Electronic Supporting Information

Laterally-Patterned Magnetic Nanoparticles

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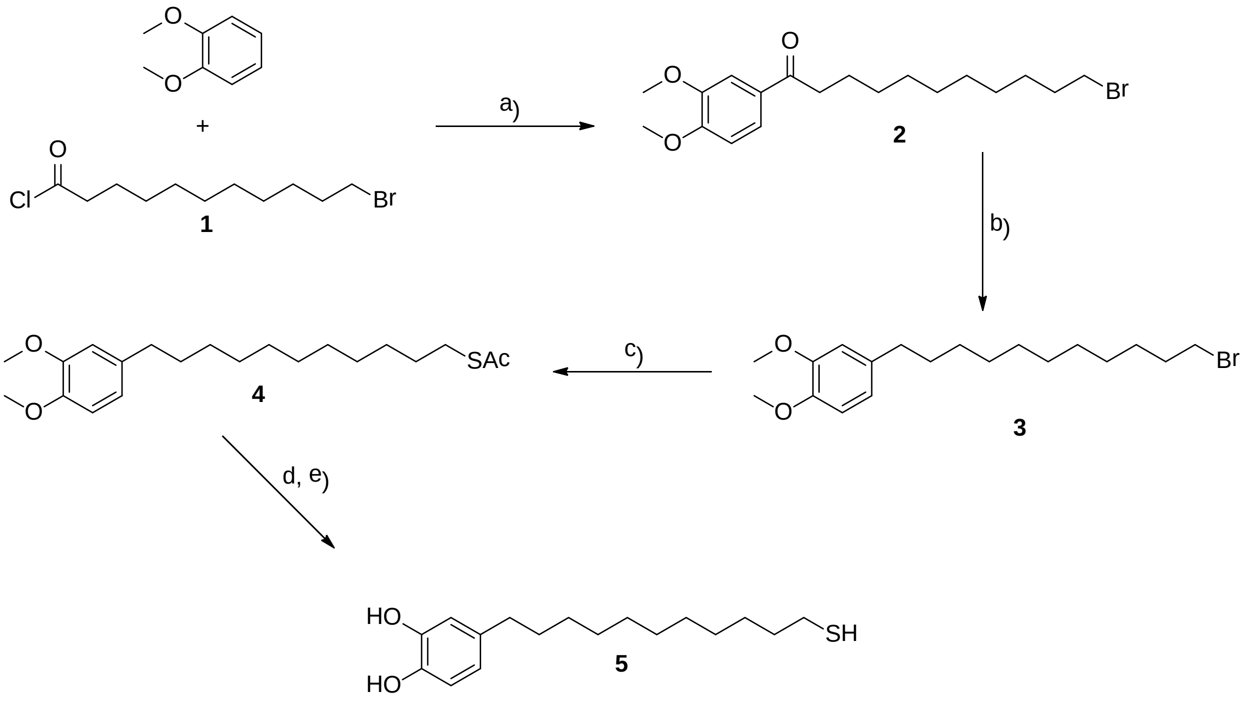
Synthesis of 4-(11-mercaptoundecyl)benzene-1,2-diol



Scheme 1. a) $AlCl_3$, reflux, 2.5 h; b) $NaBH_4$, $AlCl_3$, 0 °C→r.t., overnight; c) KSAc, reflux, 1.5 h, then r.t., 16 h; d) BBr_3, 0 °C→r.t., overnight; e) HCl, EtOH, reflux, 2.5 h.

General Methods. Unless otherwise noted, all starting materials were obtained from commercial sources and used without further purification. All reactions were conducted under argon atmosphere in flame-dried glassware. Tetrahydrofuran (THF) was distilled over sodium/benzophenone ketyl under nitrogen, and methylene chloride (CH_2Cl_2) was dried using Innovative Technology, Inc.'s PureSolv purification column. Anhydrous toluene and anhydrous diethyl ether were obtained from commercial sources and used without further drying. NMR spectra were recorded on Bruker AMX-300 or ADVANCE-400 spectrometers (at 300 or 400 MHz, respectively). Mass spectra were acquired by the University of North Carolina, Chapel Hill mass spectrometry facility.

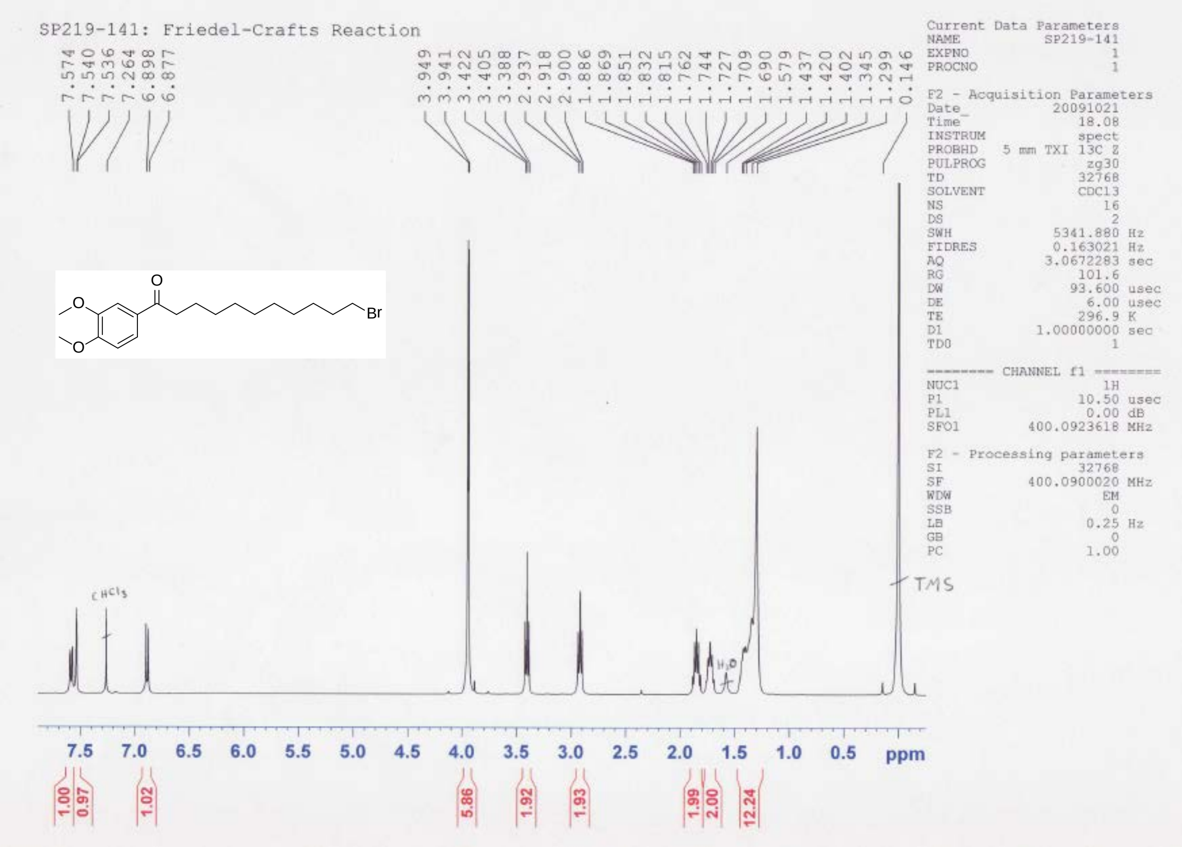
11-bromoundecanoyl chloride (1). $CHCl_3$ (190 mL), and thionyl chloride (21.8 mL, 300 mmol) were added to a round-bottomed flask fitted with a condenser containing 11-bromoundaconic acid (19.89 g, 75.0 mmol). The mixture was heated to reflux and stirred overnight. The mixture was allowed to cool and was concentrated *in vacuo*. The residue was then distilled at 120 °C and 0.8 mm Hg to yield the product (19.544 g, 91.9%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.43 (t, J = 6.8 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 1.88 (m, 2H), 1.73 (m, 2H), 1.45 (m, 2H), 1.35 (s, 10H).

