obtain the crude 2,2'-(5-hydroxy-1,3-phenylene)-bis(4,4,5,5-tetramethylimidazolidine-1,3-diol). Add the 2,2'-(5-hydroxy-1,3-phenylene)-bis (4-hydroxyphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-dione into a 250 mL round bottom flask. Then, pour in 50 mL of DCM and 50 mL of deionized water into the flask. Mix the contents in water bath at 0°C. A sodium periodate solution (856 mg dissolved in 20 mL of deionized water) was added to the flask slowly, and the reaction was monitored by TLC until the colour of the newly generated radicals became stable. The water phase was washed with DCM and then dried under vacuum at room temperature. The column chromatography (MeOH: EAC = 1:1) of this product was performed, and a dark blue crystalline powder product was obtained with a yield of 38%.
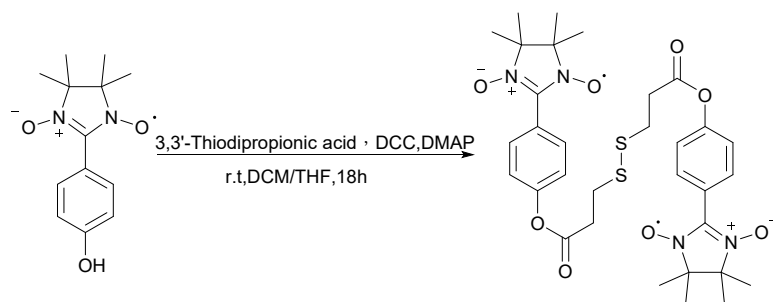
BS-NN:

Dissolve 3,3-dithiodipropionic acid (19 mg, 0.09 mmol) in anhydrous THF (0.33 mL). Add a solution of dicyclohexylcarbodiimide (DCC) (40 mg, 0.20 mmol) in anhydrous DCM (1 mL) to 3,3-dithiodipropionic acid at 0°C, and pre-react for 10 minutes under magnetic stirring. Under an ice water bath, add 4-dimethylaminopyridine (4 mg, 0.033 mmol) and a solution of S-NN (50 mg, 0.20 mmol) in 1 mL anhydrous DCM to the reaction mixture. Stir the solution at room temperature for 18 hours under argon gas. The reaction mixture was vacuum-dried at a low temperature and subjected to two column chromatography steps (DCM/EAc = 1:1) (DCM: MeOH = 30:1) to obtain the BS-NN with a yield of 45%.
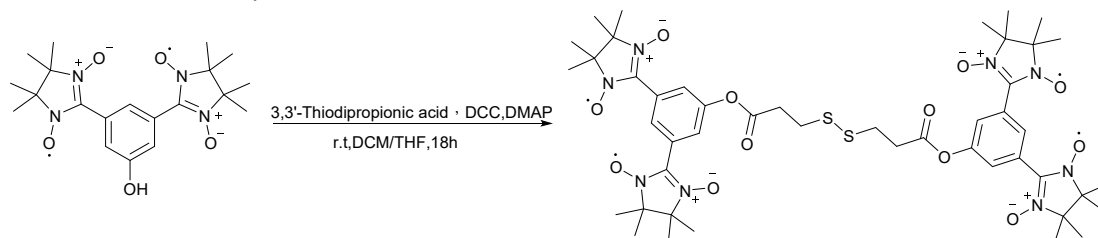
BD-NN:

Dissolve 3,3-dithiodipropionic acid (28.5 mg, 0.136 mmol) in anhydrous THF (0.50 mL). Add a solution of DCC (60 mg, 0.30 mmol) in anhydrous DCM (1.5 mL) at 0°C to 3,3-dithiodipropionic acid, and pre-react for 10 minutes under magnetic stirring. Under an ice water bath, 4-dimethylaminopyridine (6 mg, 0.05 mmol) and a solution of D-NN (121.2 mg, 0.30 mmol) in 2 mL of anhydrous DCM were added to the reaction mixture. The solution was stirred at room temperature for 18 hours under argon gas. The reaction mixture was vacuum-dried at a low temperature and subjected to two column chromatography steps (DCM/EAc = 1:1) (DCM: MeOH = 50:1) to obtain the BD-NN with a yield of 42%.

