Preparation and Self-Assembly of Dendronized Janus Fe_3O_4-Pt and Fe_3O_4-Au Heterodimers

Davit Jishkariani,[†,‡,1] Yaoting Wu,[†,1] Da Wang,[‼,1] Yang Liu,[‼,#] Alfons van Blaaderen[‼] and Christopher B. Murray[*,†,§]

[†]Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States

[‡]Complex Assemblies of Soft Matter Laboratory (COMPASS), UMI 3254, CNRS-Solvay-University of Pennsylvania, CRTB, 350 George Patterson Boulevard, Bristol, PA 19007, United States

[‼]Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC, Utrecht, The Netherlands

#Department of Earth Sciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands

[§]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States

[1]These authors contributed equally.

KEYWORDS Janus nanoparticles, heterodimers, dendritic ligands, ligand exchange, self-assembly.

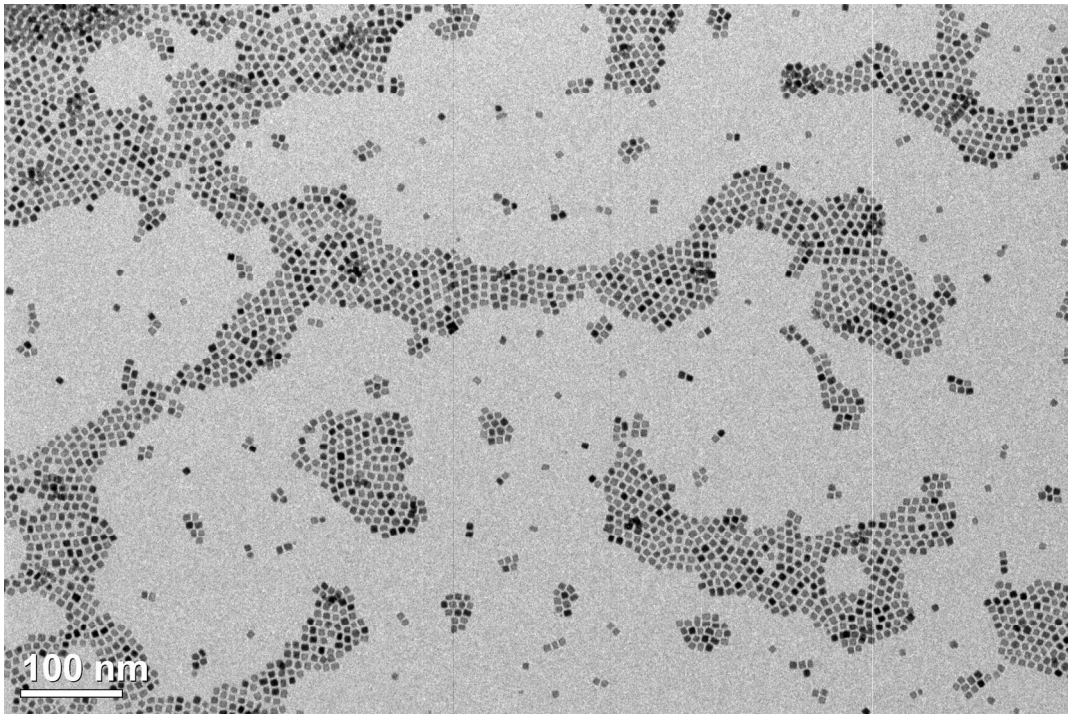


Figure S1. TEM image of Pt seeds.

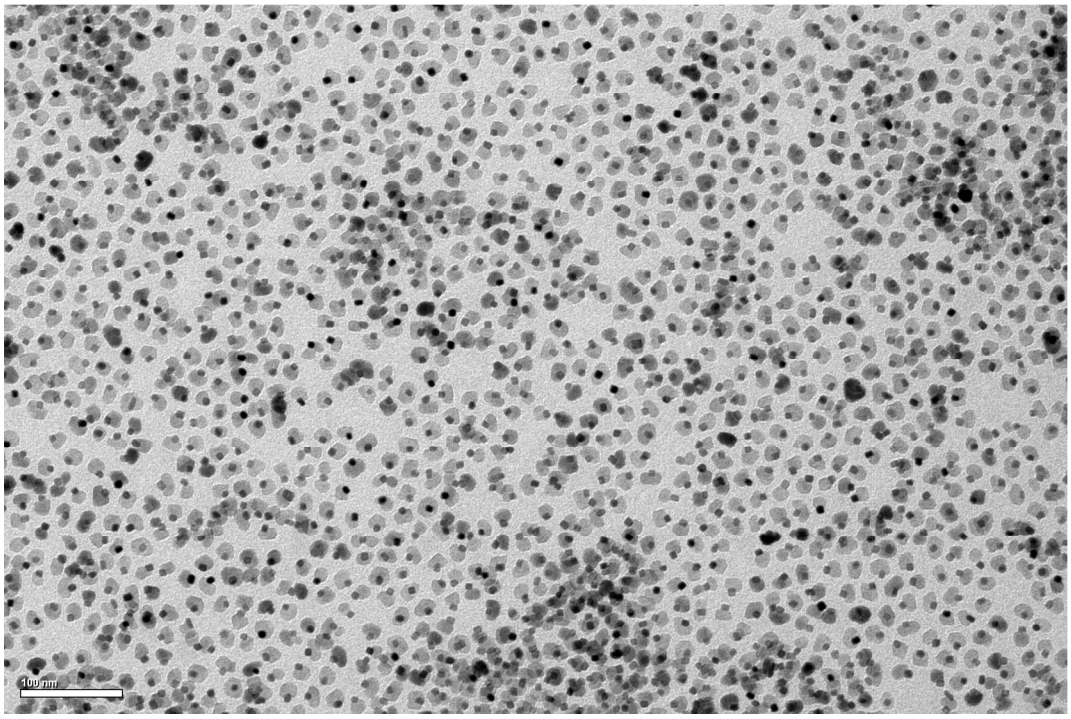


Figure S2. TEM image of Fe_3O_4-Pt particles (after functionalizing the Fe_3O_4 part with **7** and the Pt part with **2**).

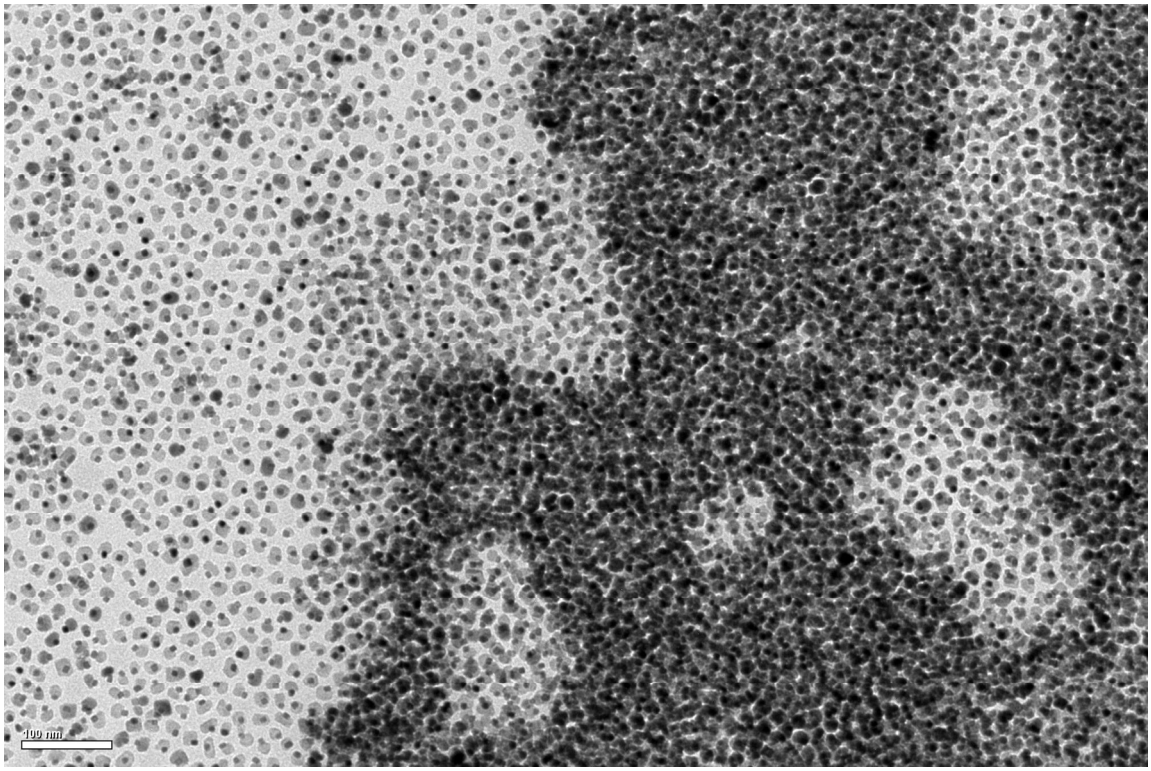


Figure S3. TEM image of Fe_3O_4-Pt particles (after functionalizing the Fe_3O_4 part with **7** and the Pt part with **4**).