11-bromo-1-(3,4-dimethoxyphenyl)undecan-1-one (2). Under an inert argon atmosphere, 1,2-dimethoxybenzene (8.81 mL, 68.9 mmol), aluminum chloride (10.11 g, 75.79 mmol), **1** (19.544 g, 68.9 mmol), and CH_2Cl_2 (340 mL) were added to a round-bottomed flask fitted with a condenser. The mixture was heated to reflux and stirred for 16 hours. After cooling, the mixture was poured into 6 *N* HCl, washed with water (3×), and filtered through a plug of silica using 2:1 hexanes:EtOAc. The mixture was concentrated *in vacuo*. The residue was recrystallized from toluene to yield 12.878 g (48.5%) of a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.56 (d, J = 13.6 Hz, 1H), 7.53 (s, 1H), 6.88 (d, J = 8.4 Hz, 1H), 3.94 (d, J = 3.2 Hz, 6H), 3.41 (t, J = 6.8 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 1.85 (m, 2H), 1.73 (m, 2H), 1.32 (m, 12H).

4-(11-bromoundecyl)-1,2-dimethoxybenzene (3). THF (200 mL), $NaBH_4$ (6.31 g, 167.0 mmol), and aluminum chloride (6.68 g, 50.1 mmol) were added to a round-bottomed flask. This mixture was stirred until all of the reagents were dissolved. The mixture was cooled to 0 °C, and **2** (12.878 g, 33.4 mmol) was added. The mixture was allowed to stir overnight, gradually warming to room temperature. It was then diluted with CH_2Cl_2, poured into a solution of saturated $NaHCO_3$, and the organic layers were extracted with CH_2Cl_2 (3 × 100 mL). The combined organics were washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in* *vacuo* to yield 9.88 g (80%) of product. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 6.78 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 6.8 Hz, 2H), 3.86 (d, *J* = 7.2 Hz, 6H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.85 (m, 2H), 1.57 (m, 2H), 1.42 (t, *J* = 6.8 Hz, 2H), 1.28 (s, 12H).

***S*-(11-(3,4-dimethoxyphenyl)undecyl) ethanethioate (4).** Potassium thioacetate (4.55 g, 39.9 mmol, 1.5 eq) was added to a round-bottomed flask containing **3** (9.88 g, 26.6 mmol, 1.0 eq) in THF (150 mL). The mixture was heated to reflux for 1.5 h, followed by stirring at room temperature for 16 hours. The reaction mixture was then poured into water and extracted with Et_2O. The combined organics were washed with water (3×), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by flash chromatography (4:1 hexanes:EtOAc) afforded the 5.403 g (55.4 %) of product. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 6.79 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.5 Hz), 2.32 (s, 3H), 1.56 (m, 5H), 1.27 (m, 15H).

4-(11-mercaptoundecyl)benzene-1,2-diol (5). A round-bottomed flask containing a solution of **4** (5.403 g, 14.74 mmol) in CH_2Cl_2 (100 mL) was cooled to 0 °C, and BBr_3 (28.99 g, 115.7 mmol) was added. The mixture was stirred at this temperature for 2 hours. Water was added slowly until gas evolution ceased. The mixture was then poured into water and extracted with Et_2O. The combined organics were washed with water, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield a pale brown solid. This solid was then combined with EtOH (150 mL), and hydrochloric acid (12 *M*, 15 mL). This mixture was heated to reflux, stirred for 2.5 hours and allowed to cool to room temperature. The mixture was concentrated, diluted with Et_2O, and washed with water (3×). The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (2:1 hexanes:EtOAc) to yield a pale yellow powder. This was recrystallized from 300 mL of an 8:1 mixture of hexanes/toluene to yield 3.15 g of the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 6.70 (d, *J* = 2.0 Hz, 1H), 6.62 (s, 1H), 6.60 (d, *J* = 2.0 Hz), 5.11 (s, 1H), 4.97 (s, 1H), 2.50 (m, 4H), 1.57 (m, 5H), 1.26 (m, 15H). MS: *m/z* calc'd for [M]+ ($C_{17}H_{28}O_2S$): 296.18; [M+H]+ found: 297.19.



