

Electronic Supplementary Information

Characterization of Surface Ligands on Functionalized Magnetic Nanoparticles Using Laser Desorption/Ionization Mass Spectrometry (LDI-MS)

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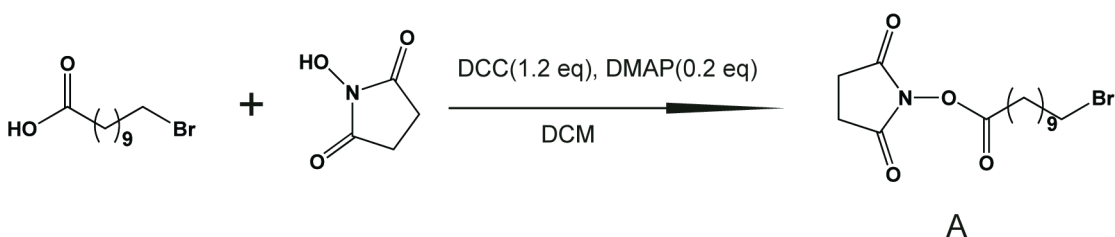
SI-I FePt NPs preparation

Synthesis of thiolalkyl tetra (ethylene glycol)lyated trimethyl ammonium ligand (TTMA, Ligand T)

This ligand was synthesized via a previously reported method.¹

Synthesis of dopamine trimethyl ammonium ligand (DTMA, Ligand D)

Step 1.

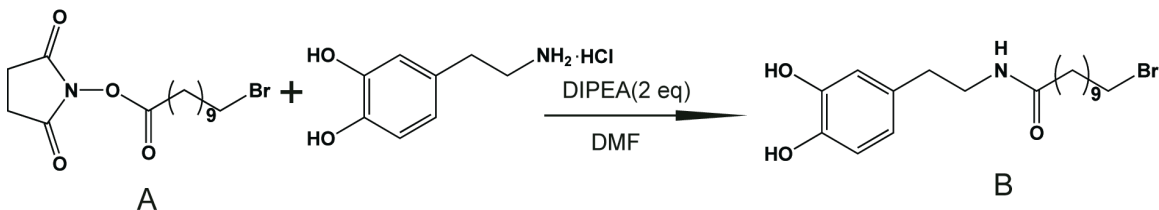


1-Bromoundecanoic acid (500 mg, 1.88 mmol) was dissolved in dry dichloromethane (DCM). To this solution N-hydroxysuccinimide (216 mg, 1.88 mmol) was added followed by a solution of N,N'-Dicyclohexylcarbodiimide (DCC) (456 mg, 2.26 mmol) in 5 mL of dry DCM at 0 °C. The mixture was stirred for 15 min, and then 4-dimethylaminopyridine (DMAP) (46 mg, 0.38 mmol) was added. After 1 h, the reaction was allowed to reach room temperature, upon which time a

white precipitate began to form, indicating the advancement of the reaction. The reaction was allowed to continue for 24 h. The white precipitate was filtered and the solvent was removed from the filtrate to give a residue that was then re-dissolved in DCM and washed with water. The organic layer was dried over Na₂SO₄, filtered and evaporated and the crude product that was obtained was purified by flash chromatography with 3/1-hexane / Ethylacetate as eluent to give the activated acid in 90 % yield.

¹H NMR_(400 MHz, CDCl₃): 1.24-1.42 (m, 12H, CH₂); 1.56 (m, 2H, CH₂); 1.77 (m, 2H, CH₂); 2.25 (t, 2H, CH₂); 2.72 (t, 4H, CH₂); 3.31(t, 2H, CH₂)

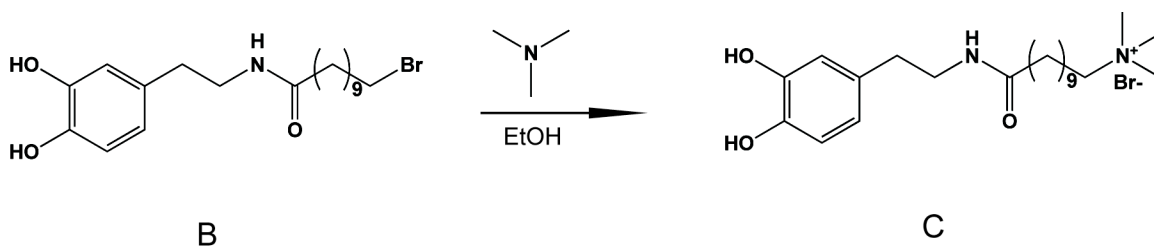
Step 2.



Hydroxytyramine•HCl (356 mg, 1.88mmol) was dissolved in dry dimethylformamide (DMF), and the solution was purged for 10 min with N₂ gas. N,N-Diisopropylethylamine (DIPEA)(507 mg, 3.76 mmol) was slowly added to the reaction mixture. The mixture was stirred for another 5 min and then compound A (670 mg, 1.18 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 64 h. After that the DMF was evaporated under reduced pressure. The residue was dissolved in ethyl acetate. The soluble part was taken out and washed with 1 M HCl and brine water. The organic component was dried over Na₂SO₄ and evaporated to obtain the crude product. The crude product obtained was purified by flash chromatography with 3/1- EtOAc / hexane as eluent to give the activated acid in 55 % yield.

¹H NMR_(400 MHz, CDCl₃): 1.24-1.42 (m, 12H, CH₂); 1.56 (m, 2H, CH₂); 1.81 (m, 2H, CH₂); 2.18 (t, 2H, CH₂); 2.65 (t, 2H, CH₂); 3.31 (t, 2H, CH₂); 3.55 (t, 2H, CH₂); 6.42 (d, 1H, H_{arom}); 6.66-6.74 (m, 2H, H_{arom})

Step 3.

