Supplemental Information

Core Size Effects on the Reactivity of Organic Substrates as Monolayers on Gold Nanoparticles

Arnold J. Kell, Robert L. Donkers and Mark S. Workentin*

Materials and Methods

Preparation of small MPN (C\textsubscript{12}MPN\textsubscript{small})

Preparation of medium MPN (C\textsubscript{12}MPN\textsubscript{medium})

Preparation of large MPN (C\textsubscript{12}MPN\textsubscript{large})

Preparation of aryl ketone probes

Place exchange reactions

1-4-C\textsubscript{12}MPN\textsubscript{large}

1 and 2-C\textsubscript{12}MPN\textsubscript{small}

1(edge)-C\textsubscript{12}MPN\textsubscript{medium}

1(terrace)-C\textsubscript{12}MPN\textsubscript{medium} 1-C\textsubscript{12}MPN\textsubscript{medium}

Stoichiometry for MPNs

Irradiation of the MPNs:

Description of spectral changes for each MPN studied

Determination of Extents of Reaction (how we did it)

Decomposition after Irradiations

Core sizes and histograms for 1-4-C\textsubscript{12}MPN\textsubscript{X}

Irradiation of the MPNs:

\textsuperscript{1}H NMR spectra of each decomposed MPN

Histograms comparing 1-C\textsubscript{12}MPN\textsubscript{small}, 2-C\textsubscript{12}MPN\textsubscript{small} and 1-C\textsubscript{12}MPN\textsubscript{medium}
Materials and Methods

The compounds thionyl chloride, 11-bromoundecanoic acid, 1-phenylhexane, hexanoic acid, undecanoic acid, 1, 11-dibromoundecane, phenyllithium, potassium thioacetate, aluminum chloride, dodecanethiol, methoxyethoxymethylchloride, triethyl amine, 48% hydrobromic acid, sodium borohydride and hydrogen tetrachloroaurate (II) trihydrate were purchased from Aldrich and used as received. Dichloromethane, benzene, toluene, potassium carbonate, hydrochloric acid and hexanes were purchased from Caledon, spectroscopy grade benzene was purchased from EM Science and 95 % ethanol was purchased from Commercial Alcohols Inc and were all used as received. Benzene-$d_6$, chloroform-$d$ and dichloromethane-$d_2$ were purchased from Cambridge Isotope Laboratories.

Irradiations were carried out in pyrex NMR tubes containing ~15 mg of MPN dissolved in 0.5-0.6 mL of nitrogen or argon saturated benzene-$d_6$ sealed with a septum. The light source was a medium pressure Hg Hanovia arc lamp cooled in a quartz immersion well and a constant temperature bath, where the temperature was maintained at 23 ± 3 °C and was filtered by the pyrex NMR tube. Earlier investigations indicate that the absorption of light by the plasmon absorption band at 520 nm does not affect the photochemistry of the aryl ketones or the overall stability of the MPN.

Proton NMR spectra were recorded on a Varian Mercury 400 (400.087 MHz) spectrometer in benzene-$d_6$, chloroform-$d$ or dichloromethane-$d_2$ solvent using the solvent resonances at 7.15, 7.26 or 5.33 ppm as the reference. UV-visible spectra were carried out on a Cary 100 BioUV spectrometer in spec-grade benzene and IR spectra were recorded on a Bomem MB100 or Bruker Vector33 spectrometer using a dropcasting technique on NaCl plates or in a
solution cell with carbon tetrachloride solvent. TEM images were recorded on a Phillips CM12 electron microscope operating at 120 keV. The samples were prepared by dropcasting toluene solutions of the MPNs (~1 mg/mL) onto standard carbon-coated Formvar films on copper grids. The grids were allowed to dry for at least 1 hour before the images were recorded. Size distributions of the MPN cores were determined from enlarged TEM image photographs, where 120-300 MPNs were measured for each sample.