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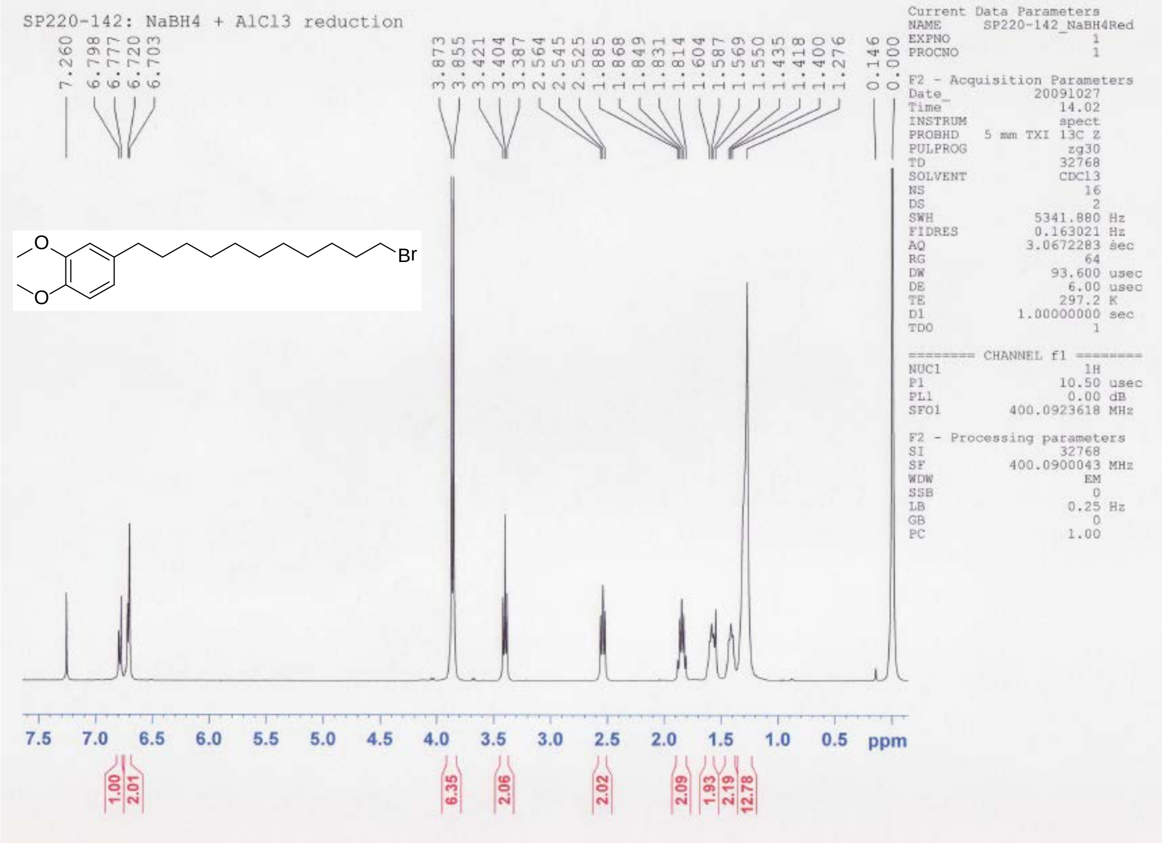

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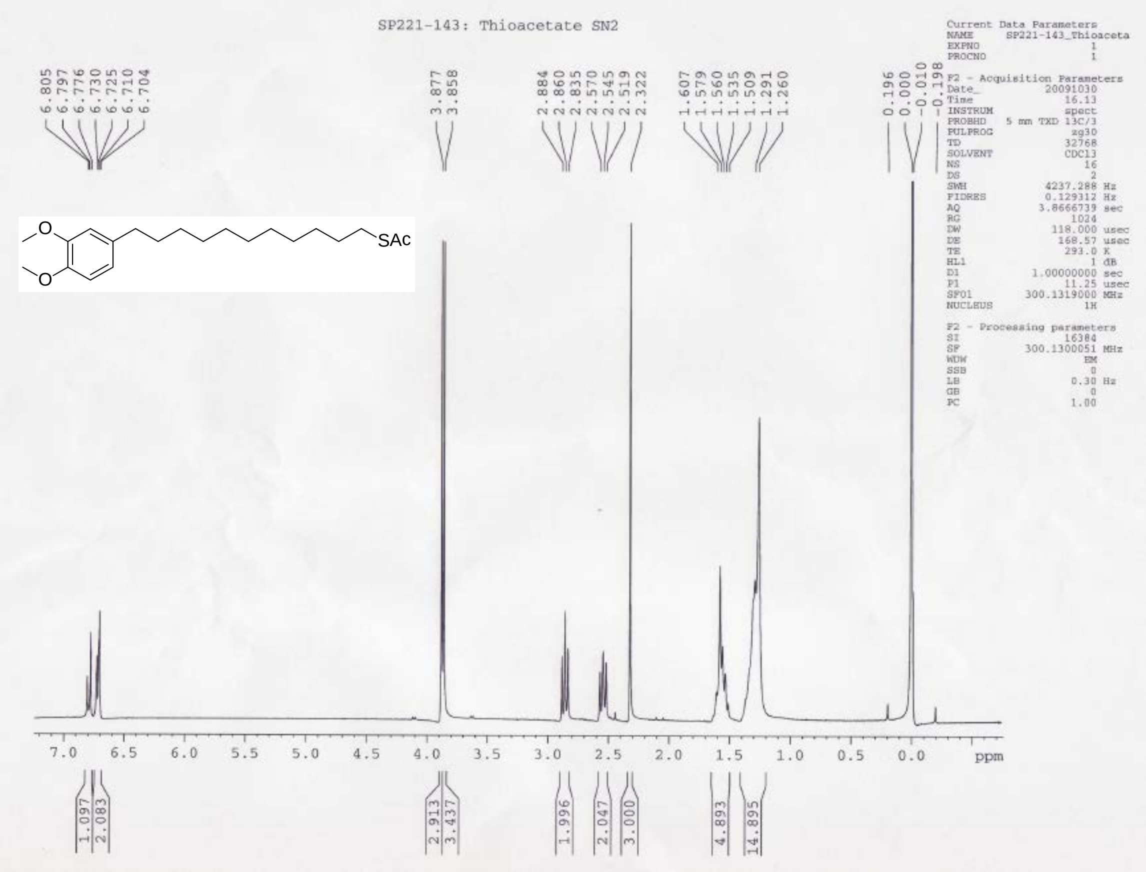