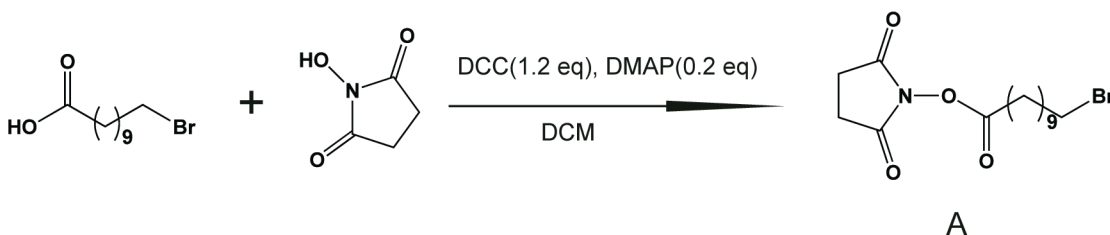


Compound B (230 mg, 0.59 mmol) and trimethylamine (696 mg, 11.8 mmol) were dissolved in 1 mL of ethanol. The solution was degassed with N₂ gas. The reaction mixture was stirred at room temperature for 64 h, and then the solvent was evaporated under vacuum. The residue was purified by washing with hexane and ether several times to obtain C in 99% yield.

¹H NMR (400 MHz, MeOD): 1.24-1.42 (m, 12H, CH₂); 1.56 (m, 2H, CH₂); 1.81 (m, 2H, CH₂); 2.18 (t, 2H, CH₂); 2.78 (t, 2H, CH₂); 3.19 (s, 9H, CH₃); 3.31 (t, 2H, CH₂); 3.55 (t, 2H, CH₂); 6.42 (d, 1H, H_{arom}); 6.66-6.74 (m, 2H, H_{arom})

Synthesis of dopamine trimethyl ammonium ligand (DTMA)

Step 1.

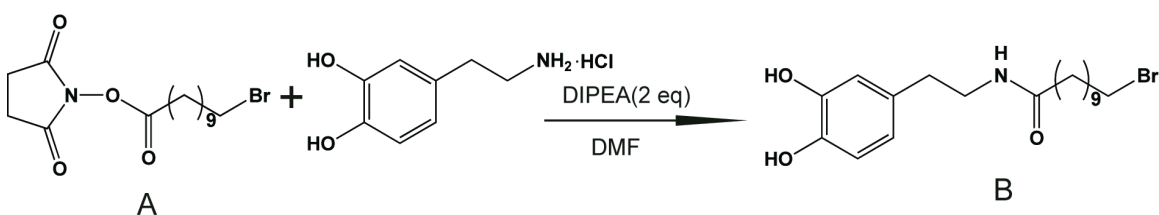


1-Bromoundecanoic acid (500 mg, 1.88 mmol) was dissolved in dry DCM. To this solution N-hydroxysuccinimide (216 mg, 1.88 mmol) was added followed by a solution of DCC (456 mg, 2.26 mmol) in 5 mL of dry DCM at 0 °C. The mixture was stirred for 15 min, and then DMAP (46 mg, 0.38 mmol) was added. After 1 h, the reaction was allowed to reach room temperature upon which time a white precipitate began to form, indicating the advancement of the reaction. The reaction was continued for 24 h. The white precipitate was filtered, and the solvent was removed from the filtrate to give a residue that was then re-dissolved in DCM and washed with water. The organic layer was dried over Na₂SO₄, filtered and evaporated and the crude product

obtained was purified by flash chromatography with 3/1-hexane / EtOAc as eluent to give the activated acid in 90 % yield.

^1H NMR_(400 MHz, CDCl_3): 1.24-1.42 (m, 12H, CH_2); 1.56 (m, 2H, CH_2); 1.77 (m, 2H, CH_2); 2.25 (t, 2H, CH_2); 2.72 (t, 4H, CH_2); 3.31(t, 2H, CH_2)

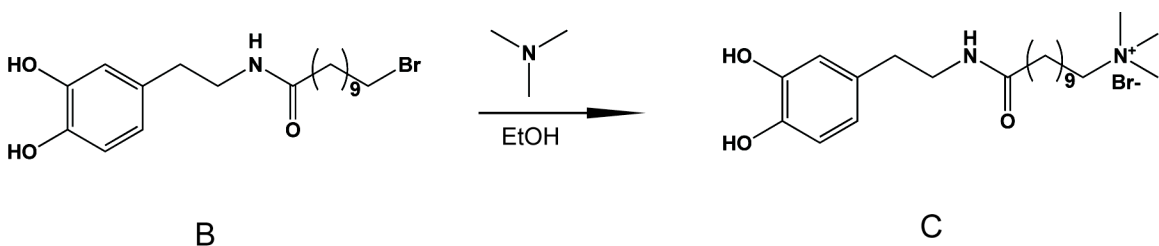
Step 2.



Hydroxytyramine•HCl (356 mg, 1.88 mmol) was dissolved in dry DMF and the solution was purged for 10 min with N_2 gas. DIPEA (507 mg, 3.76 mmol) was slowly added to the reaction mixture. The mixture was stirred for another 5 min, and then compound A (670 mg, 1.18 mmol) was added o the reaction mixture. The mixture was stirred at room temperature for 64 h. After that the DMF was evaporated under reduced pressure. The residue was dissolved in ethyl acetate. The soluble part was taken out and washed with 1 M HCl and brine water. The organic component was dried over Na_2SO_4 and evaporated to get the crude product. The crude product obtained was purified by flash chromatography with 3/1- EtOAc / hexane as eluent to give the activated acid in 55 % yield.

^1H NMR_(400 MHz, CDCl_3): 1.24-1.42 (m, 12H, CH_2); 1.56 (m, 2H, CH_2); 1.81 (m, 2H, CH_2); 2.18 (t, 2H, CH_2); 2.65 (t, 2H, CH_2); 3.31 (t, 2H, CH_2); 3.55 (t, 2H, CH_2); 6.42 (d, 1H, H_{arom}); 6.66-6.74 (m, 2H, H_{arom})

Step 3.