**Preparation of small MPN (C12MPN\textsubscript{small})**

Following the procedures of Brust\textsuperscript{1} and Murray,\textsuperscript{2} to a 250 mL round bottom flask was added hydrogen tetrachloroaurate (III) trihydrate (0.30 g, 0.768 mmol) dissolved in 28 mL distilled water (resulting in a bright yellow solution) and tetraoctylammonium bromide (2.30 g, 4.21 mmol) dissolved in 70 mL toluene (a clear and colorless solution). The contents were rapidly stirred for 30 minutes at room temperature in order to facilitate phase transfer the hydrogen tetrachloroaurate (III) trihydrate into the toluene layer, which resulted in the organic layer turning to a dark orange color and the aqueous layer becoming clear and colorless. After phase transfer the aqueous layer was removed, the contents of the flask cooled to 0°C with an ice filled dewer bath and dodecanethiol (0.47 g, 0.56 mL, 2.32 mmol) was added to the solution via a volumetric pipet and allowed to stir for ten minutes. The addition of dodecanethiol resulted in a color change from brownish-orange to colorless. A fresh solution of sodium borohydride (0.33 g, 8.68 mmol) in 28 mL water was then added to the rapidly stirring toluene solution over 5 seconds. Almost immediately the solution darkened, eventually becoming dark brown. The mixture was allowed to stir overnight (~18 hours) as it warmed to room temperature after which time the aqueous layer was removed and the toluene layer washed with 3 x 20 mL distilled water.
and dried over MgSO₄. The toluene layer was then isolated by gravity filtration and evaporated
to dryness. The resulting mixture of C₁₂MPNsmall and tetraoctylammonium bromide was
suspended in 200 mL of 95 % ethanol and placed in the freezer overnight during which the
C₁₂MPNsmall precipitated from solution. When the MPN had precipitated the supernatant was
decanted, and the precipitate dissolved in benzene and concentrated resulting in the formation of
a film in the round bottom flask. This film was washed repeatedly with 10 x 15 mL of 95%
ethanol, resulting in pure MPN as judged by ¹H-NMR spectroscopy, which showed no signs of
dodecanethiol, dodecyldisulfide or tetraoctylammonium bromide. The resulting MPN was dark
brown in color.

**Preparation of medium MPN (C₁₂MPNmedium)**

The procedure was identical to that described for C₁₂MPNsmall, however the
stoichiometries of the reagents were different. In this procedure HAuCl₄ (0.6 g, 1.54 mmol),
tetraoctylammonium bromide (4.60 g, 8.41 mmol), dodecanethiol (0.31 g, 1.54 mmol) and
sodium borohydride (0.66 g, 17.36 mmol) were employed. The MPN was dark brown in color.

**Preparation of large MPN (C₁₂MPNlarge)**

The procedure was identical to that described for C₁₂MPNsmall, however the
stoichiometries of the reagents were different. In this procedure HAuCl₄ (0.6 g, 1.54 mmol),
tetraoctylammonium bromide (4.60 g, 8.41 mmol), dodecanethiol (0.05 g, 2.24 mL, 0.062 mmol)
and sodium borohydride (0.66 g, 17.36 mmol) were employed. The MPN was deep purple-red
in color, quite different from the analogous C₁₂MPNsmall and C₁₂MPNmedium derivatives, which
were dark brown in color.
Preparation of aryl ketone probes

The aryl ketones employed in this study are 11-mercaptoundecaphenone (1), 1-(4-hexyl-phenyl)-11-mercaptoundecanone (2), 1-[4-(11-mercaptoundecyl)phenyl]hexanone (3) or 1-[4-(11-mercaptoundecyl)phenyl]undecanone (4). The conditions for their preparation have been described in earlier publications.3,4

Place exchange reactions

1-4-C_{12}MPN_{large}

The MPNs are identified using the following nomenclature. Aryl ketone 1 place exchanged onto a base C_{12}MPN with a small core diameter is represented as 1-C_{12}MPN_{small}. The place exchange reactions were carried out on 0.120 – 0.150 g of the MPN.5,6 It was assumed that the mass of dodecanethiolate on each MPN was ~25% of the total mass of the MPN. From this, the moles of dodecanethiolate surrounding the MPN can be calculated. In general C_{12}MPN_{large} was dissolved in 35 mL of toluene and the appropriate aryl ketone probe was added to the solution. Specifically, a 6 times molar excess of 1, 2 times excess of 2, a 5 times excess of 3 and a 5 times excess of 4 were stirred under nitrogen for 4-5 days. Each of the MPNs was purified after concentration by repeatedly washing with warm absolute ethanol and warm acetone. We found these large MPNs to be extremely temperamental. Heating above 35 – 40 °C seems to randomly cause the irreversible aggregation of the MPNs.
1 and 2-C\textsubscript{12}MPN\textsubscript{small}

The C\textsubscript{12}MPN\textsubscript{small} (0.100 g, 0.025 g dodecanethiolate, 0.12 mmol dodecanethiolate) was stirred under a nitrogen atmosphere in 30 mL toluene in the presence of a 3-4 times excess of either 1 or 2. The modified 1 and 2-C\textsubscript{12}MPN\textsubscript{small} were purified after place exchange via repeated washing with warmed (40\textdegree C) 95 % absolute ethanol. The stoichiometries of the MPNs were determined via \textsuperscript{1}H NMR spectroscopy after I\textsubscript{2} induced decomposition.