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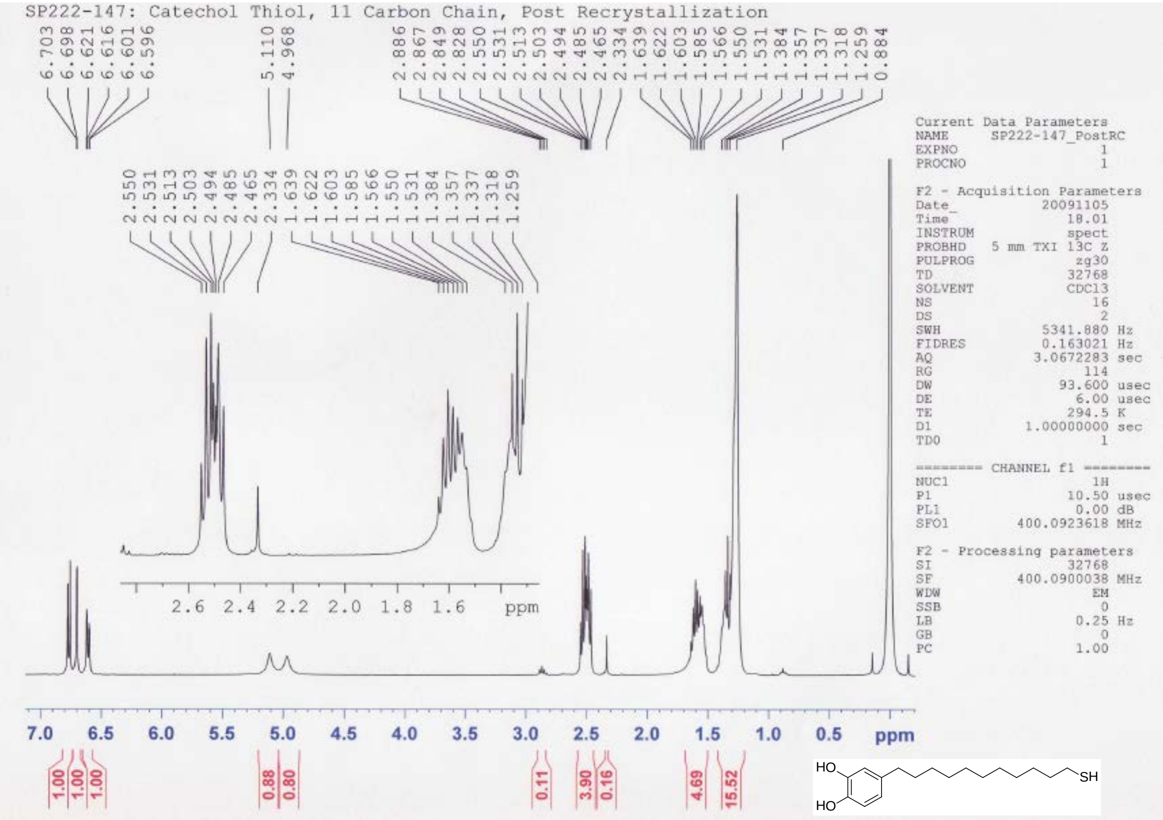

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Nanoparticle Synthesis:

All nanoparticle (NP) syntheses were performed using standard airless procedures and commercially available reagents without further purification. The following synthetic methods are based on previously reported procedures.

Gold, Following Hiramatsu, et al.[1] Au NPs were synthesized under ambient atmosphere by first bringing a solution of 1.45 mL (4.41 mmol) oleylamine (97%, Pfaltz & Bauer) in 25 mL of toluene to reflux, followed by the fast injection of a solution of 0.60 mL (1.82 mmol) oleylamine, 0.0863 g (0.219 mmol) of $HAuCl_4 \cdot 3H_2O$ (99.99%, Alfa Aesar), and 1.0 mL toluene. The mixture was heated at 110 °C for two hours before cooling to room temperature.

Magnetite (Fe_3O_4), Following Sun, et al.[2] Fe_3O_4 NPs were prepared by the thermal decomposition and reduction of 0.700 g (1.98 mmol) of $Fe(acac)_3$ (acac = acetylacetonate, 98%, Strem) dissolved in a mixture of 1.50 g (5.80 mmol) 1,2-hexadecanediol (90%, Sigma Aldrich), 3.0 mL (9.1 mmol) oleylamine, and 1.0 mL (3.2 mmol) oleic acid (99%, Alfa Aesar) in 20 mL of benzyl ether (99%, Sigma-Aldrich) in a 100 mL three-necked, round-bottomed flask. After degassing under vacuum at room temperature for 1 h and backfilling with nitrogen, the solution was heated at 200 °C for two hours and then refluxed at ~300 °C for 30 min before cooling to room temperature.

Nickel, Following Johnston-Peck, et al.[3] Nickel NPs were prepared by the thermally-driven reduction of 0.20 g (0.78 mmol) $Ni(acac)_2$ (98%, TCI America) in a mixture of 2.0 mL (6.1 mmol) oleylamine and 5.0 g (11.6 mmol) of trioctylphosphine oxide (TOPO, 90%, Sigma-Aldrich) in a 100 mL three-necked, round-bottomed flask. After degassing under vacuum at 60 °C for 2 h and backfilling with nitrogen, the solution was heated to 240 °C and held at this temperature for 30 min. As the temperature was increasing, when the temperature reached

100 °C, 0.3 mL trioctylphosphine (TOP, 97%, Strem) was added by syringe. After heating, the mixture was cooled to room temperature and ~5 mL toluene was added to prevent crystallization of the TOPO.

Cobalt, Following Bao, et al.[4] Cobalt NPs were prepared through a thermal decomposition approach by first combining 0.20 g (0.51 mmol) of trioctylphosphine oxide (TOPO, 99%, Strem), 0.40 mL (1.25 mmol) oleic acid (99%, Alfa Aesar), and 12 mL of 1,2 dichlorobenzene (DCB, anhydrous, EMD Chemicals) in a 100 mL three-necked, round-bottomed flask. After degassing under vacuum at room temperature for 1 h and backfilling with nitrogen, the solution was heated to reflux (181 °C), and then 0.54 g (1.50 mmol) dicobalt octacarbonyl (Strem) freshly dissolved in 3.0 mL DCB was quickly injected by syringe. The mixture was then refluxed for an additional 8 min before cooling to room temperature.

FePt, Following Nandwana, et al.[5] FePt NPs were prepared by first adding 0.101 g (0.25 mmol) $Pt(acac)_2$ (97%, Strem) to 15 mL of benzyl ether (99%, Acros) in a 100 mL three-necked, round-bottomed flask. After degassing under vacuum at room temperature for 1 h and backfilling with nitrogen, the solution was heated to 100 °C. When the temperature reached 100 °C, 0.40 mL (1.17 mmol) oleylamine, 0.26 mL (0.82 mmol) oleic acid, and 48 μL (0.36 mmol) iron pentacarbonyl (99.5%, Alfa Aesar) were immediately injected into the solution by syringe. The solution was slowly heated to 260 °C and then held at this temperature for 30 min before cooling to room temperature. Elemental analysis by energy dispersive spectroscopy (EDS) gave an average NP composition of $Fe_{43}Pt_{57}$.

Post-Synthesis Purification of Fe_3O_4, Ni, Co, FePt, and Au Nanoparticles. For each mL of the cooled reaction mixtures of Fe_3O_4, Ni, Co, and FePt NPs, 2 mL of ethanol was added to cause flocculation. For Au NPs, 1 mL of methanol was added per mL of the cooled reaction mixture. The NPs were then separated from the solvent, excess ligands, and reaction by-products by centrifugation at 4000 rpm for 75 s. After discarding the supernatant, the NPs were immediately re-dispersed in hexanes.