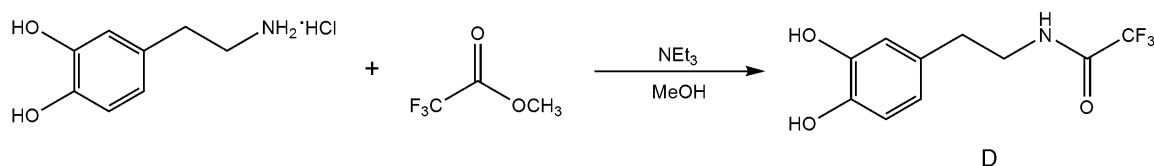


Compound B (230 mg, 0.59 mmol) and trimethylamine (696 mg, 11.8 mmol) were dissolved in 1 mL of EtOH. The solution was degassed with N₂ gas. The reaction mixture was stirred at room temperature for 64 h, and then the solvent was evaporated under vacuum. The residue was purified by washing with hexane and ether several times to obtain C in 99% yield.

¹H NMR (400 MHz, MeOD): 1.24-1.42 (m, 12H, CH₂); 1.56 (m, 2H, CH₂); 1.81 (m, 2H, CH₂); 2.18 (t, 2H, CH₂); 2.78 (t, 2H, CH₂); 3.19 (s, 9H, CH₃); 3.31 (t, 2H, CH₂); 3.55 (t, 2H, CH₂); 6.42 (d, 1H, H_{arom}); 6.66-6.74 (m, 2H, H_{arom})

Synthesis of ligands L1 and L2

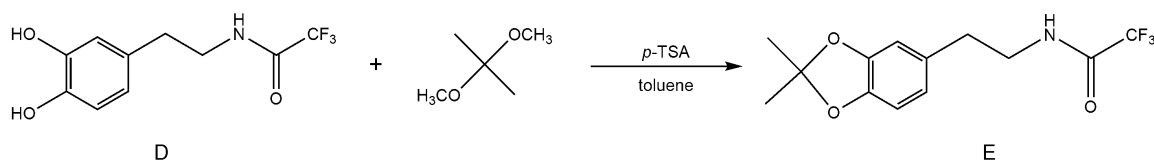
Step 1.



Hydroxytyramine•HCl (2.6 g, 13.7 mmol) was dissolved in 50 mL methanol and the solution was purged for 30 min with N₂ gas. Methyl trifluoroacetate (2.8 mL, 28.1 mmol) and triethylamine (8.0 mL) was added to the reaction mixture. The mixture was stirred at room temperature overnight. The volatile solvents were removed by rotary evaporation and the residue was treated with HCl to a pH of about 1 and extracted by ethyl acetate. The organic layer was washed with water, dried over MgSO₄, and evaporated to give D in 88% yield.

¹H NMR (400 MHz, MeOD): 2.61 (t, 2H, CH₂); 3.31 (t, 2H, CH₂); 6.43 (dd, 1H, H_{arom}); 6.58 (d, 1H, H_{arom}); 6.63 (d, 1H, H_{arom}); 8.66 (s, 2H, OH); 9.39 (s, 1H, NH).

Step 2.

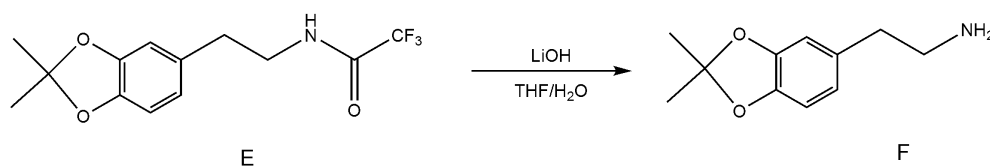


Compound D (3.0 g, 12.0 mmol) and 2,2-dimethoxypropane (6.0 mL, 48.0 mmol) were dissolved in toluene (100 mL) and stirred under reflux for 10 min. To the reaction mixture *p*-

toluenesulfonic acid monohydrate (104 mg) was added and stirred for 24 h under reflux. After cooling, the volatile solvent was removed by rotary evaporation. The crude product obtained was purified by flash chromatography with 3/1- hexane/EtOAc as eluent to give E in 90 % yield.

^1H NMR_(400 MHz, MeOD): 1.61 (s, 6H, CH_3); 2.70 (t, 2H, CH_2); 3.31 (t, 2H, CH_2); 6.60 (dd, 1H, H_{arom}); 6.68 (d, 1H, H_{arom}); 6.72 (d, 1H, H_{arom}); 9.41 (s, 1H, NH).

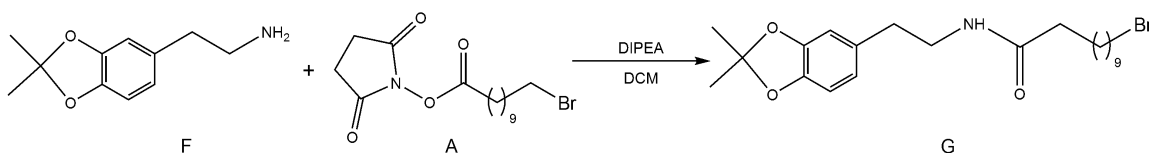
Step 3.



Compound E (1.5 g, 5.20 mmol) was dissolved in tetrahydrofuran (THF) (10 mL). Lithium hydroxide (1.1 g, 26.0 mmol) in 5 mL water was added to the reaction mixture. The mixture was stirred at room temperature for 48 h. After that the THF was evaporated under reduced pressure, the residue re-dissolved in DCM and washed with water, dried over MgSO_4 , and evaporated to give F as light yellow oil in 87% yield

^1H NMR_(400 MHz, CDCl_3): 1.65 (s, 6H, CH_3); 2.43 (br, 2H, NH_2); 2.69 (t, 2H, CH_2); 6.59-6.66 (m, 3H, H_{arom}).

