Monolayer Exchange Chemistry of $\gamma$-Fe$_2$O$_3$ Nanoparticles

Andrew K. Boal, Kanad Das, Mark Gray, and Vincent M. Rotello*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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Monolayer modification of alkylamine-protected $\gamma$-Fe$_2$O$_3$ nanoparticles using functionalized alcohols and diols is presented. The stabilization of the modified nanoparticles was found to be dependent on the nature of the introduced alcohol: both bidentate surface–ligand bonding and steric blocking by bulky tail groups were necessary to produce systems resistant to agglomeration. EPR, UV–vis, and powder XRD analyses of the pre- and post-modified nanoparticles demonstrated that the core $\gamma$-Fe$_2$O$_3$ functionality was unaffected by the change in monolayer composition. Finally, multiple ligands could be readily incorporated into the monolayer using a simultaneous displacement reaction.

Introduction

Inorganic core nanoparticles coated with organic monolayers are a fundamental building block in nanotechnology. The nanoscopic size of the inorganic core provides optical, magnetic, and conductive properties unique to quantum-confined materials. Uses for such systems include fluorescent biomacromolecule tags for activity assays, magnetic resonance imaging (MRI) contrast agents, and components for nanoscale electronic devices or data storage elements.

Molecular-scale properties can then be introduced into nanoparticle systems by the attachment of complex molecules to the nanoparticle surface as part of a monolayer, allowing for the creation of highly functional systems. Nanoparticles functionalized with molecular recognition elements add the capacity to act as selective chemical and biomacromolecular sensors, building-block components in the controlled assembly of nanoparticle structures, and biologically active agents. One of the key aspects for the realization of the potentially powerful applications presented by the incorporation of small molecule functionality, however, is the development of divergent synthetic pathways by which such hybrid nanoparticle–monolayer systems can be created.

Numerous methods for the synthesis of nanoscopic magnetic particles, including Co$_x$, Ni$_{1-x}$Fe$_2$, and alloy-based materials have been developed. The preparation of iron oxide nanoparticles is a prevalent example of matrix-free nanoparticle synthesis and most com-


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Monolayer Displacement. Our initial attempt to modify the monolayer of MPN 2 was based on the incorporation of dodecanol into the nanoparticle monolayer (Scheme 1). In this case, we dissolved both MPN 2 and a large excess of dodecanol in toluene and stirred the reaction mixture for 48 h at room temperature. After removal of the bulk of the solvent, the nanoparticles could be precipitated by the addition of a large excess of EtOH. Once precipitation was complete and the solid had been collected and rinsed, the resulting MPN could be fully resuspended in toluene or CHCl₃ (Figure 2a).

Results and Discussion

Monolayer Displacement. Our initial attempt to modify the monolayer of MPN 2 was based on the incorporation of dodecanol into the nanoparticle monolayer (Scheme 1). In this case, we dissolved both MPN...
MPNs slowly formed a precipitate over several days (Figure 2b), with the ultimate formation of an intractable black solid. This material could not be redissoled in any standard solvent, and a similar irreversible agglomeration was observed if the nanoparticles were dried in vacuo after precipitation from the reaction mixture. Sonication of this precipitate in CHCl₃ yielded a cloudy gray suspension consisting mostly of nanoparticle agglomerates ranging from tens to several hundreds of nanometers in size (Figure 2c).

To probe the cause of the observed instability of MPN 4 and to develop a ligand system capable of stabilizing these nanoparticles over long periods of time in both the solution and the solid state, a series of alkane alcohol ligands was prepared (Figure 3). In this series, ligands 5 and 6 contain more bulky alkane tail groups designed to prevent agglomeration of the nanoparticles in the solid state. To improve the stability of the ligand–nanoparticle core interaction, bidentate diols 7 and 8 were prepared with either one or two dodecyl groups. This was done to separate the possible stabilization effects of increasing the strength of the nanoparticle core–ligand interaction from the effects of increasing steric bulk.