Preparation of the Au Substrate:

Gold metal thin films were prepared by thermal evaporation onto a Si wafer (1 µm thick surface oxide, Addison Engineering). Prior to thermal evaporation, the Si substrates were cleaned in a solution of DI water, ammonium hydroxide (14.8 *M*, Fisher Scientific), and hydrogen peroxide (30%, ACS certified, Fisher Scientific) in a 2:1:1 ratio for 15 minutes. The substrates were then rinsed thoroughly with water and ethanol (100%, Pharmco), dried with a stream of dry nitrogen, and treated with ultraviolet light and ozone (UVO, Bioforce Nanosciences ProCleaner) for 20 min. Au thin films (60 nm) were deposited on top of a 3 nm titanium adhesion layer by thermal evaporation onto the Si/SiO_x substrates. The Ti adhesion layer was deposited at a rate of 2 Å/s, and the Au deposition rate was initially 1 Å/s for the first 10 Å and then was quickly increased to 15 Å/s for the rest of the deposition. Au pellets (99.999%, Kurt J. Lesker) and Ti slugs (99.995%, 3.175 mm × 3.175 mm, Alfa Aesar) were used as metal sources, and evaporation boats were purchased from R. D. Mathis Company (type S4-.015W for Ti and S42-.015W for Au). Thermal evaporation was performed using an MBraun evaporator within an MBraun nitrogen glovebox. The film thicknesses were measured using a quartz crystal microbalance located just below the substrate holder in the evaporator. The tooling factors were determined by measuring the true thicknesses of thin films with a profilometer.

Preparation of PDMS Stamps:

PDMS molds were replicated from silicon wafers with recessed features defined by conventional photolithography techniques within an epoxy-based negative photoresist (Su-8, Micro Resist Technology). Photolithography was carried out at the Chapel Hill Analytical and Nanofabrication Laboratory. Silicon wafers (Addison Engineering) were cleaned in a solution of DI water, ammonium hydroxide, and hydrogen peroxide (2:1:1) for 15 min, as detailed above. After an additional 30 min of UVO cleaning, a 10:1 (w:w) Su-8 50 (MicroChem): γ-butyrolactone (Alfa Aesar) solution was spincoated onto the substrate at 3000 rpm using a Chemat Technology (KW-4A) spincoater. Profilometry measurements showed that the Su-8 film was 7 μm thick. The Si/Su-8 substrate was cured on a hotplate at 90 °C for 3 min, cooled for 10 min, and exposed using a Karl Suss MA6/BA6 mask aligner (350 W lamp, 365 nm) for 6 s. The Si/Su-8 substrate was post baked on a hotplate for 2 min then allowed to cool for 10 min. The substrate was developed in Su-8 developer (MicroChem) for 4.5 min, rinsed with isopropyl alcohol, dried with nitrogen, and cured in a vacuum oven for 2 h at 200 °C. The aspect ratio (depth:width) of the master was determined to be 1:5 by profilometry. The master was placed in a Petri dish, and a minimal amount of the liquid PDMS prepolymer (Dow Corning, Sylgard 184) and cross-linker mixture was poured into the Petri dish (10:1 w:w ratio) to cover the master, resulting in a layer less than 1 mm thick. The Petri dish was placed under vacuum at 1 mbar for 20 min to remove residual air pockets and to ensure complete filling of the features of the master. After removal from the vacuum, the material was cured at 70 °C overnight. The cured stamp was removed from the master with tweezers and cut to size with a razor blade. Each master was reused multiple times without a loss of fidelity.

Patterned Au Nanoparticles:

As mentioned in the main text, Au NPs were patterned by the same procedure as the magnetic nanoparticles. A TEM image of the Au NPs is shown in Figure S-1. Using decanedithiol active monolayers, a distinct pattern can be seen in Figure S-2.

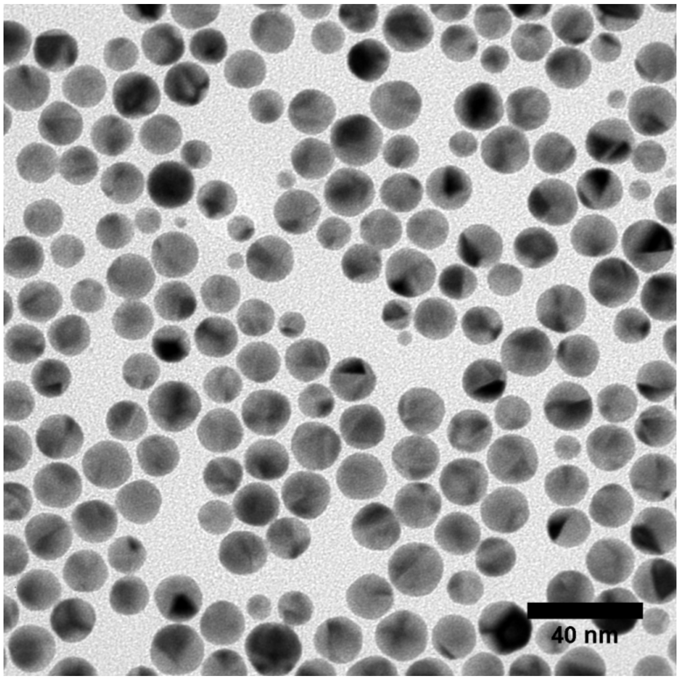

Figure S-1. TEM of Au NPs.