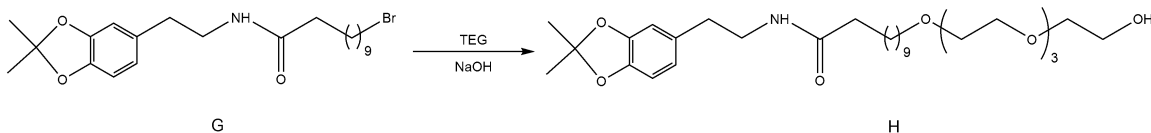
Step 4.



Compound F (1.0 g, 5.18 mmol) was dissolved in dry DCM. The mixture was stirred for another 5 min and then DIPEA (1.3 mg, 10.4 mmol) and compound A (1.66 g, 5.18 mmol) were added to the reaction mixture. The mixture was stirred at room temperature for 24 h. After that the DCM was evaporated under reduced pressure. The crude product obtained was purified by flash chromatography with 3/1- EtOAc / hexane as eluent to give G in 75 % yield.

^1H NMR_(400 MHz, CDCl_3): 1.24 (m, 12H, CH_2); 1.45 (m, 2H, CH_2); 1.61 (s, 6H, CH_3) 1.78 (m, 2H, CH_2); 2.01 (t, 2H, CH_2); 2.58 (t, 2H, CH_2); 3.19 (t, 2H, CH_2); 3.51 (t, 2H, CH_2); 6.57 (d, 1H, H_{arom}); 6.66 (d, 1H, H_{arom}); 6.69 (d, 1H, H_{arom}); 7.74 (br, 1H, NH).

Step 5.



NaOH (0.2 g, 5.00 mmol) in a minimum amount of water was added to 7.8 mL of tetraethyleneglycol (TEG: 8.8 g, 45.3 mmol) and stirred for 1 h under reflux. To this reaction mixture, 2.0 g of compound G was added and stirred for 24 h at 100 °C. The reaction mixture once completed was extracted by washing with water and ethyl acetate three times. Afterward, the organic layer was separated and concentrated at reduced pressure. The crude product was purified by flash chromatography using ethyl acetate as an eluent. The solvent was removed in vacuum to obtain compound H as yellow oil in 60 % yield.

^1H NMR_(400 MHz, CDCl_3): 1.29 (m, 14H, CH_2); 1.58 (m, 2H, CH_2); 1.68 (s, 6H, CH_3) 2.13 (t, 2H, CH_2); 2.72 (t, 2H, CH_2); 3.46 (m, 4H, CH_2); 3.67 (m, 16H, CH_2); 5.51 (br, 1H, NH); 6.59 (m, 2H, H_{arom}); 6.66 (d, 1H, H_{arom}).

Step 6.

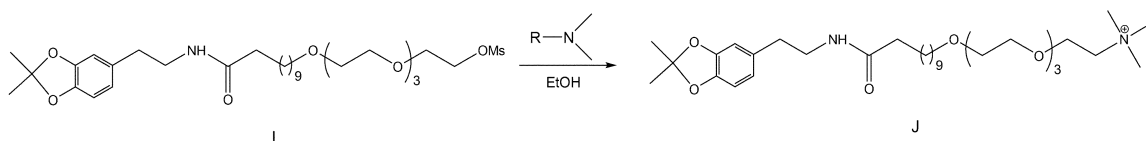


To a solution of compound H (1.0 g, 1.81 mmol) in dry DCM at 0 °C, triethylamine (0.5 mL, 3.61 mmol) was added. Methanesulfonyl chloride (MsCl) (0.2 mL, 2.72 mmol) was injected drop by drop to the solution maintaining the temperature less than 5 °C. After 30 minutes the reaction mixture was warmed up to room temperature and stirred for another 24 hours. Once the reaction was completed, the DCM was evaporated. The crude product was purified by flash

chromatography using ethyl acetate as an eluent. The solvent was removed in vacuum to obtain compound I in 85 % yield.

^1H NMR_(400 MHz, CDCl_3): 1.28 (m, 14H, CH_2); 1.59 (m, 4H, CH_2); 1.68 (s, 6H, CH_3); 2.13 (t, 2H, CH_2); 2.72 (t, 2H, CH_2); 3.10 (s, 3H, CH_3); 3.46 (m, 4H, CH_2); 3.58 (m, 2H, CH_2); 3.66 (m, 10H, CH_2); 3.78 (m, 2H, CH_2); 5.48 (br, 1H, NH); 6.59 (m, 2H, H_{arom}); 6.66 (d, 1H, H_{arom}).

Step 7.

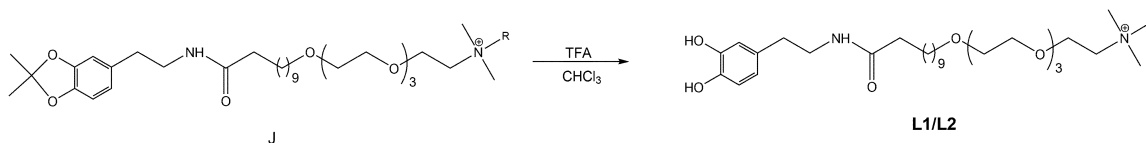


Compound I (700 mg, 1.11 mmol) and trimethylamine (**L1**) or *N,N*-dimethylhexylamine (**L2**) (22.2 mmol) were dissolved in 5 mL of ethanol. The solution was degassed with N_2 gas. The reaction mixture was stirred at 35 °C for 48 h, and then the solvent was evaporated under vacuum. The residue was purified by washing with hexane and ether several times to obtain J in 95% yield.