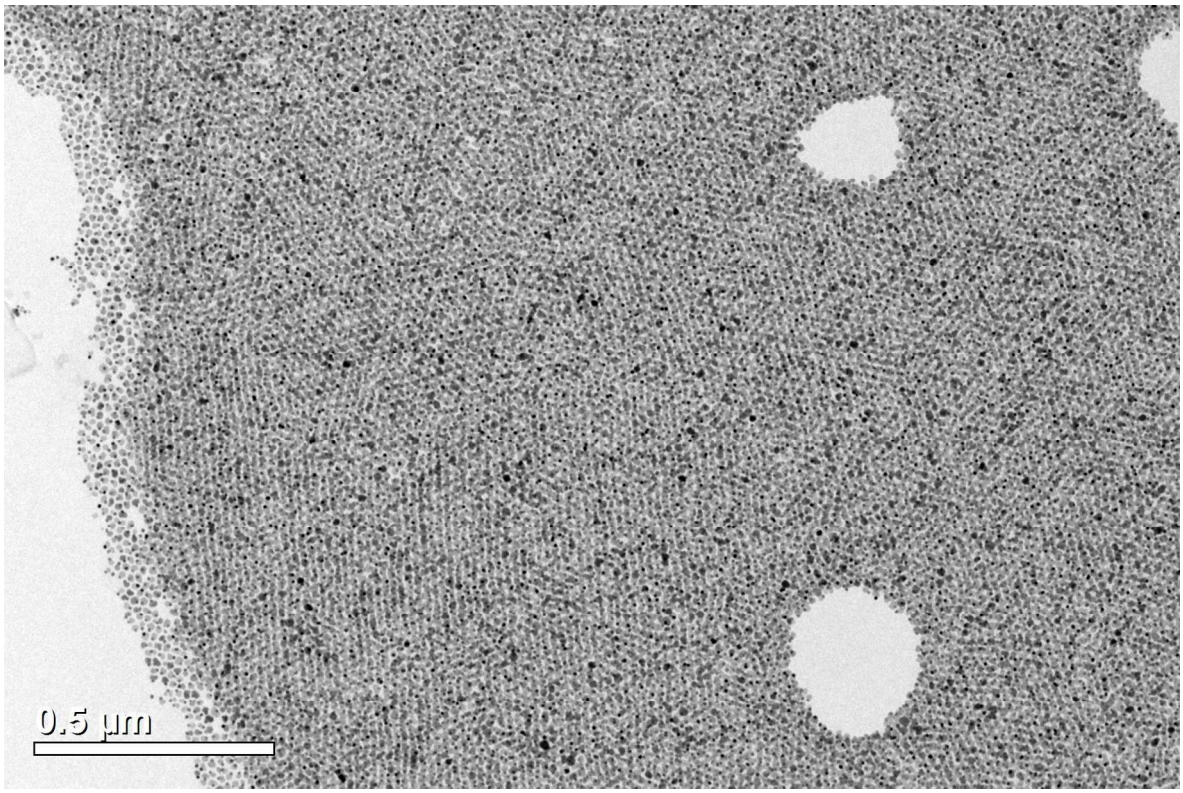


Figure S4. TEM image of Fe_3O_4-Pt particles (after functionalizing the Fe_3O_4 part with **7** and the Pt part with **6**).

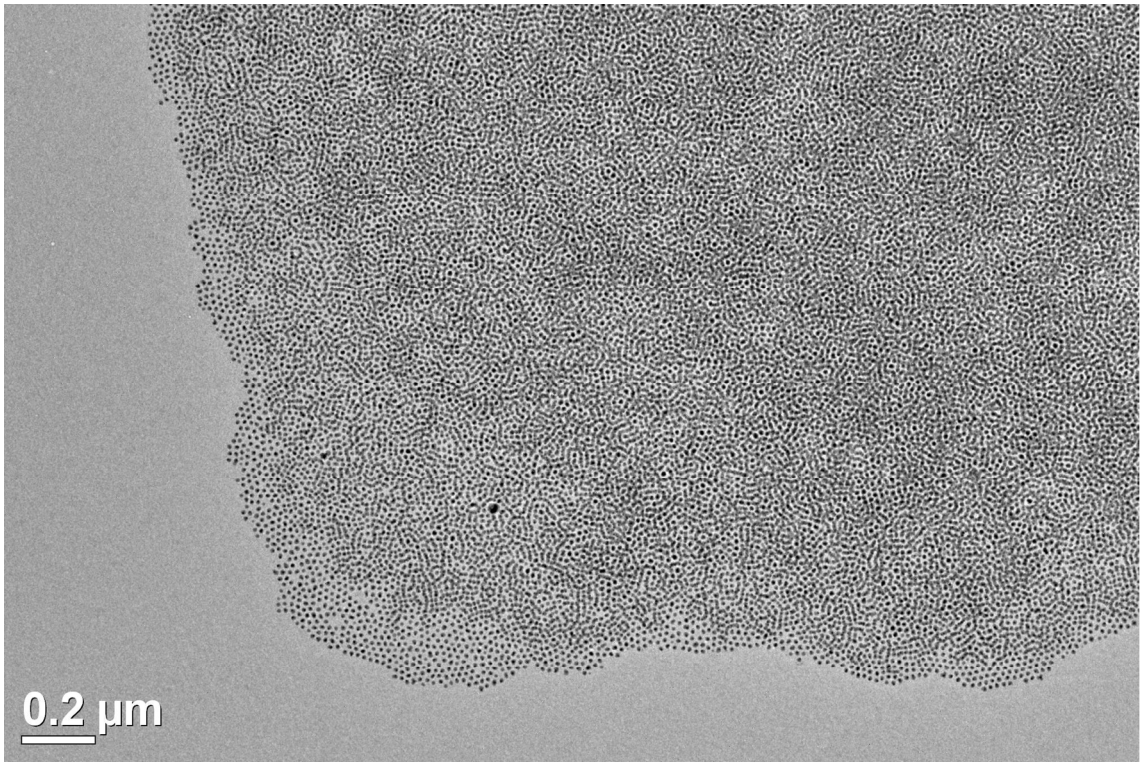


Figure S5. TEM image of Fe_3O_4-Au particles (after functionalizing the Fe_3O_4 part with **7** and the Au part with **2**).

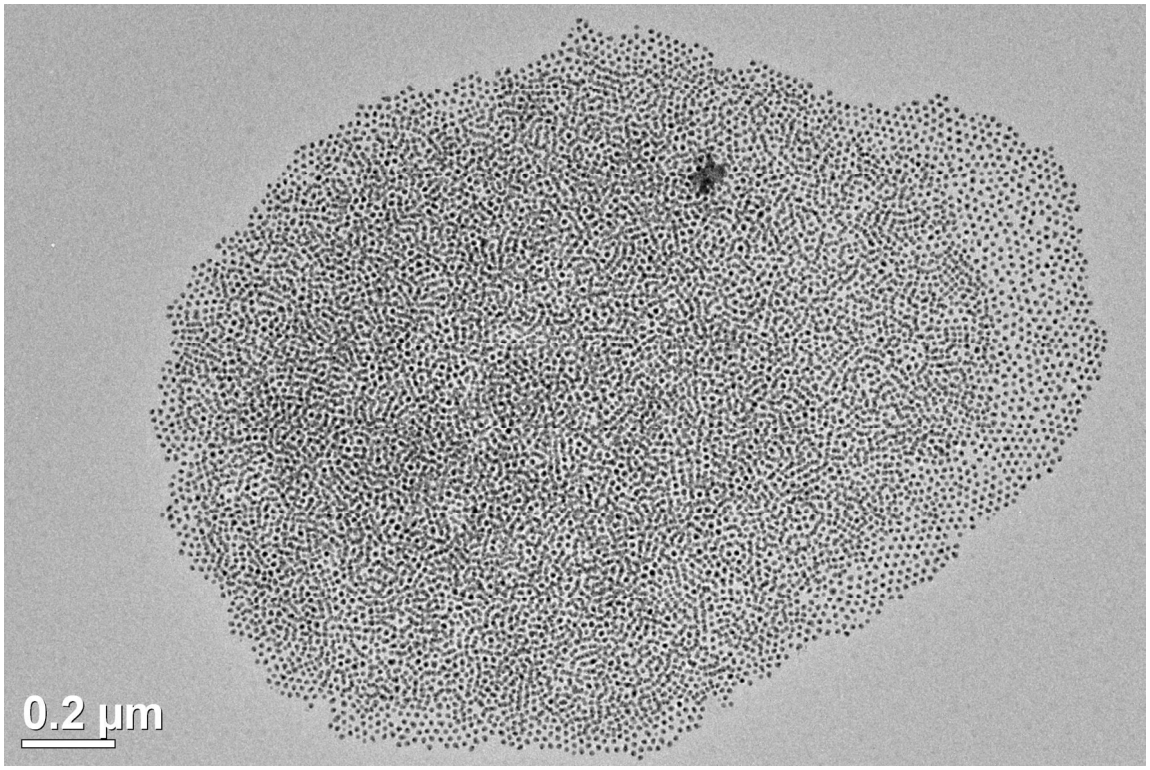


Figure S6. TEM image of Fe_3O_4-Au particles (after functionalizing the Fe_3O_4 part with **7** and the Au part with **4**).