1(edge)-C\textsubscript{12}MPN\textsubscript{medium}

The selective population of the edge and vertex sites was carried out using 60 mg of C\textsubscript{12}MPN\textsubscript{medium} and 15 mg of 1 dissolved in 25 mL of toluene under a nitrogen gas atmosphere. The contents of the flask were stirred for 45 minutes at which time the MPN was concentrated and any remaining 1 and displaced dodecanethiol were washed away from the MPN with 95 % ethanol. The resulting 1(edge)-C\textsubscript{12}MPN\textsubscript{medium} has 1 residing primarily at the edge and vertex sites.

1-C\textsubscript{12}MPN\textsubscript{medium} and 1(terrace)-C\textsubscript{12}MPN\textsubscript{medium}

The selective population of the terrace sites was carried out using 0.120 g of C\textsubscript{12}MPN\textsubscript{medium} and 0.185 g of 1 dissolved in 40 mL of toluene under a nitrogen gas atmosphere. The contents of the flask were stirred for 5 days at which time the MPN was concentrated and any remaining 1 and displaced dodecanethiol were washed away from the MPN with 95 % ethanol. The resulting 1-C\textsubscript{12}MPN\textsubscript{medium} has 1 distributed over all sites on the MPN surface. Half of this MPN (0.068 g) was dissolved in 20 mL of toluene then subjected to a short place
exchange reaction with 0.150 g of dodecanethiol for 45 minutes where the edge and vertex sites will be populated with dodecanethiol and any 1 on the MPN will be trapped predominantly at the terrace sites. The MPN was washed free of and liberated 1 and dodecanethiol with 95 % ethanol. The resulting MPN is referred to as 1(terrace)-C_{12}MPN_{medium}.

**Stoichiometry for MPNs**

The stoichiometries of the MPNs were determined via I$_2$ decomposition: this was accomplished by comparison of the aromatic resonance signals for the protons $\alpha$ to the carbonyl at 7.93-7.96 ppm with the resonance signal consistent with the terminal methyl group at 0.9 ppm in CDCl$_3$. For 2, 3 and 4 modified MPNs the contribution for the resonance signal of the terminal methyl group on the molecule must be taken into account when the stoichiometries are calculated. The stoichiometries are listed in Table 1 of the manuscript.

**Irradiation of the MPNs: Monitoring Spectral changes**

A $^1$H NMR spectrum ~15-20 mg of 1-4-C$_{12}$MPN$_X$ dissolved in nitrogen or argon saturated benzene-$d_6$ was taken prior to irradiation and at intermittent times during the irradiation until no further spectral changes could be detected. In general, the spectral changes were identical to those observed in our earlier study.$^{3,4}$ Where the probe is 1 or 2 the broad resonances at 7.90, 7.10 and 2.70 ppm decrease in intensity as broad resonances at 5.90, 5.10 and 2.10 ppm increase in intensity indicating that MPN bound alkene is generated (Figure S1-S4). There is also an increase in the intensity of sharp resonance signals at 7.80 and 7.03 ppm and a singlet at 2.10 ppm indicating that an acetophenone is liberated from the MPN. When the probe was 2 a $p$-
alkylacetophenone is liberated from the MPN surface and sharp resonances also appear at 2.38, 1.22 and 0.89 ppm. Generally irradiations were deemed complete when no further changes accompanied extended irradiation.

Where the probe molecule was 3 and 4 the broad resonances at 7.96, 7.13, 2.68, 1.29 and 0.90 ppm decrease in intensity concomitant with a growing in of broad resonances at 7.84, 7.04, 2.21 ppm (Figure S5 and S6). The resonance signals due to the alkene liberated to solution appear as sharp resonances at 5.73 and 5.02, 1.97, 1.22 and 0.89 ppm (Figure S5 and S6).