L1: ^1H NMR_(400 MHz, MeOD): 1.28 (m, 14H, CH_2 / CH_3); 1.66 (s, 6H, CH_3); 2.63 (m, 2H, CH_2); 2.86 (m, 4H, CH_2); 3.29 (m, 10H, CH_2); 3.47 (m, 5H, CH_2 / CH_3); 3.64 (m, 12H, CH_2); 3.81 (m, 2H, CH_2); 5.65 (br, 1H, NH); 6.62 (m, 2H, H_{arom}); 6.69 (d, 1H, H_{arom}).

L2: ^1H NMR_(400 MHz, MeOD): 0.91 (m, 3H, CH_3); 1.33 (m, 18H, CH_2); 1.58 (m, 4H, CH_2); 1.68 (s, 6H, CH_3); 1.76 (m, 2H, CH_2); 2.14 (m, 2H, CH_2); 2.75 (m, 4H, CH_2); 3.29 (m, 4H, CH_2); 3.47 (m, 5H, CH_2 / CH_3); 3.63 (m, 13H, CH_2 / CH_3); 3.81 (m, 2H, CH_2); 3.98 (m, 2H, CH_2); 5.63 (br, 1H, NH); 6.60 (m, 2H, H_{arom}); 6.67 (d, 1H, H_{arom}).

Step 8.



Compound J was dissolved in chloroform and an excess of trifluoroacetic acid (TFA, ~ 20 equivalents) was added. The reaction mixture was stirred for 24 hours at room temperature. The

light brown residue was purified by washing with hexane and ether several times to obtain ligands **L1** and **L2** in 95% yield.

L1: ^1H NMR (400 MHz, MeOD): 1.23 (m, 14H, CH_2/CH_3); 2.68 (m, 2H, CH_2); 2.86 (m, 4H, CH_2); 3.29 (m, 15H, CH_2/CH_3); 3.59 (m, 12H, CH_2); 3.81 (m, 2H, CH_2); 6.54 (m, 1H, H_{arom}); 6.79 (m, 2H, H_{arom}); 7.74 (br, 1H, NH).

L2: ^1H NMR (400 MHz, MeOD): 0.88 (m, 3H, CH_3); 1.27 (m, 18H, CH_2); 1.54 (m, 4H, CH_2); 1.69 (m, 2H, CH_2); 2.28 (m, 2H, CH_2); 2.71 (m, 4H, CH_2); 2.90 (m, 3H, CH_3); 3.09 (m, 6H, CH_2); 3.28 (m, 2H, CH_2); 3.50 (m, 5H, CH_2/CH_3); 3.63 (m, 12H, CH_2/CH_3); 3.87 (m, 2H, CH_2); 6.55 (dd, 1H, H_{arom}); 6.76 (d, 1H, H_{arom}); 6.79 (d, 1H, H_{arom}).

Functionalization of FePt and Fe_3O_4 NPs

Functionalized FePt and Fe_3O_4 NPs were obtained following previous methods.²⁻⁴ In a typical experiment 10 mg of oleic acid and oleylamine stabilized FePt or Fe_3O_4 NPs were mixed with different amount of ligands in 5 mL of DCM. The mixture was stirred at room temperature overnight under an inert atmosphere. A black precipitate was observed after 12 hours. Water (5 mL) was added to dissolve the resultant NPs. Functionalized NPs were purified by dialysis using 10,000 molecular weight dialysis bag for 12 h.

SI-II Experimental Techniques

TEM instrumentation

JEOL 100 S microscope was used to determine the size of FePt NPs.

LDI-MS instrumentation

The LDI-MS analyses were performed on a Bruker Autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) (Autoflex III). The Autoflex III is equipped with a Smartbeam 2 laser, and a MTP 384 ground steel sample target. Operating conditions were as follows: ion source 1 = 19.00 kV, ion source 2 = 16.60 kV, lens voltage = 8.44 kV, reflector voltage = 20.00 kV, reflector voltage 2 = 9.69 kV, pulsed ion extraction time = 10 ns, suppression

= 100 Da, and positive reflectron mode. Laser strength was optimized to around 50 $\mu\text{J/pulse}$. Three 2 μL solution samples of each NP were applied to target with great care to provide a homogeneous sample area. These samples were allowed to air-dry before LDI-MS analyses. Six spectra were collected per sample, where each spectrum was obtained at different locations across the target surface.

ICP-MS Quantification

Each FePt NP was diluted 100 times using deionized water after place exchange reaction and purification. 50 μL of each diluted solution was transferred to 15 mL centrifuge tubes. 0.5 mL of *aqua regia* was added to each sample and then the sample was allowed to react for 1 h. *Aqua regia is very corrosive and must be treated with great caution!* The sample solution was then diluted to 10 mL with 1% v/v nitric acid.

ICP-MS (Elan 6100, Perkin-Elmer, Shelton, CT, USA) was used to determine the ^{195}Pt in the NPs. A series of Pt standard solutions (20, 10, 5, 2, 1, 0.5, 0.2, and 0 ppb) were measured to build the calibration curve before each experiment. Each sample was repeated 3 times, and each replicate was measured 5 times by ICP-MS. ICP-MS operating conditions are as follows: rf power: 1600 W; plasma Ar Flow rate: 15 L/min; nebulizer Ar flow rate: 0.98 L/min; dwell time: 45 ms. All the magnetic NPs solutions were diluted to 10 $\mu\text{g/mL}$ (Pt concentration) for further experiments.

HPLC-MS Sample preparation

30 μL of each 30 $\mu\text{g/mL}$ (based on Pt concentration) FePt NP water solution was added to 1.5 mL plastic tubes. 30 μL of *aqua regia* was added to each sample and then the sample was allowed to react for 3 h. *Aqua regia is highly corrosive and must be treated with extreme caution!* The sample solution was then neutralized by 60 μL ammonium hydroxide (34~36 % v/v) to pH around 7. 10 μL of each neutralized solution was subjected to HPLC-ESI-MS analyses. A series of ligand standard solutions (200, 100, 50, and 20 μM) were prepared following the same

procedure described above and measured to build the calibration curve before each experiment.