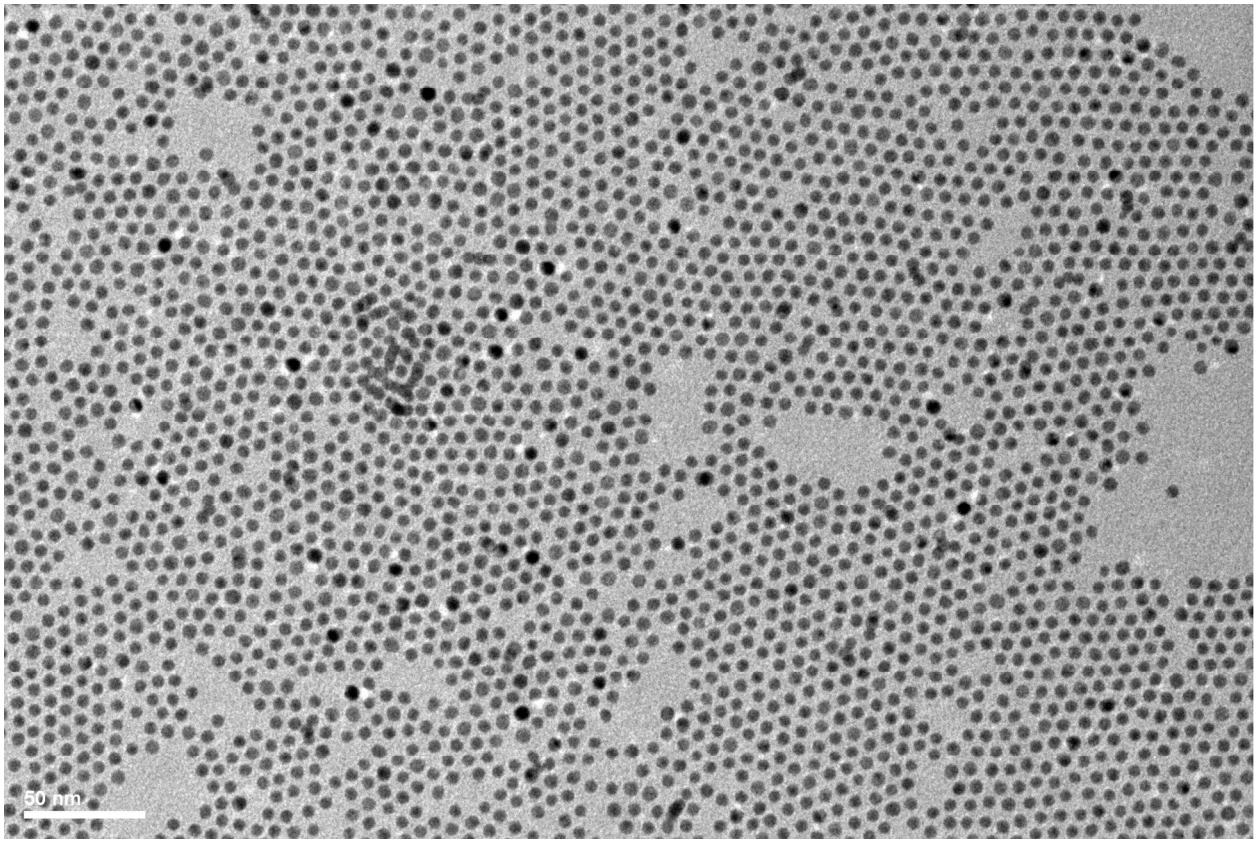


Figure S7. TEM image of Au seeds.

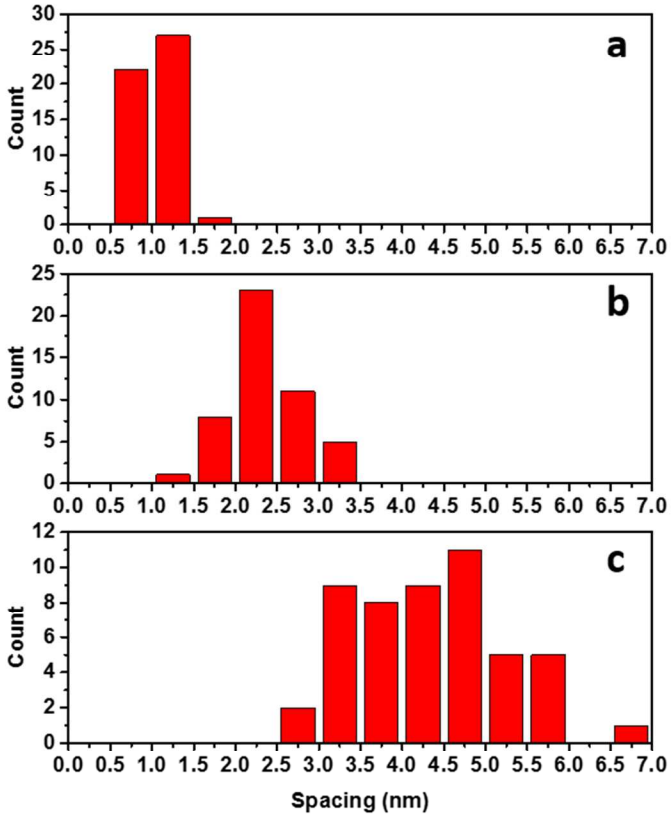


Figure S8. Interparticle spacing and distribution of (a) as synthesized Fe_3O_4-Pt heterodimers (Figure 4b, 1.0 ± 0.2 nm) (b) Fe_3O_4-Pt heterodimers after functionalization of the Fe_3O_4 part with dendron **7** (Figure 4c, 2.4 ± 0.5 nm) (c) Fe_3O_4-Pt Janus heterodimers (prepared after functionalizing the Fe_3O_4 part with dendron **7** and the Pt part with dendron **6**) (Figure 4d, 4.4 ± 0.9 nm).

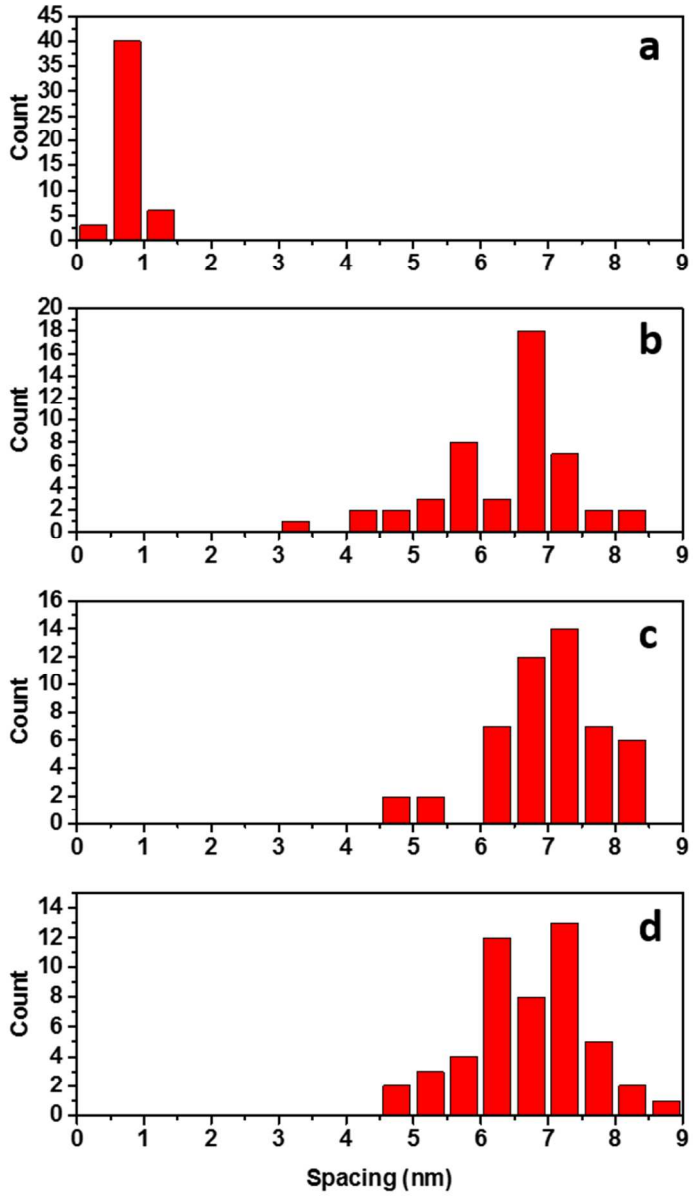
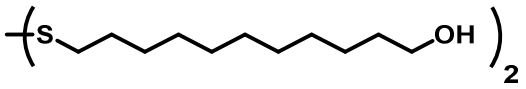