**Determination of Extents of Reaction**

The extents of reaction or conversions were determined either directly from the MPN (as for 1 and 2-C_{12}MPN_{small}, 1-C_{12}MPN_{medium} 1(terrace)-C_{12}MPN_{medium} 1(edge)-C_{12}MPN_{medium} ) or via an I\textsubscript{2} or cyanide induced decomposition reaction where the substrate is liberated from the surface as a mixed disulfide (as for 1-4-C_{12}MPN_{large}). The decomposition reaction was required for the 1-4-C_{12}MPN_{large} and the corresponding reaction products because the broadness of the \textsuperscript{1}H NMR spectra would not allow accurate integration of the resonance signals attributed to 1-4 and their corresponding reaction product.

**Decomposition after Irradiations**

The decomposition reactions carried upon completion of the irradiations were promoted by sodium cyanide in tetrahydrofuran or I\textsubscript{2} in dichloromethane. The I\textsubscript{2} induced decompositions resulted in some I\textsubscript{2} reaction with the alkene (where possible), resulting in 1,2-diiodo-based disulfides (see Figure S7 and S8). In a test reaction we verified that I\textsubscript{2} adds across the alkene functionality. The addition of I\textsubscript{2} to a mixture 1 and 11-mercaptopundecene in dichloromethane
generates disulfide products consistent with the parent functional groups (i.e. alkene and aryl ketone) and disulfide products consistent with the addition of I\textsubscript{2} across the olefin bond to produce a 1,2-diiodo-based product. The chemical shifts and splitting patterns present in the \textsuperscript{1}H NMR spectra of these products are consistent with the analogous dibromides in the Aldrich book of NMR spectra (i.e. 1,2-dibromohexane). In general the MPNs were washed clean of any alkene or acetophenone prior to decomposition and dissolved in dichloromethane, dichloromethane-\textit{d}\textsubscript{2} or tetrahydrofuran. For decompositions carried out in dichloromethane, an I\textsubscript{2} solution of dichloromethane was added dropwise to the MPN solution. Upon addition of the minimum amount of I\textsubscript{2} the solution turned from its original dark purple-red color to a faint orange color with brown precipitate. At this point a \textsuperscript{1}H-NMR spectrum was run on the resulting mixed disulfide to determine the extent of reaction. For decompositions carried out in THF, the MPN was dissolved in THF and an aqueous solution of sodium cyanide was added dropwise until the solution turned from purple-red to colorless. At this point the solution was concentrated and a \textsuperscript{1}H NMR spectrum was run on the mixed disulfide product in order to determine the extent of reaction.
Core sizes and histograms for $1$-$4$-$\text{C}_{12}\text{MPN}_X$, where $X=$small, medium and large.

Core sizes for $1$-$\text{C}_{12}\text{MPN}_\text{small}$.

Core sizes for $1$-$\text{C}_{12}\text{MPN}_\text{medium}$.
Core sizes for $1(\text{terrace})$-$C_{12}\text{MPN}_{\text{medium}}$.

Core sizes for $1(\text{edge})$-$C_{12}\text{MPN}_{\text{medium}}$. 
Core sizes for $1$-$C_{12}$MPN$_{\text{large}}$.

Core sizes for $2$-$C_{12}$MPN$_{\text{small}}$. 

Core sizes for $2\text{-C}_{12}\text{MPN}_{\text{large}}$.

Core sizes for $3\text{-C}_{12}\text{MPN}_{\text{large}}$. 
Core sizes for 4-C12MPN_{large}.
Figures for Supporting Information