Each sample was repeated three times.

HPLC-MS condition

HPLC separations were performed on an Agilent 1100 (Agilent Technologies, Wilmington, DE) HPLC system with a C18 column (15 cm × 2.1 mm, 5 μm particle size, Supelco Inc., Bellefonte, PA). The mobile phase gradient is shown in Table S1 (phase A: deionized water; phase B: methanol with 0.1 % trifluoroacetic acid). The smaller fraction of the LC effluent was fed into the mass spectrometer (split ratio of about 1:4).

A Bruker Esquire-LC (Billerica, MA) quadrupole ion trap mass spectrometer, which is equipped with an electrospray ionization source, was used in this study. All the experiments were performed in positive mode, and the electrospray needle voltage was kept at 3.5 kV, and the capillary temperature was set to 300 °C. Other operating conditions were as follows: nebulizer: 25 psi; dry gas: 10 L/min; skimmer 1: 30.0 V; skimmer 2: 6.0 V; cap exit offset: 30.0 V; octopole RF: 195.0 Vpp; lens 1: - 5.0 V; lens 2: - 60.0 V; and trap drive: 40.

HPLC Gradient condition

Mobile phase: A, H₂O; B, MeOH, 0.1% CF₃COOH

Table S1: Gradient of mobile phase in HPLC

Time (min)	A%	B%
0	95	5
15	95	5
20	80	20
25	50	50
30	50	50
40	0	100
45	0	100
50	95	5
55	95	5

SI-III. Fragmentation pathway in the LDI-MS analysis of Ligand D on FePt NPs

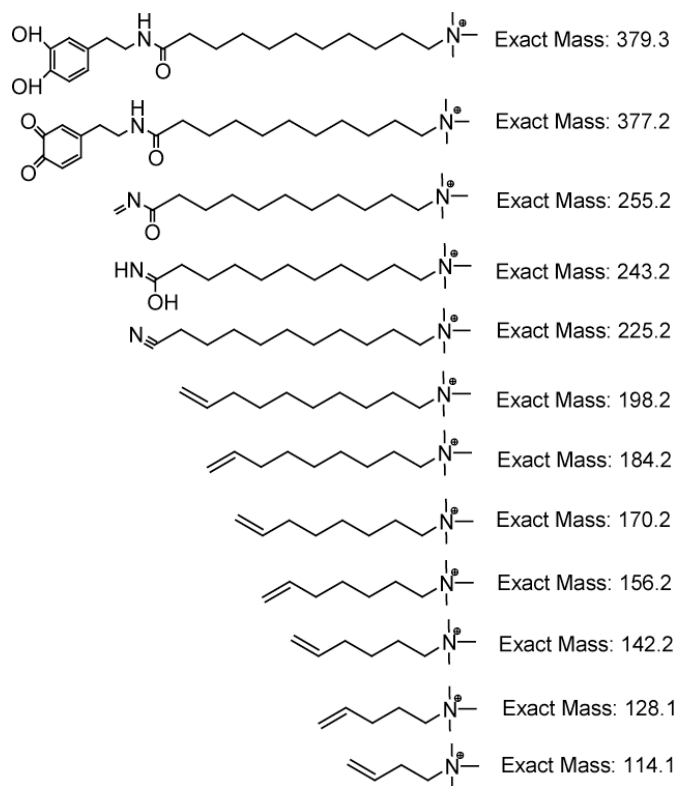


Figure S1. LDI-MS fragmentation pattern of Ligand **D** on FePt NPs

SI-IV. Fragmentation pathway in the LDI-MS analysis of Ligand M and H on Fe₃O₄ NPs

Possible fragment structure	Exact Molecular weight:		Possible fragment structure	Exact Molecular weight:	
	ligand M	ligand H		ligand M	ligand H
	555.40	625.48		318.26	388.34
	553.39	623.47		304.25	374.33
	431.35	501.43		290.23	360.31
	419.35	489.43		276.22	346.30
	401.34	471.42		262.20	332.28
	390.36	460.44		234.17	304.25
	374.33	444.41		218.18	288.26
	360.31	430.39		190.14	260.22
	346.30	416.38		174.15	244.23
	332.28	402.36		146.12	216.20
				130.12	200.20

Figure S2. LDI-MS fragmentation pattern of Ligand **M** and Ligand **H** on FePt NPs

SI-V. LDI-MS analysis of FePt NPs with Ligand D and T

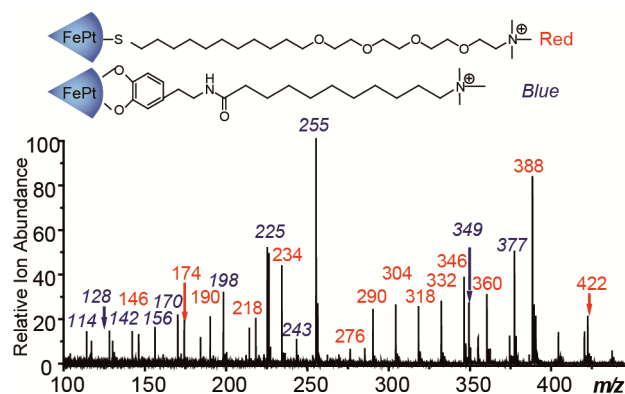


Figure S3. LDI-MS analysis of a 1:1 mixture of FePt NPs with Ligand **D** and **T**