Derivatization of MPN 2 was again accomplished by stirring a toluene solution of the nanoparticle and a large excess of the desired ligand for 48 h at room temperature. In all cases, the nanoparticle could be precipitated from toluene using EtOH and then suspended in toluene or CHCl₃. The stability of these derivatized nanoparticles was strongly dependent on the ligand: those functionalized with 5 and 6 rapidly precipitated from solution after they were resuspended but were stable for weeks in the solid state following their initial precipitation. Nanoparticles derivatized with 7 were stable for at least a month in solution, but were unstable if solvent was completely removed at any time after their initial precipitation from the derivatization reaction. Nanoparticles derivatized with 8 proved to be the most stable: they were found to remain in solution for at least a month and were dispersible even after being dried in vacuo and stored in the solid state for a month (Figure 4).

The disparity in the observed stabilities of our alcohol-modified MPNs is the result of the alcohol structure and points to a loosely packed monolayer. Nanoparticles coated with dodecanol proved to be unstable in the solid state, whereas both monoalcohol ligands 5 and 6 are stable for long periods of time in the solid state. If the monolayer is sparsely packed, nanoparticles derivatized with 3 are able to approach close enough in the solid state that their cores can agglomerate, whereas the other two molecules present enough organic bulk at the surface to prevent agglomeration. In solution, however, these nanoparticles slowly precipitated over time, indicating a possible kinetic instability in the binding of the alcohol to the nanoparticle surface. This was prevented in the case of ligands 7 and 8, which are able to participate in bidentate binding to the nanoparticle surface. In monolayers formed from 7, however, we observed instability in the solid state, indicating that the amount of organic coating was insufficient to prevent contact of the nanoparticle cores, thus allowing nanoparticle agglomeration. As ligand 8 was found to produce the most stable monolayer–nanoparticle system, we next characterized both MPN 9 and the reaction used to introduce the monolayer (Scheme 2).

**Monolayer Characterization.** Infrared (IR) spectroscopy was used to further characterize the monolayers of MPNs 2 and 9 (Figure 5). The IR spectrum of MPN 2 (Figure 5a) contained the expected methylene stretching peaks as well as a number of peaks in the fingerprint region (−1500−1000 cm⁻¹) arising from the alcohol ligands used in exchange reactions with MPN 2.

![Figure 2. TEM micrographs of MPN 4 (a) immediately after purification, (b) after aggregation, and (c) after sonication of the insoluble material.](image)

![Figure 3. Alcohol ligands used in exchange reactions with MPN 2.](image)
octylamine and trioctylamine, both of which are present during the formation of the nanoparticle. A number of changes were observed after ligand displacement (Figure 5b), the most notable of which is the appearance of a strong adsorption at ca. 1050 cm\(^{-1}\) arising from C–O single-bond stretching. Further, the CH\(_3\)/CH\(_2\) stretching region (2700–2900 cm\(^{-1}\)) also showed an increase in intensity relative to the other spectral features, indicating an increase in the amount of long-chain hydrocarbons. Analysis of the peak positions in this region can yield information about the degree of order within the monolayer. Here, both MPN 2 and 9 exhibit peaks at \(\nu_{\text{as}}(\text{CH}_3)\), \(\sim 2954\) cm\(^{-1}\) for \(\nu_{\text{as}}(\text{CH}_2)\), and \(\sim 2926\) cm\(^{-1}\) for \(\nu_{\text{s}}(\text{CH}_2)\) (inset of Figure 5b), indicating a disordered monolayer. In both cases, an intense, broad adsorption at \(\sim 550\) cm\(^{-1}\) was observed, arising from the Fe\(_2\)O\(_3\) core.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on MPNs 2 and 9 to further compare the two monolayers. The TGA trace of MPN 2 exhibits a steady decrease in mass throughout the range of the scan, with a final loss of 12% of the initial mass at 700 °C (Figure 6, solid trace). This mass loss is less than that observed for undeceneoate-coated MPNs (17.5% of the initial mass), and it might indicate that the amine monolayer is somewhat less densely packed. For MPN 9, a loss of 15% of the initial mass was observed over the same range (Figure 6, dashed trace).