**Figure S1**: Proton NMR spectra of 1-C<sub>12</sub>MPN<sub>large</sub> measured in benzene-<i>d</i><sub>6</sub> (C<sub>6</sub>H<sub>6</sub> indicated with *) a, before irradiation; b, during the irradiation and c, when the irradiation was complete and the modified MPN had been washed free of liberated acetophenone. In <sup>1</sup>H NMR spectra b, the solid arrows highlight the growing in of resonances associated with the liberation of acetophenone from the MPN surface. In spectra c the hollow arrows indicate where the resonances associated with 1 have decreased in intensity and the filled arrows indicate the resonances associated with the growing in of nonene anchored to the MPN surface.
**Figure S2:** Proton NMR spectra of 2-C_{12}MPN\textsubscript{large} measured in benzene-\textit{d}_6 (C_6H_6 indicated with *) a, before irradiation; b, during the irradiation and c, when the irradiation was complete and the modified MPN had been washed free of liberated \(p\)-hexyl acetophenone. In \(^1\)H NMR spectra b, the solid arrows highlight the growing in of resonances associated with the liberation of \(p\)-hexyl acetophenone from the MPN surface. In spectra c the hollow arrows indicate where the resonances associated with 2 have decreased in intensity and the filled arrows indicate the resonances associated with the growing in of nonene anchored to the MPN surface. Some residual toluene remains in a. This was not removed before irradiation commenced, but is not expected to effect the reaction.
**Figure S3:** Proton NMR spectra of 1-C_{12}MPN_{small} measured in benzene-\textit{d}_6 (C_6H_6 indicated with *) a, before irradiation; b, during the irradiation and c, when the irradiation was complete and the modified MPN had been washed free of liberated acetophenone. In ^1H NMR spectra b, the solid arrows highlight the growing in of resonances associated with the liberation of acetophenone from the MPN surface. In spectra c the hollow arrows indicate where the resonances associated with 1 have decreased in intensity and the filled arrows indicate the resonances associated with the growing in of nonene anchored to the MPN surface. Some residual hexanes remains in b (hexanes was used to dissolve the MPN after the liberated acetophenone had been washed away from the MPN during irradiation). This was not removed before irradiation was commenced, but is not expected to effect the reaction.
Figure S4: Proton NMR spectra of 2-C_{12}MPN_{small} measured in benzene-d_{6} (C_{6}H_{6} indicated with *) a, before irradiation; b, during the irradiation and c, when the irradiation was complete and the modified MPN had been washed free of liberated p-hexylacetophenone. In $^1$H NMR spectra b, the solid arrows highlight the growing in of resonances associated with the liberation of p-hexylacetophenone from the MPN surface. In spectra c the hollow arrows indicate where the resonances associated with 2 have decreased in intensity and the filled arrows indicate the resonances associated with the growing in of nonene anchored to the MPN surface.
Figure S5: Proton NMR spectra of $3\text{-C}_{12}\text{MPN}_{\text{large}}$ measured in benzene-$d_6$ ($C_6H_6$ indicated with *) a, before irradiation, b, during the irradiation and c, when the irradiation was complete and the modified MPN had been washed free of liberated butene. In $^1\text{H}$ NMR spectra b, the solid arrows highlight the growing in of resonances associated with the liberation of butene (barely visible, because butane is quite volatile) from the MPN surface. In spectra c the hollow arrows indicate where the resonances associated with 3 have decreased in intensity and the filled arrows indicate the resonances associated with the growing in of $p$-acetophenone anchored to the MPN surface. The lines from spectra a to c and spectra b to c help to identify the shift in resonance frequency associated with the modified acetophenone MPN with respect to the original $3\text{-C}_{12}\text{MPN}_{\text{large}}$.
Figure S6: Proton NMR spectra of 4-C\textsubscript{12}MPN\textsubscript{large} measured in benzene-\textit{d\textsubscript{6}} (C\textsubscript{6}H\textsubscript{6} indicated with *) a, before irradiation; b, during the irradiation and c, when the irradiation was complete and the modified MPN had been washed free of liberated nonene. In $^1$H NMR spectra b, the solid arrows highlight the growing in of resonances associated with the liberation of nonene from the MPN surface and resonances at 7.8 and 2.4 ppm are due to liberation of very small amounts of disulfide during the irradiation. In spectra c the hollow arrows indicate the decreased intensity of resonances associated with 4 and the filled arrows indicate the growing in of resonances associated with $p$-alkylacetophenone anchored to the MPN surface.