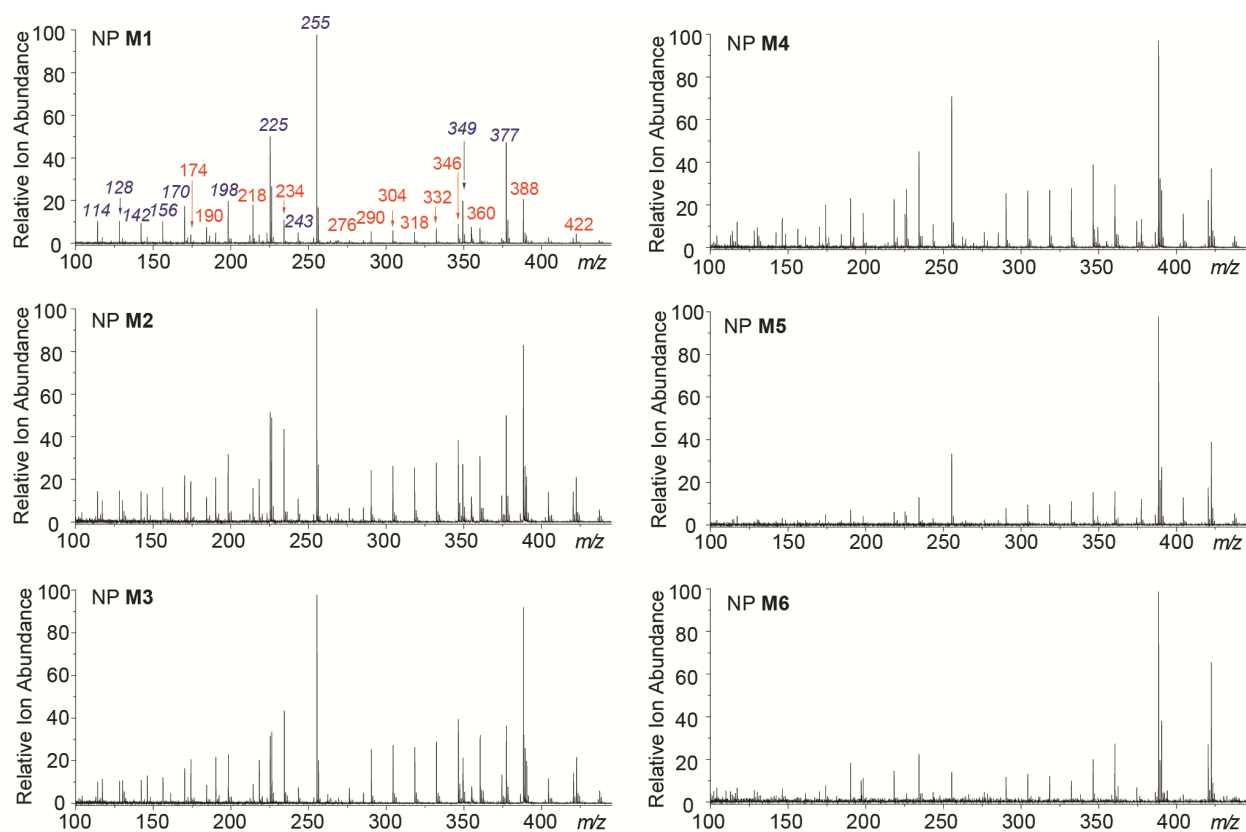


Figure S4. Representative LDI-MS analysis of mixed monolayer FePt NPs with various amount of Ligand **D** (blue, italic) and **T** (red, non-italic).