DSC can be used to provide an estimate of the degree of monolayer order on the nanoparticles, as well-packed monolayers exhibit a “melting” transition from a crystalline-like to a liquidlike state on the nanoparticle surface. In previous agglomerate Fe\(_2\)O\(_3\) nanoparticle–alkane thiol monolayer systems, this melting transition was observed at \(\sim 10 \degree \text{C}\) for a dodecane thiol monolayer. For both MPN 2 and 9, DSC traces showed only a featureless, reversible curve between \(-100\) and \(200 \degree \text{C}\) (Figure 7), in good agreement with the IR data, which

(25) See Supporting Information for IR spectra of octylamine and trioctylamine. These data do not allow us to assign the chemical structure of the native monolayer, because the IR spectra of these molecules are nearly indistinguishable in this region. Further, the broad peak observed between 1600 and 1500 cm\(^{-1}\), which neither octylamine nor trioctylamine exhibit, indicates that there might be other components of the native monolayer that are unknown at this time. Further, not all of these peaks disappear after monolayer displacement, indicating that some of the original functionality remains after exchange.

(26) A similar, strong stretch was also observed in the IR spectrum of 8; see Supporting Information.


indicate a disordered monolayer. In sum, both the IR and TGA results confirm that we were able to modify the native monolayer of MPN\textsubscript{2} with diol 8, and the DSC results indicate a less dense monolayer, suggested by the lack of a melting transition, than was observed for other Fe\textsubscript{2}O\textsubscript{3} nanoparticle–organic monolayer systems.\textsuperscript{30}

Characterization of the Nanoparticle Core. For some nanoparticle–monolayer systems, the properties of the inorganic core material can be affected by the type of attached ligand.\textsuperscript{31} To determine whether any changes occurred in the core as a function of the monolayer, we next characterized both MPN\textsubscript{2} and 9 by electron paramagnetic resonance (EPR) and ultraviolet–visible (UV–vis) spectroscopy, as well as by powder X-ray diffraction (XRD).

The EPR spectra of both particles showed a broad, single transition at $g \approx 2$ with a line width of $\approx 1800$ G at room temperature, as is typical for nanoscopic Fe\textsubscript{2}O\textsubscript{3} (Figure 8).\textsuperscript{32,33} The UV–vis spectra of both MPN\textsubscript{2} and 9 (Figure 9) showed a broad absorbance, strong at short

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\textsuperscript{30} TGA and DSC data collected for MPNs modified with ligands 3–7 gave mass losses ranging from 12 to 22% of the initial mass and featureless DSC traces; see Supporting Information.


\textsuperscript{33} In both cases, no second signal at $g \approx 4.3$ appeared, which indicates the lack of rhombic Fe\textsuperscript{3+} sites that are sometimes observed for nanoscopic Fe\textsubscript{2}O\textsubscript{3}.

was next carried out. Here, we explored changes in the ratio between the two reactants as well as the reaction temperature (Table 1). The resulting nanoparticles were characterized by IR spectroscopy, where the degree of derivatization can be estimated by the relative strengths of the C–O and Fe–O stretches (Table 1). Room-temperature reactions were found to inefficiently incorporate into the monolayer of MPN2, even when a large excess of was used in the reaction (Table 1, entries 1–4). At 50 °C, however, significantly less ligand was needed to achieve a higher degree of surface derivatization (Table 1, entries 5–7), and an MPN2/8 mass ratio of at least 3:1 was found to produce a highly modified monolayer.