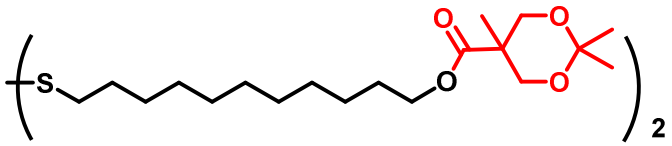
Figure S9 Interparticle spacing and distribution of (a) as synthesized Fe_3O_4-Au heterodimers (Figure 4e, 0.7 ± 0.2 nm) (b) Fe_3O_4-Au heterodimers after functionalization of the Fe_3O_4 part with dendron **7** (Figure 4f, 6.4 ± 1.0 nm) (c) Fe_3O_4-Au Janus heterodimers (after functionalizing the Fe_3O_4 part with dendron **7** and the Au part with dendron **6** (Figure 4g, 6.5 ± 0.8 nm) (d) Fe_3O_4-Au heterodimers after functionalization of the Fe_3O_4 part with dendron **7** and the Au part with dendron **9** (Figure 4h, 6.7 ± 0.8 nm).

Synthesis of hydrophilic dendritic ligands



11,11'-Disulfanediylbis(undecan-1-ol) 2.[1] White powder. To a stirred solution of 11-mercaptoundecan-1-ol **1** (5.0g, 24.5 mmol) in CH_2Cl_2 was added a solution of iodine in CH_2Cl_2 (50 mL) until the solution remained purple/brown and the resulting solution was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with 1M sodium thiosulfate (2 x 100 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford pure 11,11'-disulfanediylbis(undecan-1-ol) **2** (4.72g, 95%). ^{1}H NMR ($CDCl_3$) δ 3.64 (t, J = 6.6 Hz, 4H), 2.68 (t, J = 7.3Hz, 4H), 1.67 (p, J = 7.4 Hz, 4H), 1.61 – 1.51 (m, 4H), 1.39 – 1.25 (m, 28H);13C NMR ($CDCl_3$) δ 77.41, 77.16, 76.91, 63.23, 39.39, 32.96, 29.72, 29.65, 29.63, 29.57, 29.37, 28.67, 25.89; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{22}H_{46}O_2S_2Na$, 429.2837; found 430.473.

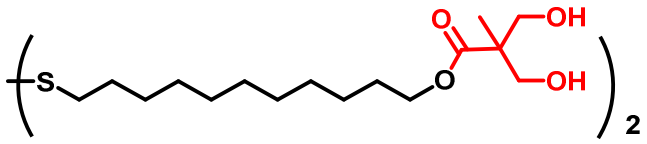
General procedure 1. The synthesis of 3 and 5.



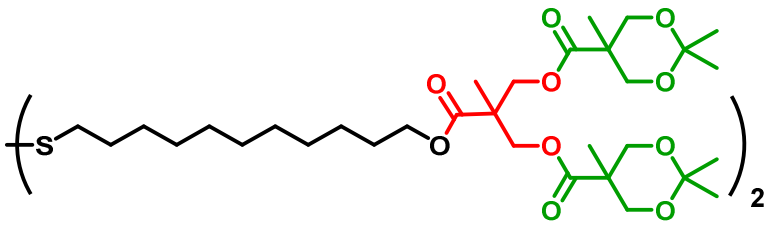
Disulfanediylbis(undecane-11,1-diyl)bis(2,2,5-trimethyl-1,3-dioxane-5-carboxylate) 3. Colorless oil. To a stirred solution of 11,11'-disulfanediylbis(undecan-1-ol) **2** (2.5 g, 6.2 mmol) in CH_2Cl_2 (30 mL) was added 2,2,5-trimethyl-1,3-dioxane-5-carboxylic anhydride (5.0 g, 15 mmol), pyridine (1.45g, 22 mmol) and DMAP (0.24g, 2 mmol) and the resulting mixture was stirred at rt for an additional 12h. The reaction was quenched by water (5 mL), diluted with CH_2Cl_2 and washed with water (3 x 100 mL). The Organic layer was dried over Na_2SO_4, concentrated under reduced pressure and the residue purified by flash chromatography (SiO_2, 0-10% EtOAc/Hexanes) to afford pure disulfanediylbis(undecane-11,1-diyl)bis(2,2,5-trimethyl-

1,3-dioxane-5-carboxylate) **3** (4.03g, 91%). ^{1}H NMR ($CDCl_3$) δ 4.17 (d, J = 11.7 Hz, 4H), 4.12 (t, J = 6.7 Hz, 4H), 3.62 (d, J = 11.8 Hz, 4H), 2.67 (t, J = 7.5 Hz, 3H), 1.71 – 1.58 (m, 8H), 1.42 (s, 6H), 1.38 (s, 6H), 1.37 – 1.23 (m, 28H), 1.19 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.38, 98.14, 66.15, 65.06, 41.90, 39.30, 29.60, 29.35, 29.32, 28.70, 28.65, 25.94, 24.31, 23.28, 18.89, 0.12; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{38}H_{70}O_8S_2Na$, 741.4410; found 742.658.

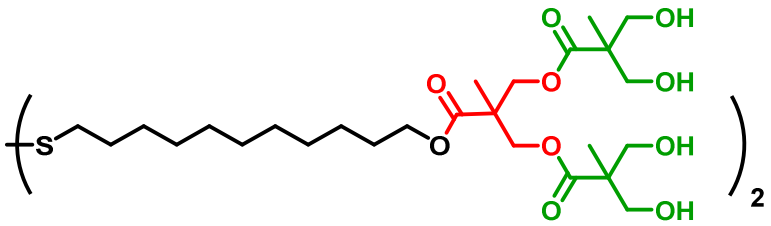
General procedure 2. The synthesis of 4 and 6



Disulfanediylbis(undecane-11,1-diyl) bis(3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate) 4. White solid. To a stirred solution of disulfanediylbis(undecane-11,1-diyl)bis(2,2,5-trimethyl-1,3-dioxane-5-carboxylate) **3** (1.2 g 1.7 mmol) in MeOH was added DOWEX resin (2 g) and the resulting suspension stirred at 50 °C for 7 h, after which ^{13}C NMR showed the disappearance of the acetonide quaternary carbon signal (~98 ppm). The suspension was filtered through Celite and the filtrate concentrated under reduced pressure to afford title compound **4** (1.06g, 99%). ^{1}H NMR ($CDCl_3$) δ 4.13 (t, J = 6.7 Hz, 4H), 3.87 (d, J = 11.2 Hz, 4H), 3.69 (d, J = 11.3 Hz, 4H), 3.02 (s, 4H), 2.66 (t, J = 7.4 Hz, 4H), 1.64 (h, J = 6.6 Hz, 8H), 1.39 – 1.23 (m, 28H), 1.05 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 176.09, 68.10, 65.29, 49.26, 39.29, 29.56, 29.31, 29.29, 28.63, 28.60, 25.95, 17.28, 0.10; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{32}H_{62}O_8S_2Na$, 661.3784; found 662.720.

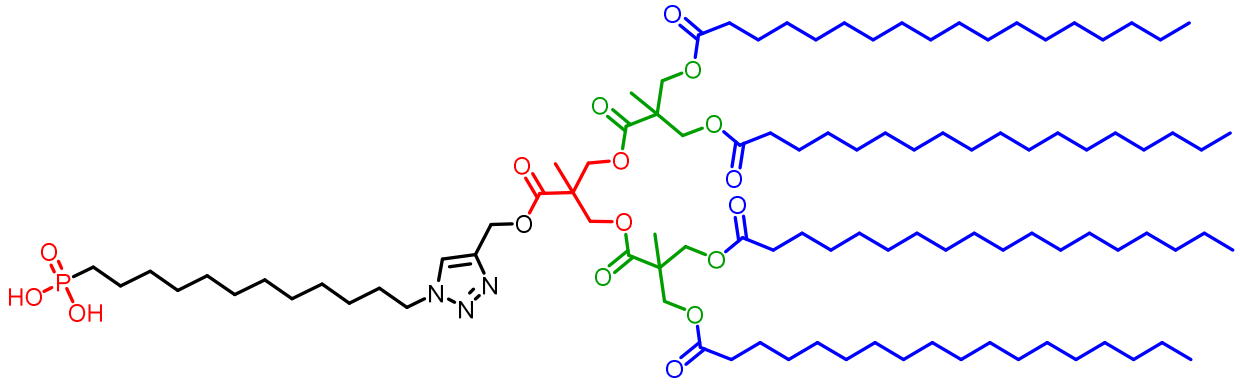


(((Disulfanediylbis(undecane-11,1-diyl))bis(oxy))bis(carbonyl))bis(2-methylpropane-2,1,3-triyl) tetrakis(2,2,5-trimethyl-1,3-dioxane-5-carboxylate) 5. Colorless oil. The compound was prepared according to the general procedure 1 (See above). The molecule was taken into next step without isolation.