SI-VI. LDI-MS characterization of various types of Fe₃O₄ NPs

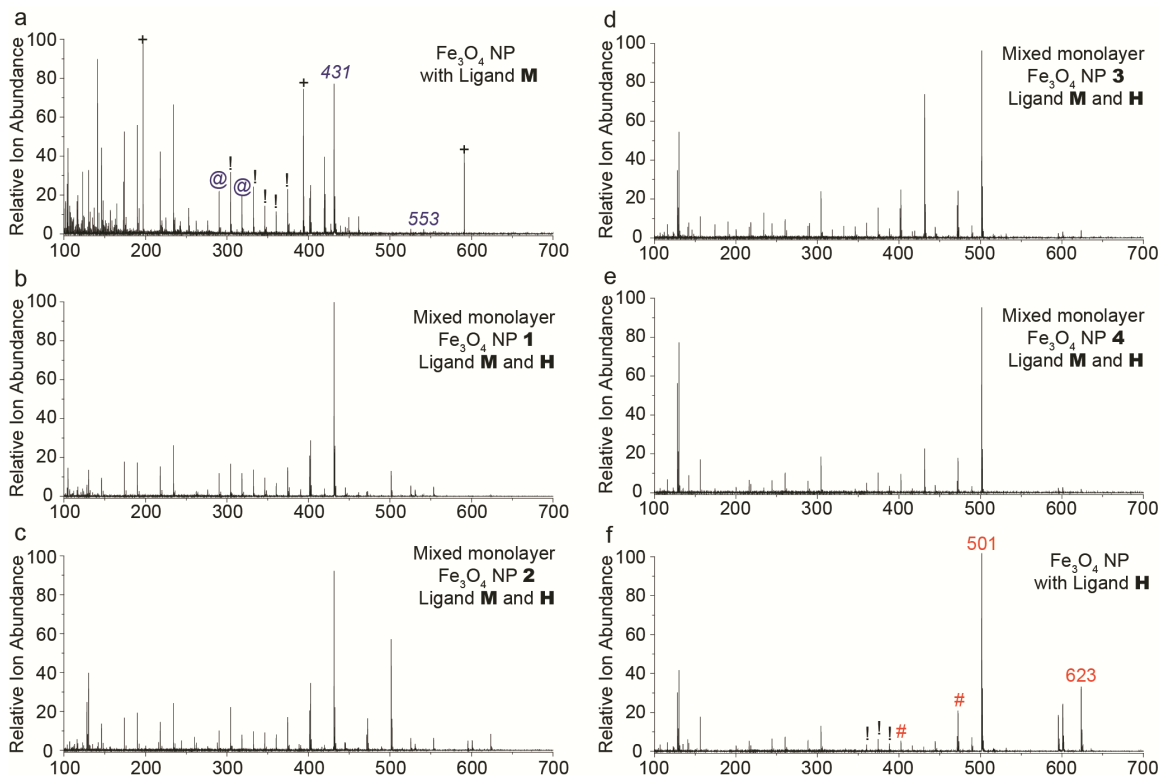


Figure S5. Representative LDI mass spectra of Fe₃O₄ NPs with various amount of Ligand **H** and **M**. The fragmentation patterns can be found in Figure S2. Selected representative ions have been marked as below: the m/z ratios in red or marked # correspond to the ions generated from the ligand **H**, while the m/z ratios in blue or marked @ (italic) indicate ions from the ligand **M**. Some of the fragments from Ligand **H** and **M** may overlapped in the mass spectra of mixed monolayer Fe₃O₄ NPs, and those ions are labelled using (!). Some contamination ions generated from the trace amount of gold on the sample target have been marked + in the mass spectrum of Fe₃O₄ NP with Ligand **M**.

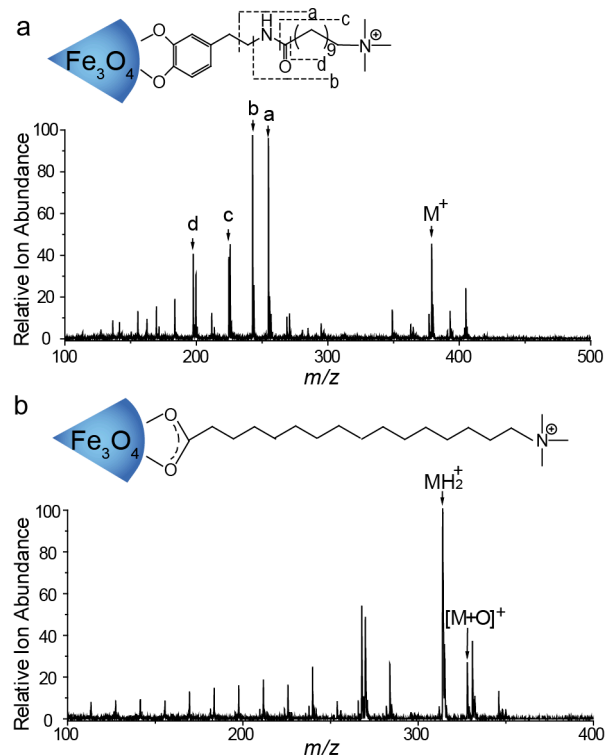


Figure S6. LDI mass spectra of Fe_3O_4 NPs with various ligands.

SI-VII. HPLC-MS analysis of ligand composition in mixed monolayer magnetic NPs

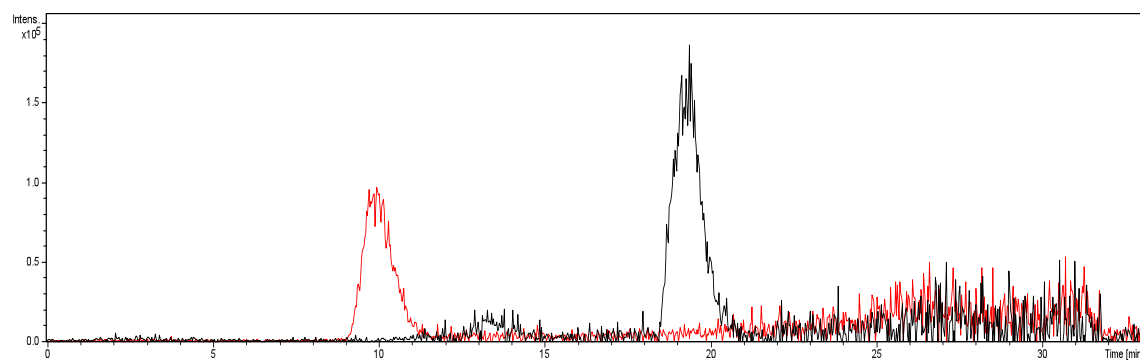


Figure S7. Representative extracted ion chromatogram of Ligand T (black line) and D (red line).

The ESI-MS data was collected 15 min after the HPLC sample injection to avoid the high salt concentration in the first 15 min.

Table S2 HPLC-MS quantification of ligand composition in mixed monolayer magnetic

FePt NPs

FePt NPs	Ligand T (%)	STD (%)	RSD
NP M1	42.2	0.7	1.8%
NP M2	54.3	3.1	5.7%
NP M3	58.2	4.9	8.4%
NP M4	64.0	4.9	7.6%
NP M5	66.2	5.3	8.0%
NP M6	70.8	6.5	9.2%

SI-VIII. Reproducibility of the current LDI-MS technique

Table S3 3-day reproducibility of the LDI-MS technique

FePt NPs	Day 1 (%)		Day 2 (%)		Day 3 (%)		Reproducibility (%)		
	Avg	STD	Avg	STD	Avg	STD	Avg	STD	RSD
NP M1	45.4	1.6	39.3	2.3	39.8	3.7	41.5	3.4	8.1%
NP M2	59.2	1.8	57.7	4.6	58.8	0.7	58.5	0.8	1.3%
NP M3	69.5	11.0	67.6	4.6	64.7	1.5	67.3	2.4	3.6%
NP M4	79.2	5.9	78.5	5.9	75.3	3.2	77.7	2.1	2.6%
NP M5	81.7	10.7	81.9	12.6	83.5	4.2	82.4	1.0	1.2%
NP M6	88.3	11.8	91.6	13.6	88.2	13.9	89.3	1.9	2.1%

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