As mixed-monolayer systems are often used to impart complex functionality into monolayer-nanoparticle systems, we next explored the simultaneous introduction of multiple alcohol ligands into the monolayer of MPN2. Here, both 8 and an amide-functionalized derivative, 10, were stirred in different ratios with MPN2 (Scheme 3 and Table 2) using the previously described conditions. The resulting nanoparticles, MPN11, were then purified by multiple toluene/ethanol precipitations and were then characterized by IR spectroscopy (Figure 11). In addition to the C–O stretching, which arises from both 8 and 10, a new peak at ~1637 cm\(^{-1}\) arising from the amide C=O stretch is also observed for MPN11. As expected, as the ratio of 10 to 8 was increased, the relative intensity of the amide C=O stretch increased as compared to the C–O stretch, because of the relative increase of 10 in the monolayer. This indicates that it is possible to define the relative surface coverage of the two ligands by the synthetic conditions.

**Conclusions**

In summary, we have developed a divergent synthetic pathway that allows access to mixed monolayer-protected γ-Fe\(_2\)O\(_3\) nanoparticles. We found that alkane alcohols can be introduced into the monolayer by stirring amine-coated nanoparticles in solution with the desired alcohol. Here, it was found that both kinetic stabilization, in the form of multivalent ligand-nanoparticle core contacts, and steric stabilization, in the form of a bulky tail group, were necessary to prevent nanoparticle agglomeration. The relative instability of

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(35) All reactions were carried out using 20 mL of a 1:1 mixture of toluene and CHCl\(_3\), and all products were purified by precipitation with MeOH, followed by extensive MeOH washings. Full spectra of these nanoparticles are given in the Supporting Information.

(36) A stepwise reaction was also explored, but it was found to give unreliable results. See Supporting Information.

(37) This peak is insignificantly shifted from the free ligand (~1640 cm\(^{-1}\)) and indicates that the amide group is not involved in binding to the nanoparticle surface.
the nanoparticle monolayer might arise from the sparse monolayer packing observed in these systems, as inferred from TGA, DSC, and IR studies on MPNs 2 and 9. The nature of the γ-Fe₂O₃ core is unaffected by changes in the ligand shell; EPR, UV–vis, and powder XRD spectra are unchanged for nanoparticles with either their native amine monolayers or modified alcohol monolayers. This reaction was optimized to maximize the inclusion of the incoming ligand by using a 3:2 MPN 2-to-ligand mass ratio and conducting the reaction at 50 °C. Finally, we explored the creation of monolayer systems made from two molecular components and found that the most reliable method for introducing multiple functionalities in a predetermined ratio is to exchange in the two components simultaneously. Currently, we are using this ligand design and displacement reaction for the creation of recognition-element-functionalized MPNs to explore their potential application as components in magnetic materials and as biological probes.

Experimental Section

General. Unless otherwise noted, all reactions were carried out in oven-dried glassware under an argon atmosphere. Toluene and CH₂Cl₂ were distilled over CaH₂ under argon. THF was distilled over sodium/benzophenone ketyl immediately before use. 1H NMR spectra were recorded in CDCl₃ (Cambridge Isotope Labs, Inc.) at 200 MHz and referenced internally to TMS at 0.0 ppm. All reagents and other solvents were used as received from commercial sources. IR spectra were recorded on a Perkin-Elmer 783 spectrometer. Samples were prepared by drop casting concentrated CH₂Cl₂ or CHCl₃ analyte solutions onto NaCl plates. UV–vis samples were prepared as CHCl₃ solutions, and a 1-cm-path length quartz cell was used. EPR spectra were recorded on an IBM ESP-300 X-band spectrometer. TEM micrographs were obtained on a JEOL-100CX electron microscope operating at 100 keV. Samples were prepared by dropping CHCl₃ solutions of the desired nanoparticles onto 300-mesh Cu grids coated with a carbon film. TGA was performed on a TA Instruments TGA 2050 apparatus. DSC was obtained on a Perkin-Elmer Pyris 1 instrument. XRD patterns were recorded on a Nonius instrument with a KappaCCD area detector at room temperature using graphite-monochromated Mo Kα radiation.