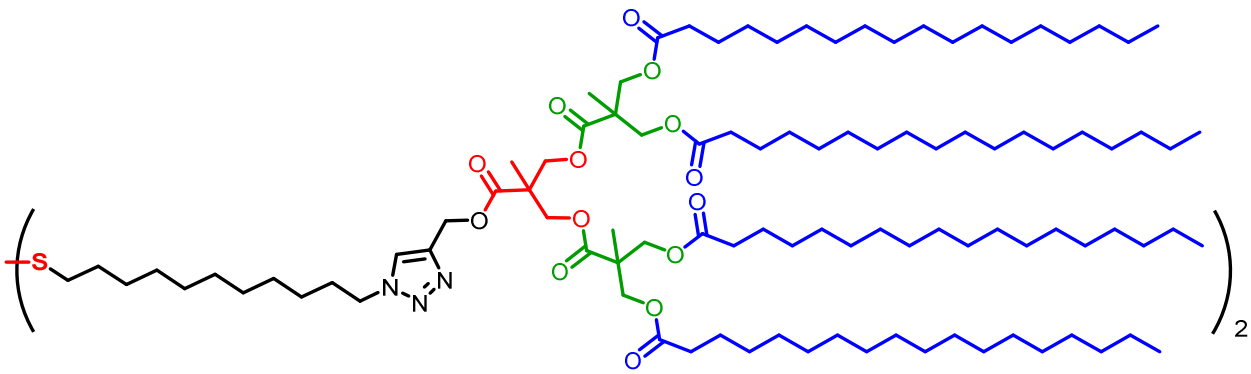
(((Disulfanediylbis(undecane-11,1-diyl))bis(oxy))bis(carbonyl))bis(2-methylpropane-2,1,3-triyl) tetrakis(3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate) 6. Colorless oil. The compound was prepared according to the general procedure 2 (See above). (1.42g, 99%). ^{1}H NMR ($CDCl_3$) δ 4.43 (d, J = 11.1 Hz, 4H), 4.26 (d, J = 11.1 Hz, 4H), 4.13 (t, J = 6.7 Hz, 4H), 3.83 (d, J = 4.2 Hz, 4H), 3.81 (d, J = 4.1 Hz, 4H), 3.73 – 3.67 (m, 8H), 3.07 (s, 8H), 2.68 (t, J = 7.3 Hz, 4H), 1.72 – 1.59 (m, 8H), 1.39 – 1.24 (m, 34H), 1.05 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 175.26, 173.19, 67.86, 65.82, 65.04, 49.86, 46.50, 39.34, 29.61, 29.58, 29.34, 29.32, 28.64, 25.98, 18.30, 17.27; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{52}H_{94}O_{20}S_2Na$, 1125.5780; found 1127.117.

Synthesis of hydrophobic dendritic ligand 7.



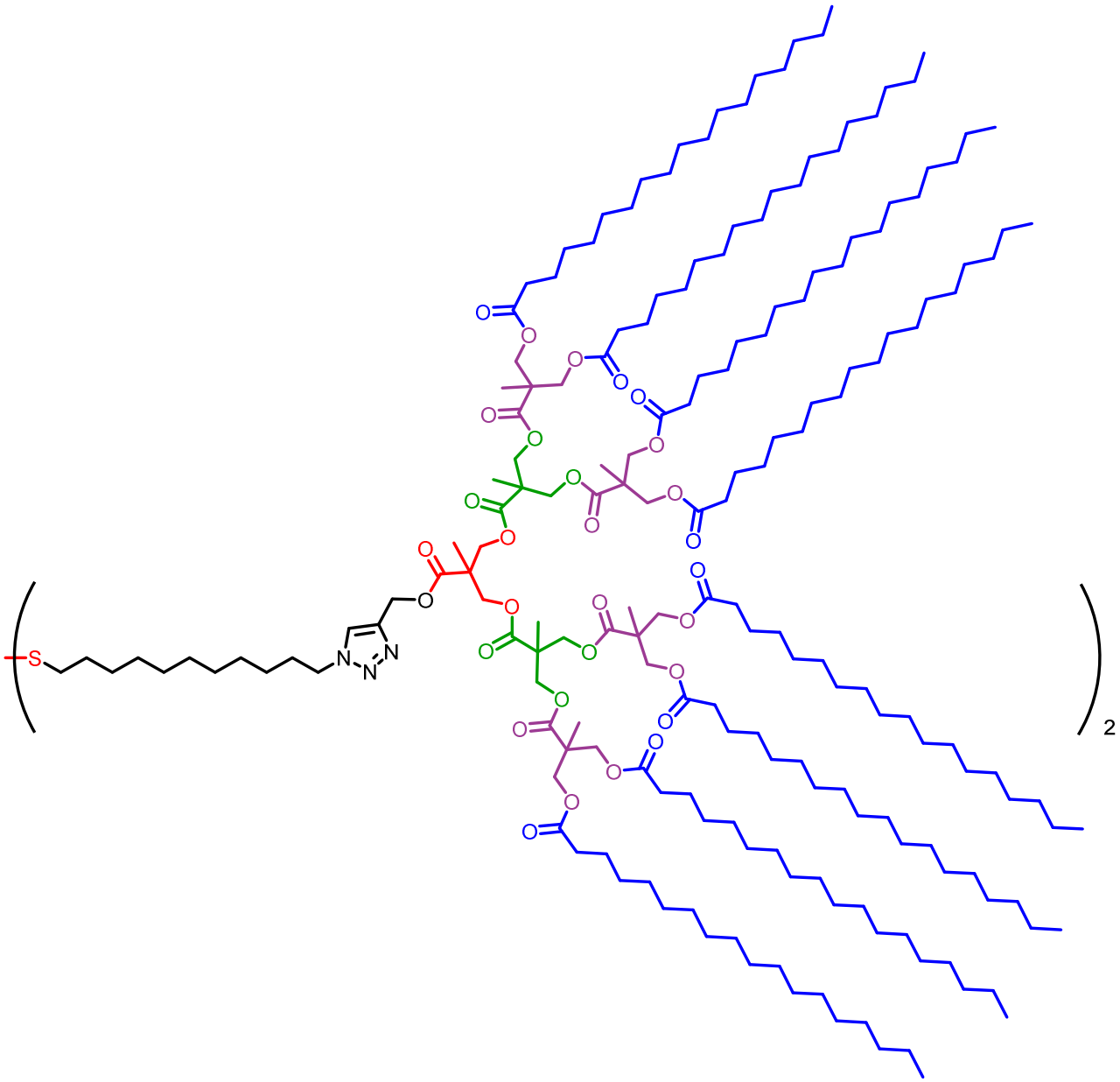
(11-(4-(((2-Methyl-3-((2-methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)-2-(((2-methyl-3-(stearoyloxy)-2-((stearoyloxy)methyl)propanoyl)oxy)methyl)propanoyl)oxy) methyl)-1H-1,2,3-triazol-1-yl)undecyl)phosphonic acid 7. Compound **7** was prepared previously in our lab. All synthetic and characterization details can be found in our previous report.[2]

Synthesis of hydrophobic dendritic ligand 8.