Gold nanoparticles (AuNPs):

The gold nanoparticles were synthesized according to the previous procedure without modification. 0.035 g (0.10 mmol) of a 1% aqueous hydrogen tetrachloroaurate trihydrate solution was dried by evaporating in a rotary evaporator at 60°C to remove the water. Then, 45 ml of toluene and 4 g (0.11 mmol) of trioctylamine were added. The mixture was sonicated for 20 minutes until a clear yellow solution was obtained, indicating that $HAuCl_4$ was fully dissolved in toluene. 5 mL of an aqueous solution containing 20 mg (0.53 mmol) of $NaBH_4$ was then added under vigorous magnetic stirring to reduce $HAuCl_4$. The color of the solution rapidly changed from yellow to red. After 2 h (with the flask opened to air), half of the flask volume was removed under vacuum, resulting in the production of deep red gold nanoparticle products.

S-NPs:

Gold nanoparticles grafted with S-NN. A DCM solution (3 mL) of BS-NN (13.5 mg, 0.02 mmol) was added to the previously synthesized AuNPs. The reaction was left to proceed for 17 h with the flask sealed from air using a septum. The excess solvent was removed under vacuum until 3 or 4 mL remained, and then 20 mL of methanol was added before centrifugation. The methanol phase was red in color and it contained the nanoparticles. The methanol was removed under vacuum to yield a violet solid. After dialysis using a 1000 molecular weight membrane for 24 hours, the solvent is removed using a rotary evaporator to obtain a purple-black solid. The purified sample was evaporated under a stream of nitrogen, dissolved in DCM, and analyzed using electron paramagnetic resonance (EPR) and superconducting quantum interference device (SQUID).

D-NPs:

Gold nanoparticles grafted with D-NN. A DCM solution (3 mL) of BS-NN (19.7 mg, 0.02 mmol) was added to the