**Scheme 4. Synthesis of Ligands 7 and 8**

![Scheme 4](image)

**Figure 11.** IR spectra from simultaneous exchange study. Spectra are for (a) MPN 2 and (b–d) entries 1–3, respectively, of Table 2. All spectra were recorded as thin films cast from CHCl₃ onto NaCl plates.

In a 250-mL three-neck round-bottom flask, diethyl malonate (2.5 g, 15.6 mmol, 2.4 mL) was dissolved in 100 mL of absolute EtOH, giving a clear solution. NaOEt (19 mmol, 8.1 mL of a 21 wt % solution in EtOH) was then added slowly, and the reaction mixture became bright orange. After the mixture had been for 30 min, dodecyl bromide (5.85 g, 23.4 mmol, 5.7 mL) was added, and the reaction mixture was refluxed for 48 h, during which time a white precipitate formed. After the reaction mixture had been cooled to room temperature, a second equal portion of NaOEt was added, followed by 30 min of stirring at room temperature, the addition of a second equal amount of dodecyl bromide, and another 48 h at reflux. The EtOH was removed in vacuo, and the resulting thick slurry was dissolved in EtOH. A solution of NaOH (1 M, 12.3 mL) was added slowly, and the reaction mixture became bright orange. After the mixture had been for 30 min, the resulting slurry was filtered through SiO₂ with 10% EtOAc/hexanes and used without further purification (6.5 g, 84% yield).

In a 100-mL round-bottom flask, the product from the preceding reaction (2.0 g, 4.02 mmol) was dissolved in 40 mL of THF and cooled to –78 °C. Lithium aluminum hydride (24 mmol, 24 mL of a 1 M solution in THF) was then added dropwise, and the reaction mixture was stirred overnight at room temperature. After careful quenching of the reaction by the dropwise addition of H₂O, the reaction mixture was...
transferred to a separatory funnel, washed once with each 1 M aqueous NaOH and saturated aqueous NaCl, and dried over MgSO₄. Solvent removal resulted in an off-white solid, which was chromatographed (SiO₂ gradient elution, EtOAc to 10% MeOH/EtOAc) to yield the product as a white solid (1.4 g, 82% yield).¹ ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 3.7 (m, 2H), 3.57 (d, 4H, J = 5.4 Hz), 2.77 (m, 4H), 1.26 (m, 40H), 0.88 (m, 6H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 3340, 2915, 2820, 2812, 1640, 1020 cm⁻¹. Anal. Calcd. for C₂₇H₅₆O₂: C, 78.57; H, 13.68. Found: C, 77.93; H, 13.41.

**Diethyl Dodecylmalonate (14).** In a 250-mL three-neck round-bottom flask, diethyl malonate (16.1 g, 100 mmol, 15.2 mL) was dissolved in 100 mL of absolute EtOH, giving a clear solution. NaOEt (100 mmol, 42 mL of a 21 wt % solution in EtOH) was then added slowly, and the reaction mixture was allowed to stir overnight at room temperature. After careful quenching of the reaction by the dropwise addition of H₂O, the reaction mixture was refluxed for 36 h under argon, during which time a white precipitate formed. The EtOH was removed in vacuo, and the resulting thick slurry was dissolved in EtoAc. The organic fraction was washed once with each 1 M aqueous HCl and saturated aqueous NaCl and dried over MgSO₄. Solvent removal gave a thick yellow/orange oil, which was chromatographed (SiO₂/hexanes) to give the product as a white solid (2.1 g, 82% yield). ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 3.58 (m, 2H), 3.22 (m, 2H), 2.25 (bs, 6H), 1.85 (m, 4H), 1.29 (m, 44H), 0.88 (m, 6H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 2915, 2810, 1735, 1720, 1460, 1150, 1015 cm⁻¹. Anal. Calcd. for C₂₉H₃₈O₂: C, 64.97; H, 11.05. Found: C, 65.89; H, 11.25.