Patterning Au nanoparticles

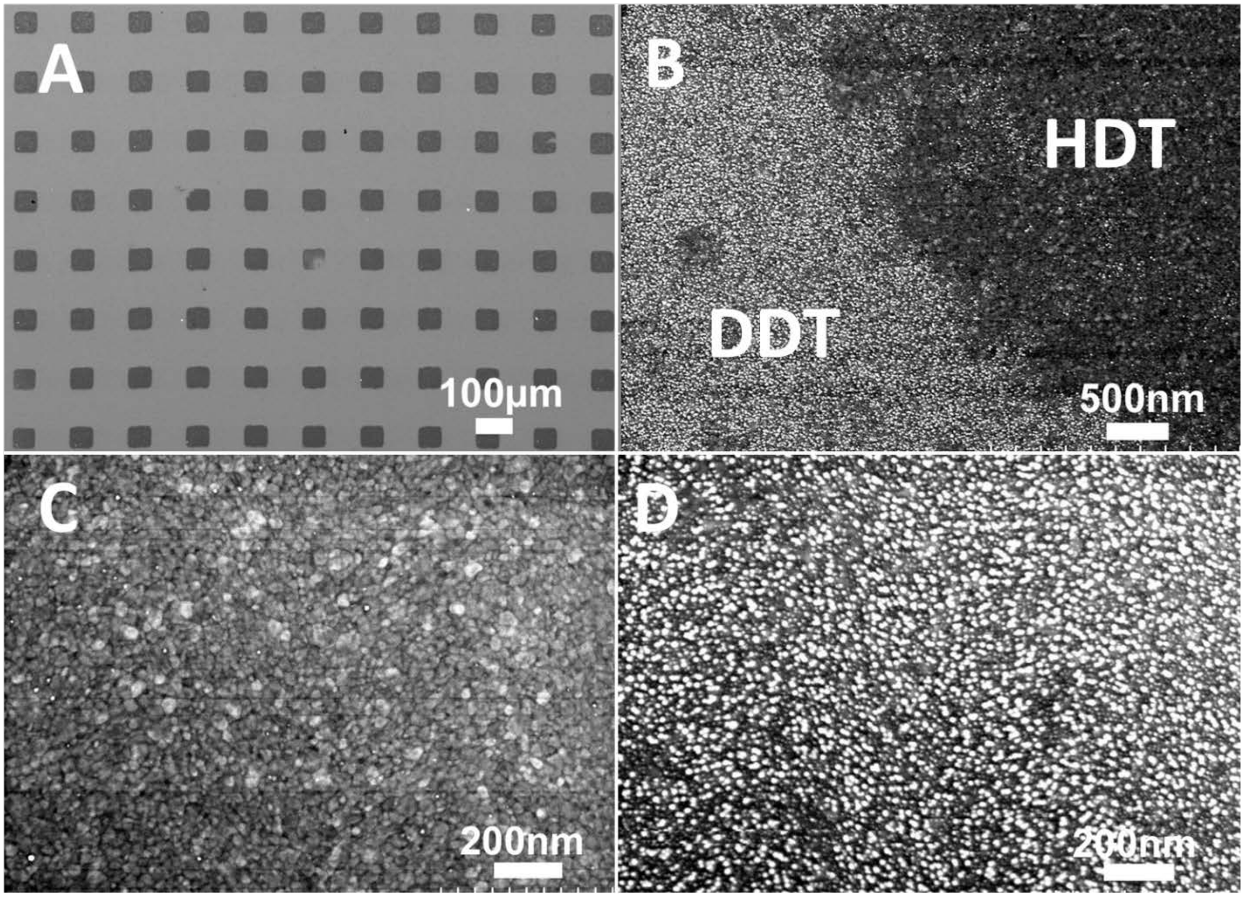

Figure S-2. SEM of patterned Au NPs. (A) 50 μm × 50 μm pattern using DDT monolayer, (B) edge of a HDT/DDT region, (C) absence of NPs in the HDT region, and (D) dense coverage in the DDT region. (Patterning conditions: 1 mg/mL NP solution, 60 min soak time)

Patterning Co nanoparticles

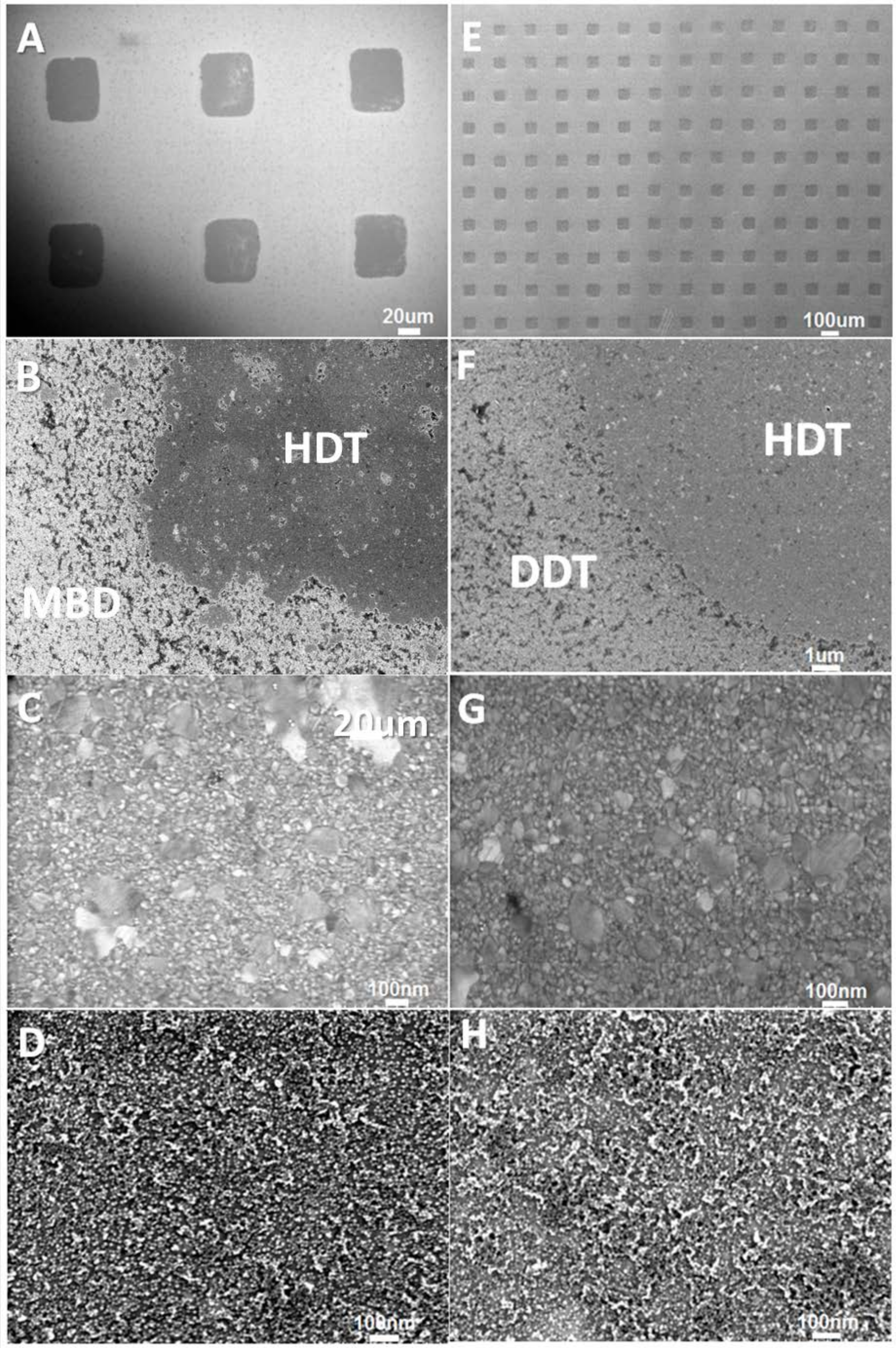

Figure S-3. SEM of patterned Co NPs. (A) 50 μm × 50 μm pattern using MBD monolayer, (B) edge of a HDT/MBD patterned region, (C) absence of NPs in the HDT region, (D) dense NP coverage in the MBD region, (E) patterned surface using DDT monolayer, (F) edge of a HDT/DDT patterned region, (G) absence of NPs in the HDT region, and (H) dense coverage of NPs in the DDT region. (Patterning conditions: 0.51 mg/mL NP solution, 30 min soak time)