aforementioned AuNPs solution. The reaction was left to proceed for 17 h with the flask sealed from air using a septum. The excess solvent was removed under vacuum until 3 or 4 mL remained, and then 20 mL of methanol was added before centrifugation. The methanol phase was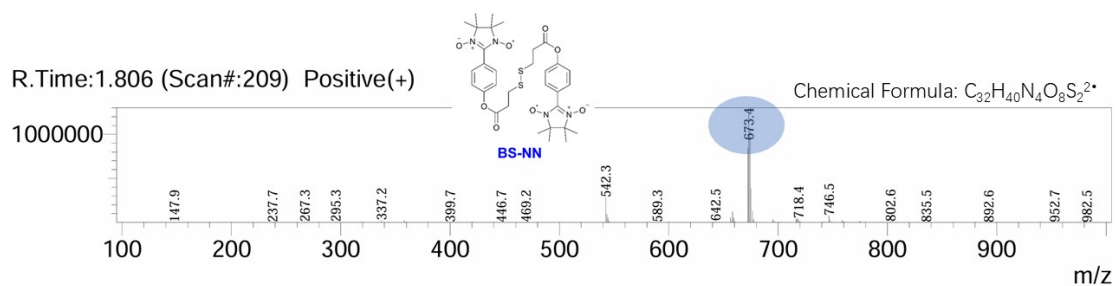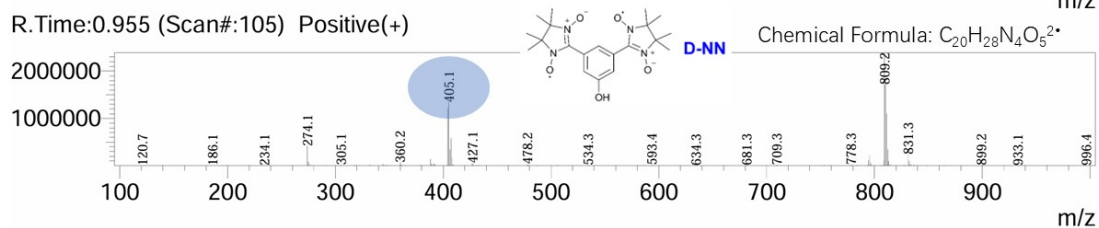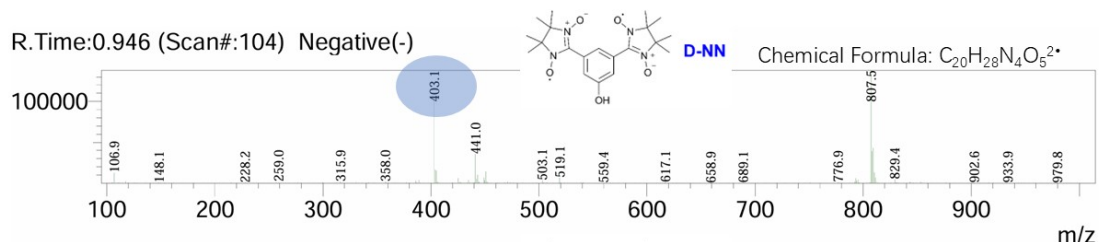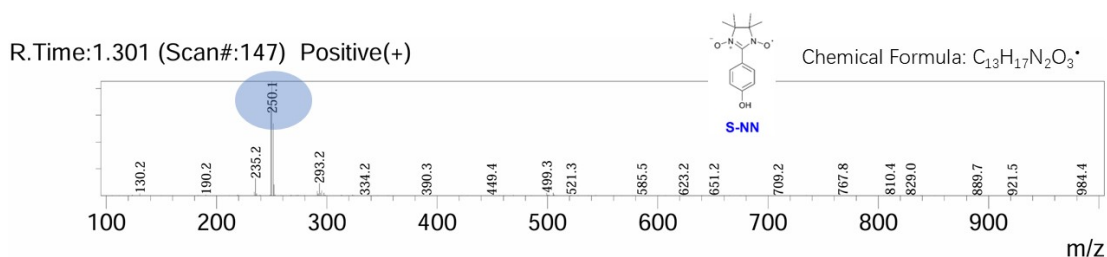 red in color and it contained the nanoparticles. The methanol was removed under vacuum to yield a dark violet solid. After dialysis using a 3000 molecular weight membrane for 24 hours, the solvent is removed using a rotary evaporator to obtain a purple-black solid. The purified sample was evaporated under a stream of nitrogen, dissolved in DCM and analyzed by EPR and SQUID.

Mass spectrum

R.Time:1.301 (Scan#:147) Positive(+)

Chemical Formula: $C_{13}H_{17}N_2O_3^{\bullet}$

S-NN

R.Time:0.946 (Scan#:104) Negative(-)

D-NN Chemical Formula: $C_{20}H_{28}N_4O_5^{2\bullet}$

R.Time:0.955 (Scan#:105) Positive(+)

D-NN Chemical Formula: $C_{20}H_{28}N_4O_5^{2\bullet}$

R.Time:1.806 (Scan#:209) Positive(+)

Chemical Formula: $C_{32}H_{40}N_4O_8S_2^{2\bullet}$

BS-NN

R.Time:1.891 (Scan#:219) Positive(+)

BD-NN Chemical Formula: $C_{46}H_{62}N_8O_{12}S_2^{4\bullet}$
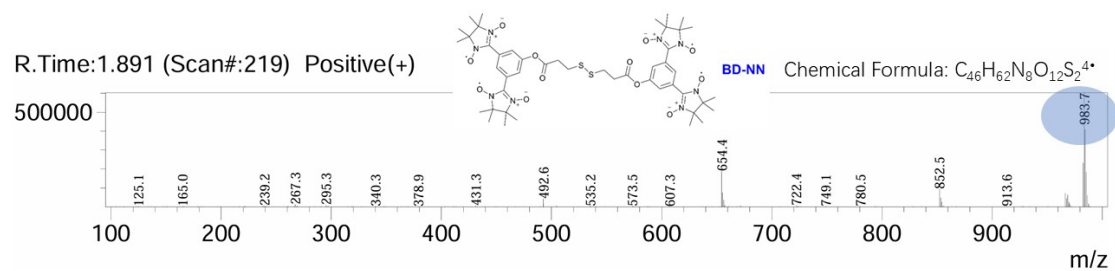
Calculated spin density data