**2-Hydroxymethyltetradecan-1-ol (7) (Scheme 4).** In a 100-mL round-bottom flask, 13 (500 mg, 1.5 mmol) was dissolved in 20 mL of THF and cooled to –78 °C. Lithium aluminum hydride (9 mmol, 9 mL of a 1 M solution in THF) was then added dropwise, and the reaction mixture was allowed to stir overnight at room temperature. After careful quenching of the reaction by the dropwise addition of H₂O, the reaction mixture was transferred to a separatory funnel, washed once with each 1 M aqueous NaOH and saturated aqueous NaCl, and dried over MgSO₄. Solvent removal gave the product as an off-white solid, which was chromatographed (SiO₂/hexanes) to give the product as a white solid (310 mg, 85% yield). ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 3.55 (s, 4H), 2.69 (t, 2H, J = 6.9 Hz), 2.15 (t, 2H, J = 7.8 Hz), 1.77 (m, 1H), 1.26 (m, 20H), 0.88 (m, 3H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 3370, 2910, 2850, 1490, 1010, 680 cm⁻¹. Anal. Calcd. for C₁₉H₃₆O₄: C, 73.71; H, 13.20. Found: C, 73.88; H, 13.35.

**3-Dodecylpentacosane-13-ol (5) (Scheme 5).** In a 100-mL round-bottom flask, dimethyl carbonate (450 mg, 5.0 mmol, 0.42 mL) was dissolved in 10 mL of THF and cooled to –78 °C. Dodecylmagnesium bromide (20 mmol, 48 mL of a 1 M solution) was then added, and the reaction mixture was allowed to stir for three nights at room temperature. The reaction was quenched by the careful addition of MeOH, the organic fraction was chromatographed (SiO₂ gradient elution, EtOAc to 10% MeOH/EtOAc) to yield the product as a white solid (310 mg, 85% yield). ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 3.60 (m, 4H), 2.34 (t, 2H, J = 7.8 Hz), 1.34 (m, 66H), 0.88 (m, 9H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 3340, 2915, 2820, 2810, 1480 cm⁻¹. Anal. Calcd. for C₃₇H₇₆O: C, 82.76; H, 14.27. Found: C, 82.84; H, 14.20.

**Pentacosane-13-ol (6) (Scheme 5).** In a 100-mL round-bottom flask, ethyl formate (500 mg, 6.67 mmol, 0.54 mL) was dissolved in 10 mL of THF and cooled to –78 °C. Dodecylmagnesium bromide (20 mmol, 48 mL of a 1 M solution) was then added, and the reaction mixture was allowed to stir for three nights at room temperature. The reaction was quenched by the addition of MeOH and then saturated aqueous NH₄Cl. The organic phase was transferred to a separatory funnel, washed once with a saturated aqueous NaCl solution, and dried over MgSO₄. After solvent removal, the crude material was recrystallized from EtOAc to yield the product as a white solid (2.1 g, 84% yield). ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 3.58 (m, 1H), 1.29 (m, 44H), 0.88 (m, 6H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 3340, 2915, 2820, 2810, 1480, 1020 cm⁻¹. Anal. Calcd. for C₂₅H₅₂O: C, 81.44; H, 14.22. Found: C, 81.38; H, 14.20.