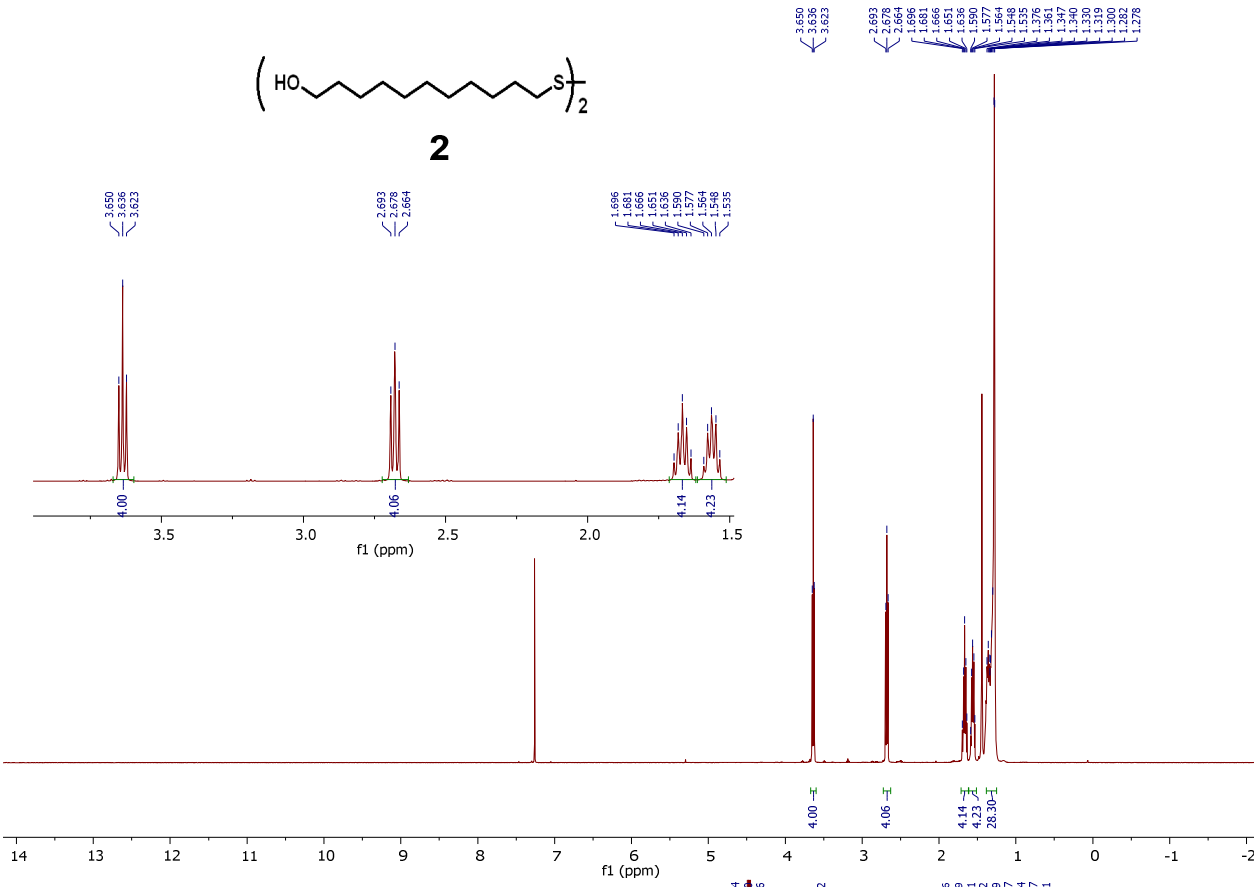


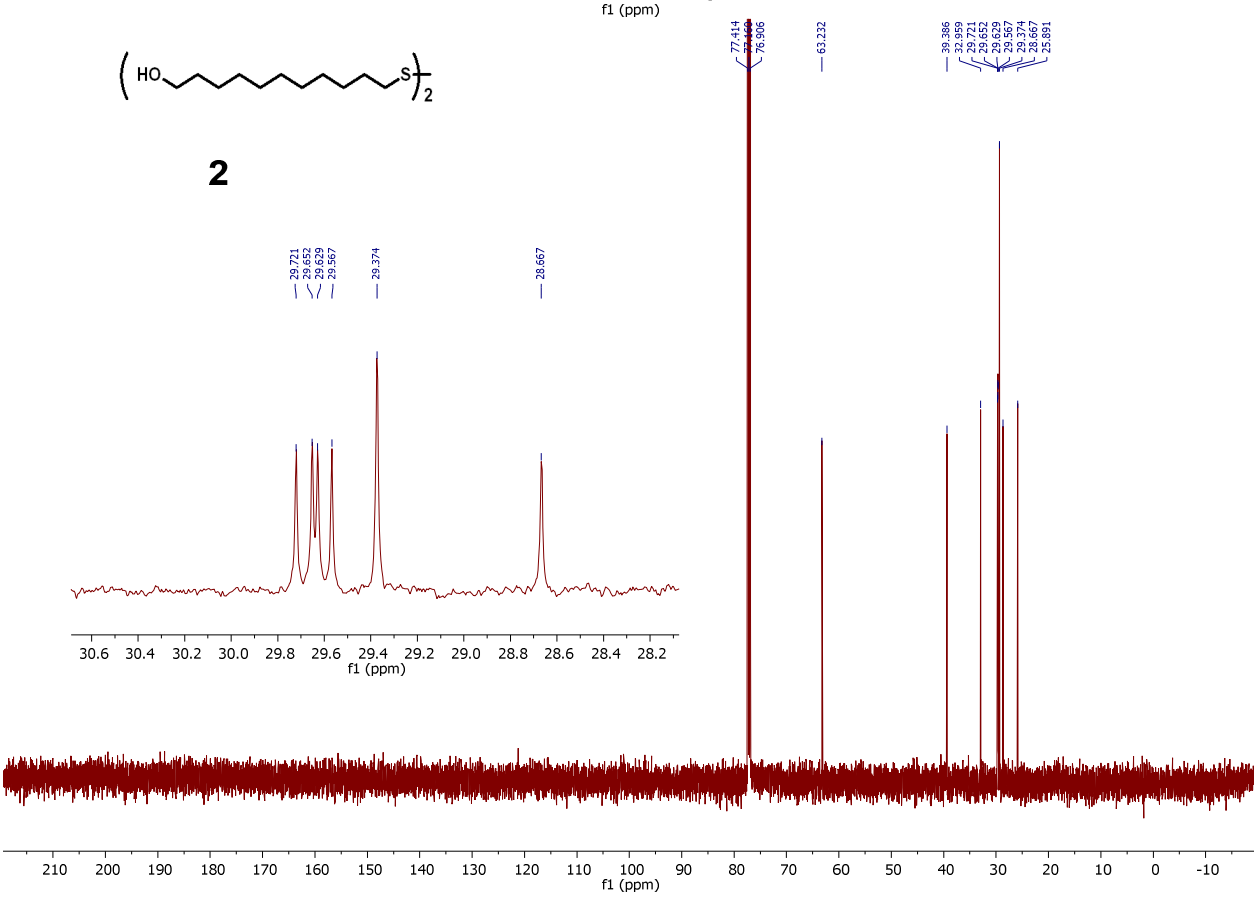
Compound **8** was prepared previously in our lab. All synthetic and characterization details can be found in our previous report.[3]

Synthesis of hydrophobic dendritic ligand 9.



Compound **9** was prepared previously in our lab. All synthetic and characterization details can be found in our previous report.[3]