Patterning FePt nanoparticles

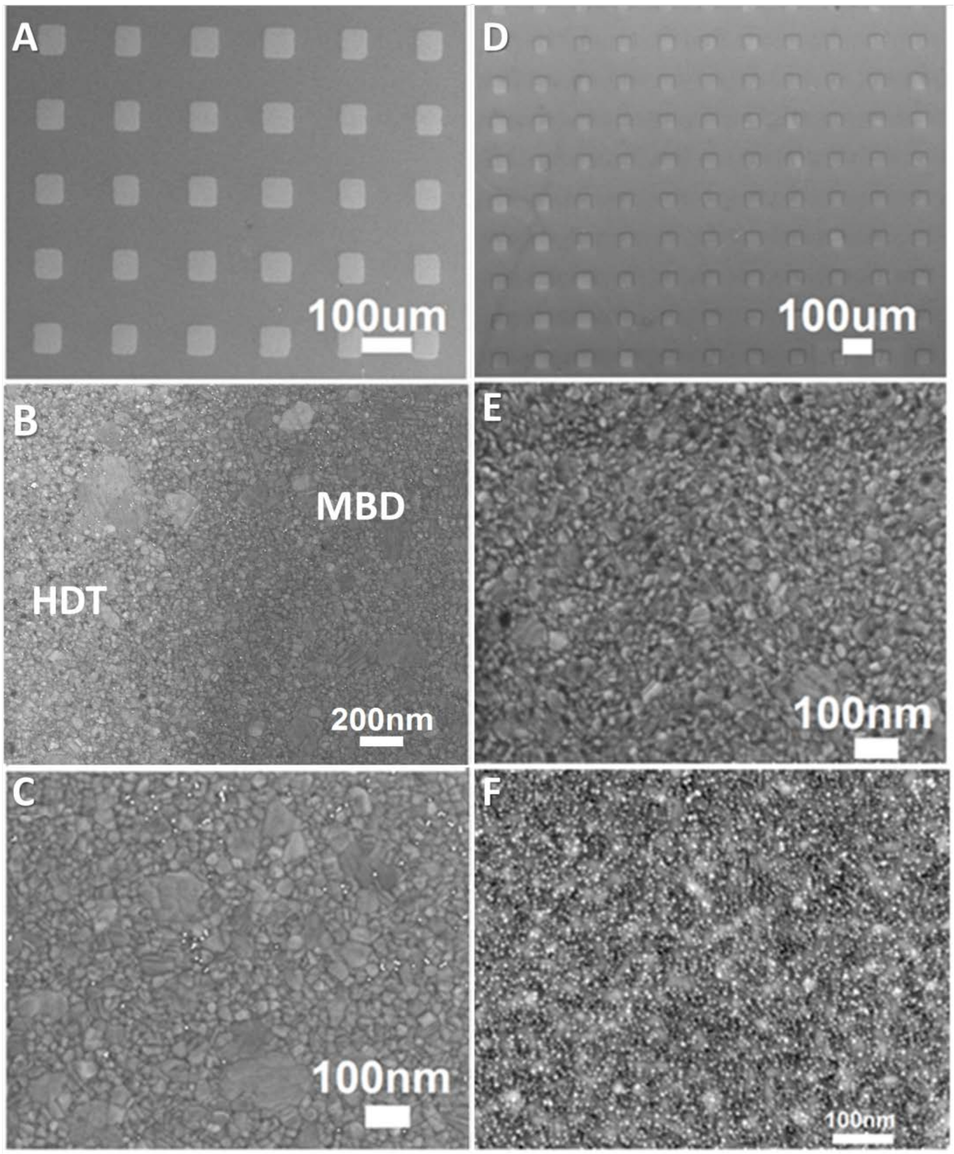

Figure S-4. SEM of patterned FePt NPs. (A) 50 μm × 50 μm pattern using MBD, (B) edge of a HDT/MBD patterned region, (C) absence of NPs in the MBD region, (D) patterned surface using DDT monolayer, (E) absence of NPs in the HDT region, and (F) dense coverage of NPs in the DDT region. (Patterning conditions: 1.36 mg/mL NP solution, 10 min soak time)