**Diethyl 5-Cyanopentyl Dodecyl Malonate (16).** In a 125-mL three-neck round-bottom flask, 14 (7.0 g, 21 mmol) was dissolved in 30 mL of THF and cooled to –78 °C. Lithium di-isopropyl amide (24 mmol, 24 mL of a 1 M THF solution) was then added and the reaction mixture was subsequently allowed to stir for an hour at room temperature. 6-Bromohexan-1-ol (25 mg, 0.24 mmol) was then added, and the reaction mixture was refluxed for 36 h under argon, during which time a precipitate formed. After the reaction had been quenched by the careful addition of MeOH, the organic fraction was washed once with each 1 M aqueous HCl and saturated aqueous NaCl, and dried over MgSO₄. Solvent removal gave a thick orange oil, which was chromatographed (SiO₂ gradient elution of hexanes to 10% EtOAc/hexanes) to give the product as a pale yellow oil (7.4 g, 85% yield). ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 4.18 (q, 4H, J = 6.88 Hz), 2.33 (t, 2H, J = 6.9 Hz), 1.89 (m, 4H), 1.56 (mm, 4H), 1.25 (m, 22H), 0.88 (m, 3H), 0.68 (m, 3H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 2920, 2840, 2245, 1620, 1480, 1020 cm⁻¹. Anal. Calcd. for C₂₇H₃₉NO: C, 70.88; H, 10.71. Found: C, 70.84; H, 10.95.

**1-Amino-7,7-bis-hydroxymethylnonadecane (17).** In a 100-mL round-bottom flask, 15 (500 mg, 0.95 mmol) was dissolved in 20 mL of THF and cooled to –78 °C. Lithium aluminum hydride (10 mmol, 10 mL of a 1 M solution in THF) was then added dropwise, and the reaction mixture was allowed to stir overnight at room temperature. After careful quenching of the reaction by the dropwise addition of H₂O, the reaction mixture was transferred to a separatory funnel, washed once with each 1 M aqueous NaOH and saturated aqueous NaCl, and dried over MgSO₄. Solvent removal gave viscous yellow oil, which was used without further purification in the next reaction (310 mg, 95% yield). ¹H NMR (CDCl₃, 200 MHz): δ (ppm) 3.55 (s, 4H), 2.69 (t, 2H, J = 6.9 Hz), 2.25 (bs, 2.1 Hz), 1.95 (m, 9H), 1.54 (m, 22H), 0.88 (m, 6H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 3025, 2910, 1735, 1680, 1480, 1020 cm⁻¹. Anal. Calcd. for C₁₉H₃₈O₅: C, 78.57; H, 13.68. Found: C, 77.93; H, 13.41.
N-Hexanoyl-1-amino-7,7-bis-hydroxymethylnonadecane (10) (Scheme 6). In a 50-mL round-bottom flask, 16 (310 mg, 0.9 mmol) was dissolved in 25 mL of CH₂Cl₂. Triethylamine (200 mg, 1.9 mmol, 0.27 mL) was added, and the light yellow solution was cooled to −78 °C. Hexanoyl chloride (100 mg, 0.76 mmol, 0.1 mL) was added dropwise, and the reaction mixture was allowed to stir for 3 h at room temperature. The mixture was then washed once with each 1 M aqueous HCl saturated aqueous NaHCO₃, and saturated aqueous NaCl before being dried over MgSO₄. Solvent removal gave a white tacky solid, which was chromatographed (SiO₂ gradient elution, 1:1 EtOAc/hexanes to 5% MeOH/EtOAc) to give the product as a thick, colorless oil (250 mg, 76% yield).

1H NMR (CDCl₃, 200 MHz): δ (ppm) 5.43 (bs, 1H), 3.57 (s, 4H), 3.24 (q, 2H, J = 8.32 Hz), 2.34 (m, 2H), 2.15 (t, 2H, J = 7.86 Hz), 1.6 (mm, 4H), 1.26 (m, 34H), 0.89 (m, 6H). IR (thin film from CH₂Cl₂ on NaCl plate): νmax 3300, 3090, 2920, 2845, 1640, 1550, 1470, 1030 cm⁻¹.

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Supporting Information Available: Additional characterization (TEM, DSC, TGA) of MPNs and spectra of intermediates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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