HO
S
2
2
3.650
3.636
3.623
2.693
2.678
2.664
1.696
1.681
1.666
1.651
1.636
1.590
1.577
1.564
1.548
1.535
4.00
4.06
4.14
4.23
28.30
f1 (ppm)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S
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2
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76.806
63.232
39.386
32.399
29.721
29.652
29.629
29.567
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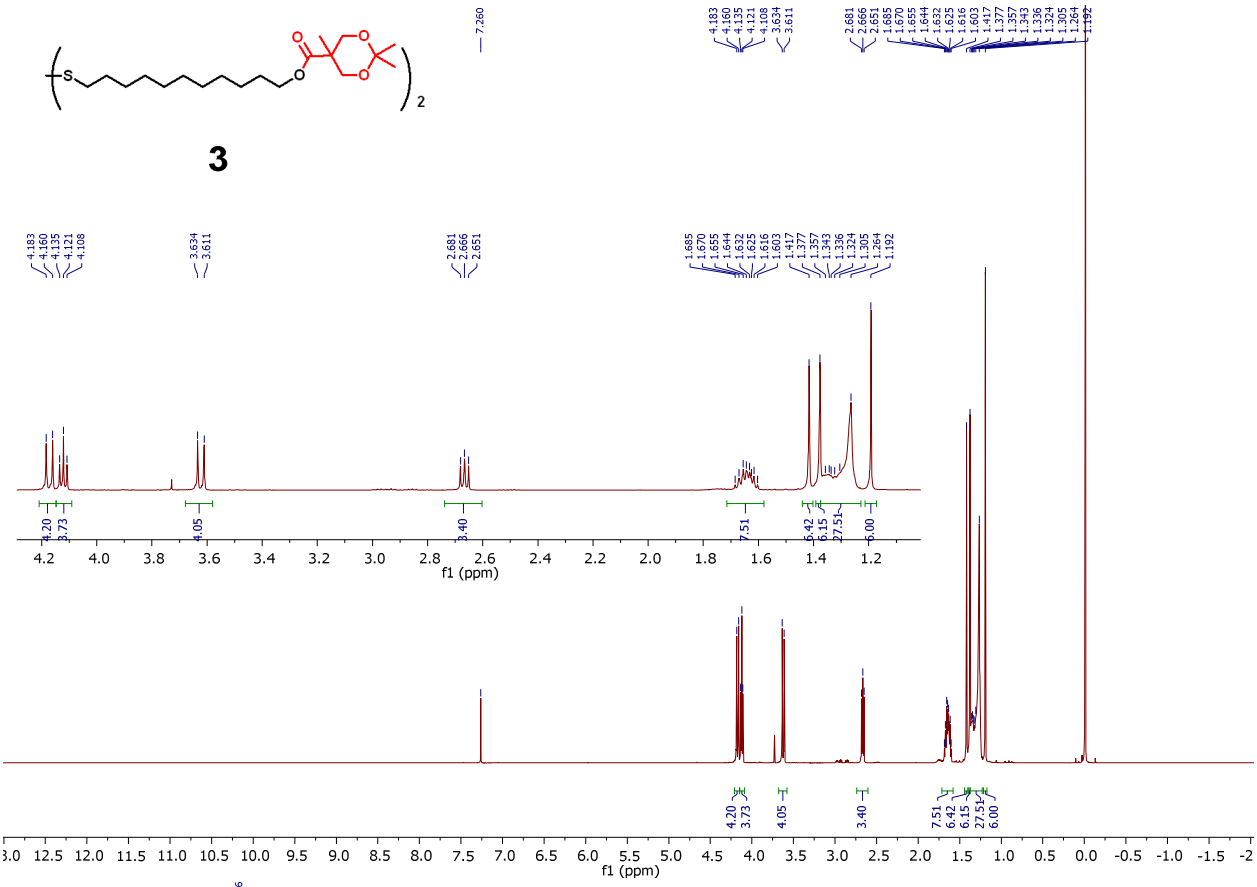
28.667
25.891
29.721
29.652
29.629
29.567
29.374
28.667
f1 (ppm)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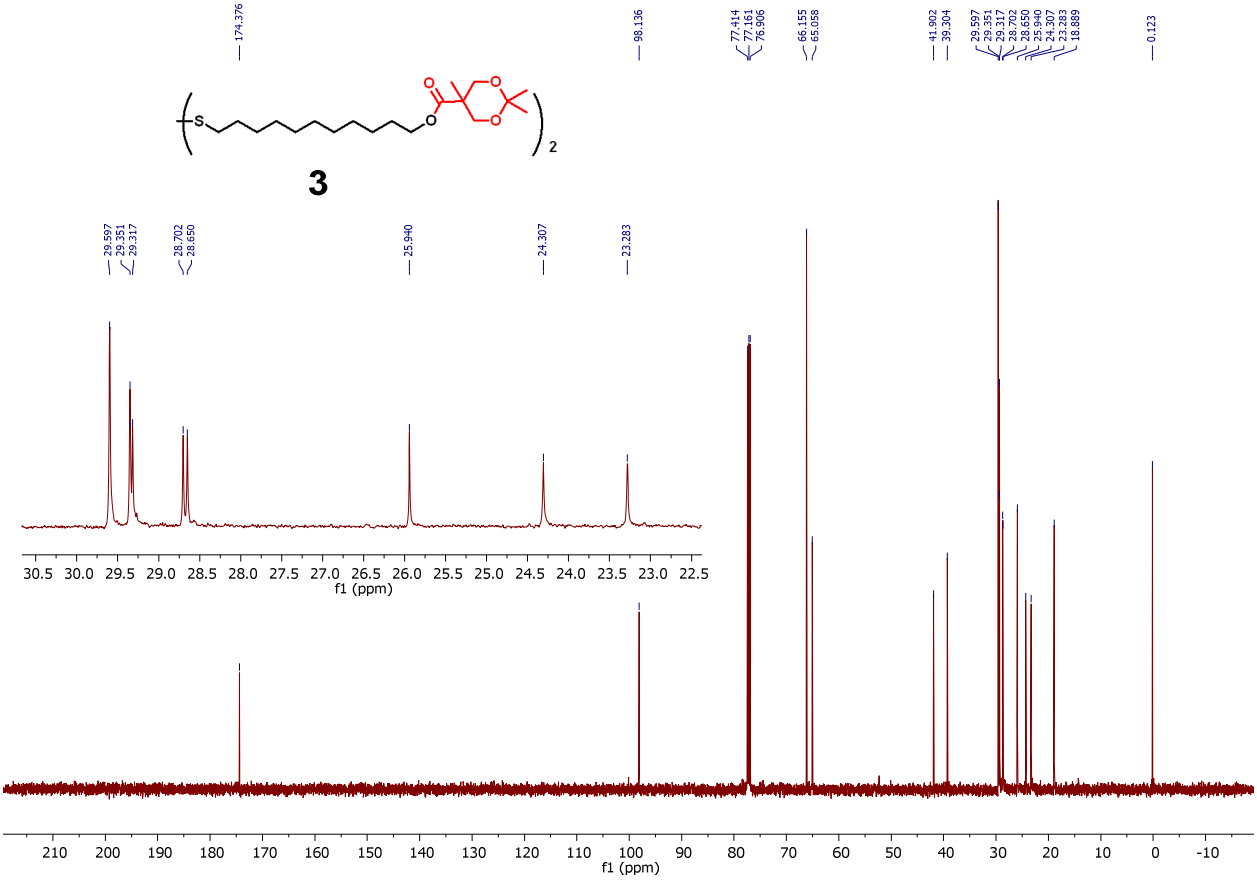
f1 (ppm)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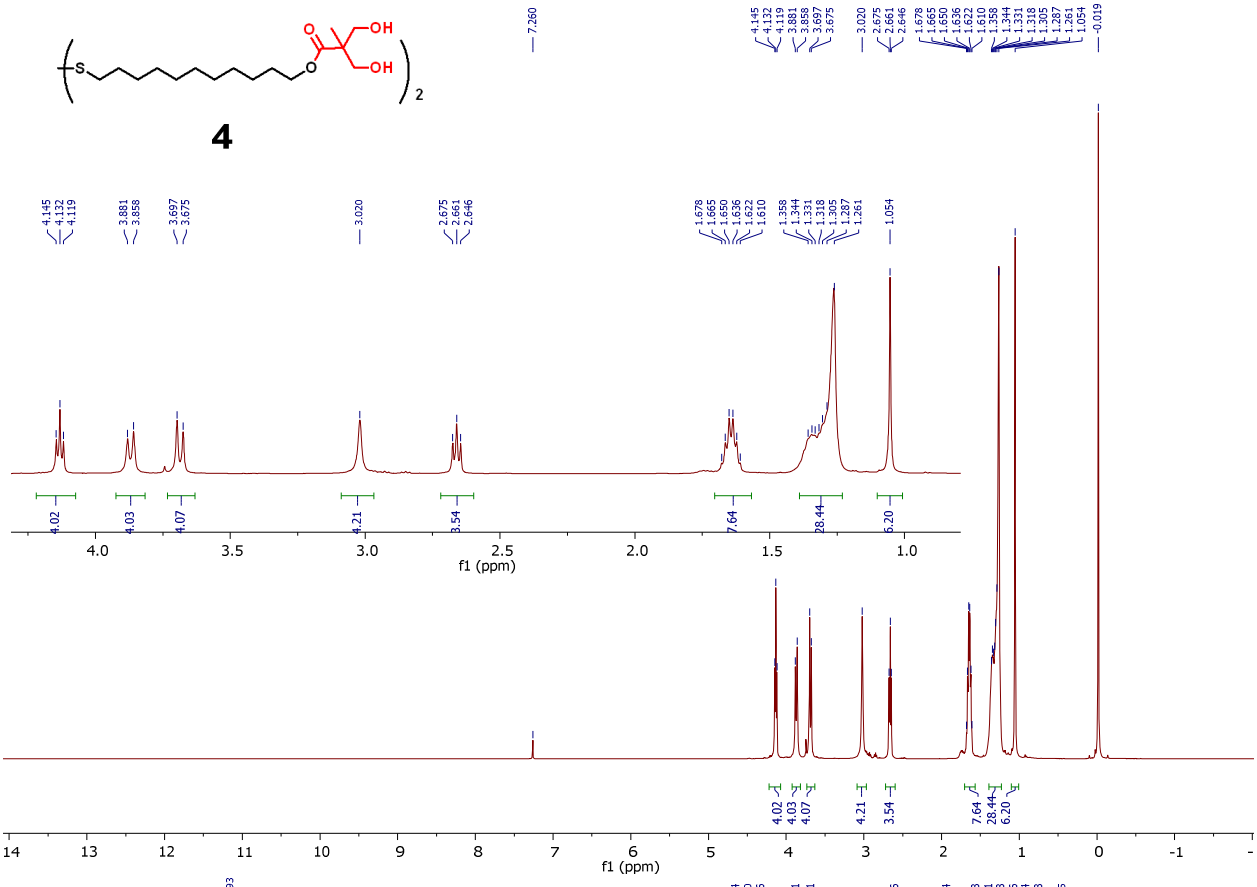
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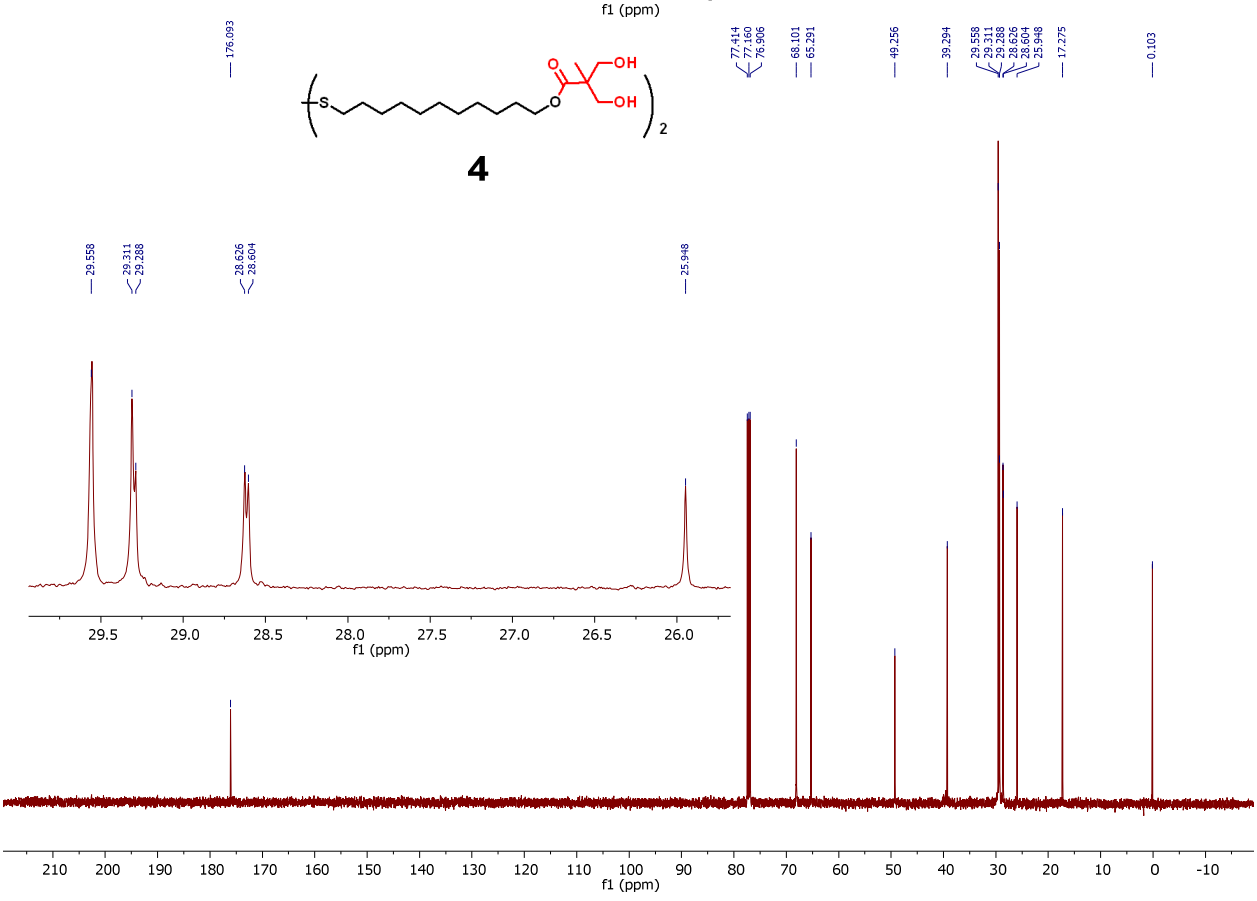