Patterning Fe3O4 nanoparticles

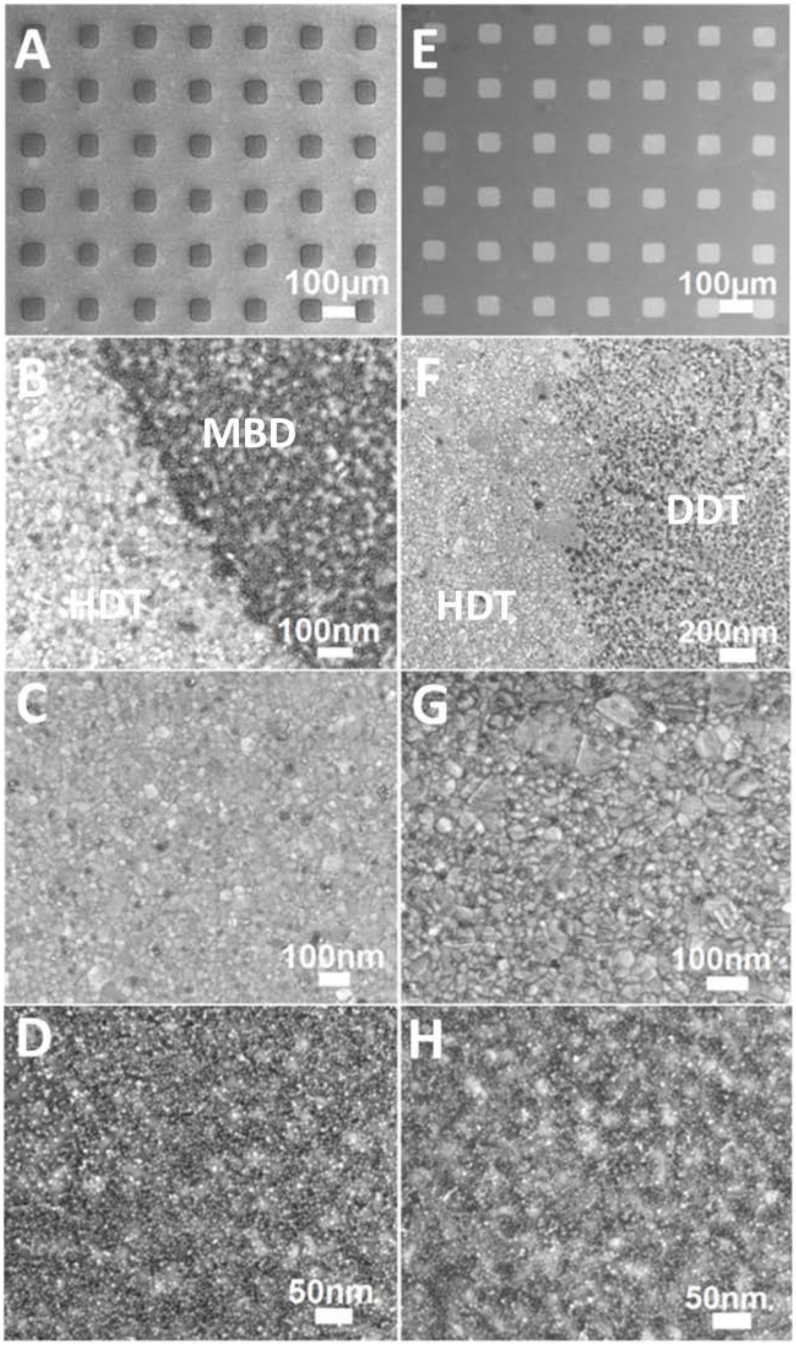

Figure S-5. SEM of patterned Fe_3O_4 NPs. (A) 50 µm × 50 µm pattern using MBD monolayer, (B) edge of a HDT/MBD patterned region, (C) absence of NPs in the HDT region, (D) dense coverage of NPs in the MBD region, (E) patterned NP surface using DDT monolayer, (F) edge of a HDT/DDT patterned region, (G) absence of NPs in the HDT region, and (H) Fe_3O_4 NPs in the DDT region. (Patterning Conditions: 1.00 mg/mL NP solution, 15 min soak time)

Patterning Ni nanoparticles

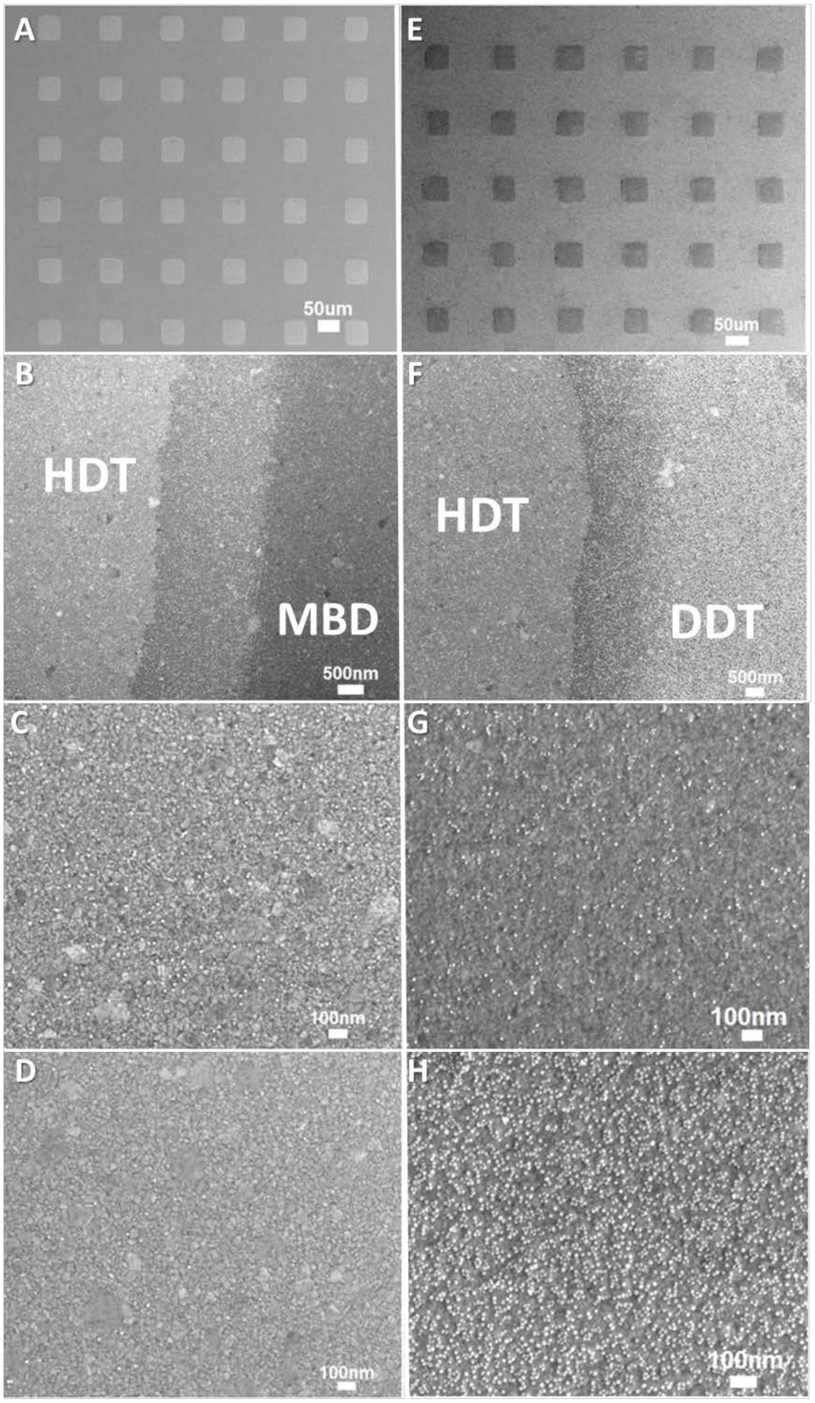

Figure S-6. SEM of patterned Ni NPs. (A) 50 μm × 50 μm pattern using MBD monolayer, (B) edge of a HDT/MBD patterned region, (C) absence of NPs in the HDT region, (D) absence of NPs in the MBD region, (E) patterned surface using DDT monolayer, (F) edge of a HDT/DDT patterned region, (G) absence of NPs in the HDT region, and (H) Ni NPs in the DDT region. (Patterning conditions: 5.69 mg/mL NP solution, 24 h soak time)

References:

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5. V. Nandwana, K. E. Elkins, N. Poudyal, G. S. Chaubey, K. Yano and J. P. Liu, *The Journal of Physical Chemistry C*, 2007, **111**, 4185-4189.