Part of the S-NN structure on S-NPs (doublet)

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

BROKEN BS-NN DOUBLET	1	2
1 C	0.033381	-0.061123
2 C	0.076480	0.032336
3 C	0.283579	-0.052172
4 C	-0.007871	0.032887
5 C	0.055425	-0.057428
6 C	0.105862	0.069506
7 C	0.655960	-0.246929
8 O	-0.572656	-0.000435
9 C	0.529710	-0.001369
10 C	0.090708	0.000183
11 C	-0.086614	-0.000070
12 O	-0.401315	-0.003033
13 S	0.069005	-0.000102
14 N	-0.339051	0.271662
15 C	0.136116	-0.016744
16 C	0.136752	-0.016753
17 N	-0.339052	0.272492
18 O	-0.377988	0.368120
19 O	-0.374716	0.371323
20 C	0.086431	0.015716
21 C	0.076328	0.003128
22 C	0.087109	0.015712
23 C	0.076418	0.003092

Part of the D-NN structure on D-NPs (singlet and triplet)

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

BROKEN BD-NN SINGLET	1	2	BROKEN BD-NN TRIPLET	1	2
1 C	0.066682	-0.035062	1 C	0.066821	0.098401
2 C	0.140413	0.001488	2 C	0.139925	-0.1062
3 C	0.234352	0.000942	3 C	0.234384	0.061899
4 C	0.091743	-0.004925	4 C	0.091677	-0.10665
5 C	0.077557	0.037401	5 C	0.077602	0.098727
6 C	0.109041	-0.00181	6 C	0.108631	-0.11673
7 C	0.641009	0.247719	7 C	0.641116	-0.25623
8 O	-0.56582	-0.000009	8 O	-0.56581	-0.0003
9 C	0.51314	-0.000012	9 C	0.513066	0.00103
10 C	0.085611	0.000006	10 C	0.085549	-7.5E-05
11 C	-0.08401	0.000002	11 C	-0.08394	0.000027
12 O	-0.39587	-0.000013	12 O	-0.39584	0.000246
13 N	-0.33455	-0.2679	13 N	-0.33503	0.271882
14 C	0.13557	0.016356	14 C	0.135679	-0.01649
15 C	0.136043	0.016474	15 C	0.136228	-0.01657
16 N	-0.33474	-0.2641	16 N	-0.3352	0.267535
17 O	-0.3636	-0.38048	17 O	-0.36297	0.383263
18 O	-0.37996	-0.3597	18 O	-0.37933	0.363057
19 C	0.07566	-0.00295	19 C	0.075643	0.003015
20 C	0.087796	-0.01539	20 C	0.087683	0.015609
21 C	0.075373	-0.00297	21 C	0.075316	0.003042
22 C	0.089004	-0.01535	22 C	0.088975	0.015608
23 C	0.644429	-0.24744	23 C	0.644419	-0.2558
24 N	-0.33714	0.267544	24 N	-0.33754	0.271456
25 C	0.136972	-0.01623	25 C	0.137082	-0.01636
26 C	0.135149	-0.01662	26 C	0.135266	-0.01673
27 N	-0.33703	0.265212	27 N	-0.33744	0.268622
28 O	-0.36241	0.382394	28 O	-0.36176	0.385296
29 O	-0.37968	0.358738	29 O	-0.37913	0.362033

1.   V. Lloveras, E. Badetti, J. Veciana and J. Vidal-Gancedo, *Nanoscale*, 2016, **8**, 5049-5058.