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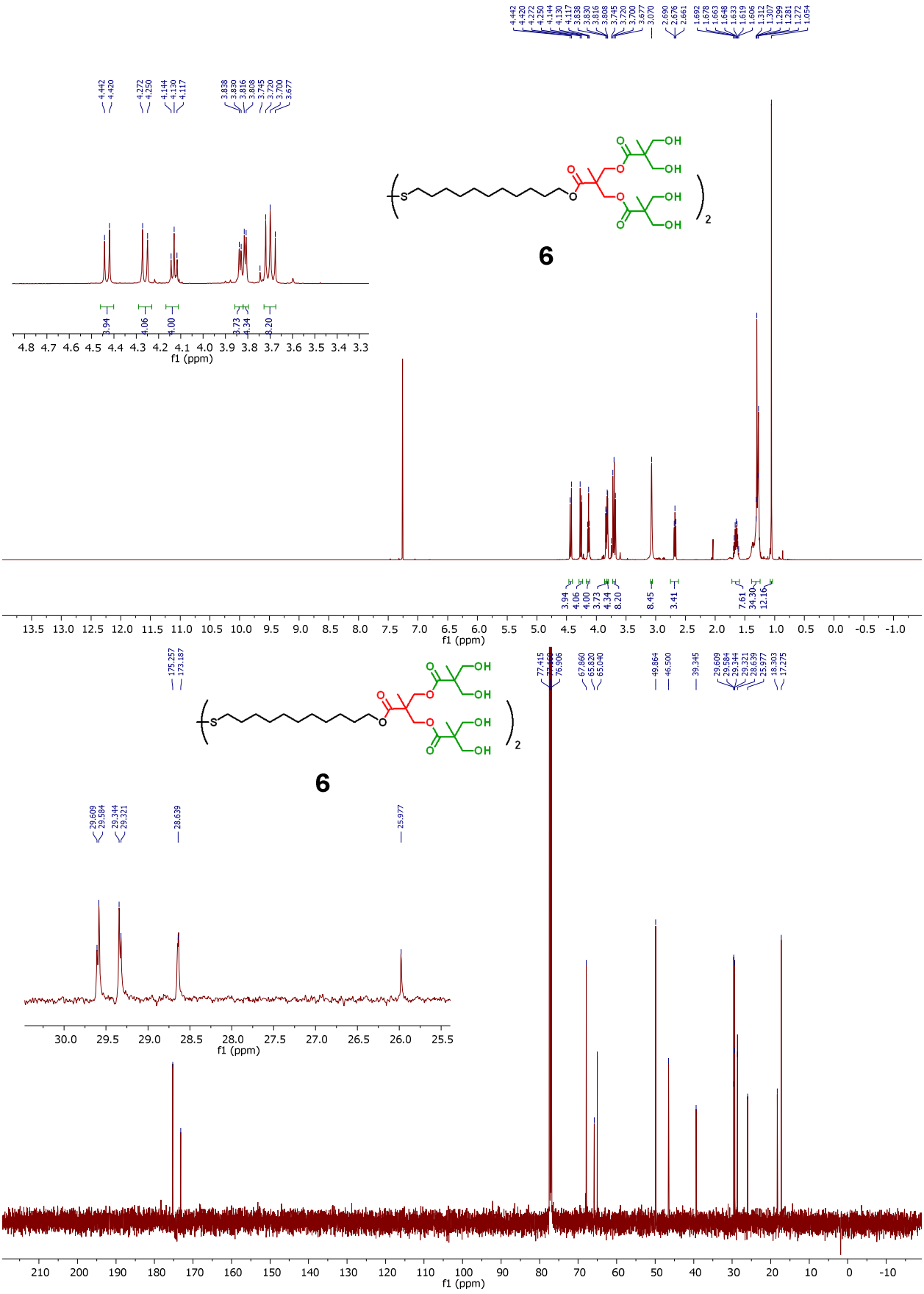
6
f1 (ppm)
6
f1 (ppm)
f1 (ppm)

References:

(1) Kell, A. J.; Alizadeh, A.; Yang, L.; Workentin, M. S. Monolayer-Protected Gold Nanoparticle Coalescence Induced by Photogenerated Radicals. *Langmuir* **2005**, *21*, 9741–9746.

(2) Jishkariani, D.; Lee, J. D.; Yun, H.; Paik, T.; Kikkawa, J. M.; Kagan, C. R.; Donnio, B.; Murray, C. B. Dendritic Effect and Magnetic Permeability in Dendron Coated Nickel and Manganese Zinc Ferrite Nanoparticles. *Submitted* **2017**.

(3) Jishkariani, D.; Diroll, B. T.; Cargnello, M.; Klein, D. R.; Hough, L. A.; Murray, C. B.; Donnio, B. Dendron-Mediated Engineering of Interparticle Separation and Self-Assembly in Dendronized Gold Nanoparticles Superlattices. *J. Am. Chem. Soc.* **2015**, *137*, 10728–10734.