Figure S7: Proton NMR spectra of $\text{1-C}_{12}\text{MPN}_{\text{large}}$ measured CDCl$_3$ after cyanide induced decomposition which results in a mixture of disulfide products. The resonance signal at 7.96 ppm is due to the protons $\alpha$ to the carbonyl on the phenyl ring in $\text{1}$, and the resonance signal at 2.94 ppm is due to the protons $\alpha$ to the carbonyl on the alkyl chain of $\text{1}$. The resonances at 5.80 and 4.95 ppm are due to the vinyl on the nonene moiety and the resonance at 2.35 ppm is due to the allyl protons of the nonene. The resonance signal at 7.36 is due to benzene.
Figure S8: Proton NMR spectra of $2\text{-C}_{12}\text{MPN}_{\text{large}}$ measured CDCl$_3$ after I$_2$ induced decomposition which results in a mixture of disulfide products. The resonance signal at 7.9 ppm is due to the protons $\alpha$ to the carbonyl on the phenyl ring in 2, and the resonance signal at 2.94 ppm is due to the protons $\alpha$ to the carbonyl on the alkyl chain of 2. The resonances at 5.83 and 5.0 ppm are due to the vinyl on the nonene moiety and the resonance at 2.05 ppm is due to the allyl protons of the nonene. Finally, the resonances at 4.33, 4.08 and 3.38 ppm are due to the diiodononane product derived from the addition of I$_2$ across the double bond of nonene (each resonance signal integrates to 1 proton). We speculate that the signal at 3.35 ppm is possibly due to a terminal iodide, which would integrate to 2 protons, so the signal is included in the calculation for the extent of reaction, but is essentially negligible. The resonance signals at 7.20 and 2.35 are due to toluene.
Figure S9: Proton NMR spectra of 3-C_{12}MPN_{large} measured benzene-$d_6$ after I$_2$ induced decomposition which results in a mixture of disulfide products. The resonance at 7.9 ppm and the shoulder at 2.62 ppm are due to the protons $\alpha$ to the carbonyl on the phenyl ring and the protons $\alpha$ to the carbonyl on the alkyl chain of 3 respectively. The resonance signals at 7.8 and 2.14 ppm are due to the protons $\alpha$ to the carbonyl on the phenyl ring of the $p$-acetophenone and the protons on the methyl ketone on the new ketone respectively. The resonance signal at 2.41 ppm is due to overlapping signals from the protons on the alkyl chain para to the ketones on the phenyl rings of both 3 and the new $p$-acetophenone moiety. Finally, the resonances at 0.93 and 0.86 ppm are due to the terminal methyl protons on the C_{12} moiety and 3, respectively.
**Figure S10:** Proton NMR spectra of 4-C\textsubscript{12}MP\textsubscript{large} measured benzene-\textit{d\textsubscript{6}} after I\textsubscript{2} induced decomposition which results in a mixture of disulfide products. The resonance at 7.9 ppm and the shoulder at 2.65 ppm are due to the protons \(\alpha\) to the carbonyl on the phenyl ring and the protons \(\alpha\) to the carbonyl on the alkyl chain of 4 respectively. The resonance signals at 7.8 and 2.14 ppm are due to the protons \(\alpha\) to the carbonyl on the phenyl ring of the \(p\)-acetophenone and the protons on the methyl ketone on the \(p\)-acetophenone, respectively. The resonance signal at 2.41 ppm is due to overlapping signals from the protons on the alkyl chain \textit{para} to the ketones on the phenyl rings of both 2 and the new \(p\)-acetophenone moiety and the resonance signal at 0.93 ppm is due to the terminal methyl protons on both 4 and the C\textsubscript{12} moiety.
**Figure S11:** Proton NMR spectra of 1-C_{12}MPN_{small} measured benzene-\textit{d}_6 after irradiation. The resonance signals at 7.9 ppm and at 2.82 ppm due to the protons α to the carbonyl on the phenyl ring and the protons α to the carbonyl on the alkyl chain of 1 respectively have completely disappeared. The resonance signals at 5.89 and 5.11 ppm are due to the vinyl protons on the nonene modified MPN and the resonance signal at 2.15 is due to the proton in the allyl position in the nonene moiety.
Figure S12: Proton NMR spectra of 2-C_{12}MPN_{small} measured benzene-\textit{d}_6 after irradiation. The resonance signals at 7.89, 2.82 and 2.45 ppm are due to the protons α to the carbonyl on the phenyl ring and the protons α to the carbonyl on the alkyl chain and the protons α to the phenyl ring on the \textit{p}-alkyl chain of 2 respectively. The resonance signals at 5.89 and 5.11 ppm are due to the vinyl protons on the nonene modified MPN and the resonance signal at 2.15 is due to the proton in the allyl position in the nonene moiety.
Figure S13: The histograms for 1-C_{12}MPN_{small} (a), 2-C_{12}MPN_{small} (b) and 1-C_{12}MPN_{medium}. Of note is the increased contribution for the 2.04 nm core in 2-C_{12}MPN_{small} in comparison to 1-C_{12}MPN_{small}. 
References


