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PAMAM dendrimers and graphene: Materials for removing aromatic contaminants from water

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Abstract

We present results from experiments and atomistic molecular dynamics simulations on the remediation of naphthalene by polyamidoamine (PAMAM) dendrimers and graphene oxide (GrO). Specifically, we investigate 3rd-6th generation (G3-G6) PAMAM dendrimers and GrO with different levels of oxidation. The work is motivated by the potential applications of these emerging nanomaterials in removing polycyclic aromatic hydrocarbon contaminants from water. Our experimental results indicate that GrO outperforms dendrimers in removing naphthalene from water. Molecular dynamics simulations suggest that the prominent factors driving naphthalene association to these seemingly disparate materials are similar. Interestingly, we find that cooperative interactions between the naphthalene molecules play a significant role in enhancing their association to the dendrimers and GrO. Our findings highlight that while selection of appropriate materials is important, the interactions between the contaminants themselves can also be important in governing the effectiveness of a given material. The combined use of experiments and molecular dynamics simulations allows us to comment on the possible factors resulting in better performance of GrO in removing polyaromatic contaminants from water.

Keywords: Dendrimers, polyaromatic hydrocarbons, remediation, graphene, molecular simulations
Introduction

Economical and effective water purification is recognized as a top 21st century challenge.\textsuperscript{(1)} Applications of water purification to environmental clean-up and removal of contaminants from drinking water will become ever more important as a growing world population places greater stress on the environment and potable water sources. Polycyclic aromatic hydrocarbons (PAHs) and other organic compounds with aromatic groups constitute a group of environmental pollutants that represent a threat to ecosystems\textsuperscript{(2)} and drinking water.\textsuperscript{(3,4)} Many PAHs including naphthalene (NPH), phenanthrene, anthracene, and pyrene are found on the US EPA’s list of priority pollutants.\textsuperscript{(5)} Other priority pollutants, such as dichlorobenzene, benzidine, and diethyl phthalate, contain aromatic groups as well. PAHs and other aromatic organic compounds accumulate in the environment from sources including incomplete combustion,\textsuperscript{(6)} industrial effluents,\textsuperscript{(7)} and large scale chemical spills such as the Deepwater Horizon accident.\textsuperscript{(8)}

Prior studies have investigated methods and materials for removing PAHs from the environment\textsuperscript{(9)} and point sources of pollution.\textsuperscript{(10,11)} A variety of materials such as polymer nanofibre networks,\textsuperscript{(12)} soybean stalk-based activated carbon,\textsuperscript{(13)} dendrimers,\textsuperscript{(14–16)} and graphene (GRA) materials\textsuperscript{(17,18)} have been explored for removing aromatic hydrocarbons from water. Our work focuses on two promising materials - polyamidoamine (PAMAM) dendrimers and graphene oxide (GrO). PAMAM dendrimer – aromatic hydrocarbon interactions have been studied previously for the purposes of oil dispersion.\textsuperscript{(19,20)} GrO is well-dispersed in water, yet retains some of the aromatic structure of GRA, which should enable $\pi-\pi$ interactions with aromatic pollutants. Recent work by Chen \textit{et al.} has explored using GrO and GRA nanosheets to remove PAHs from water.\textsuperscript{(21)} Our work highlights the molecular mechanisms involved in the PAMAM dendrimer–NPH and GrO–NPH interactions and compares the respective materials’ potential for water purification applications.

Dendrimers are polymeric materials with a symmetric dendritic structure comprising
a core from which branches emanate.\textsuperscript{(22,23)} The dendrimer generation is determined from
the number of branch iterations. In addition to varying core and branch chemistries, the
terminal groups on the branches can be modified to alter dendrimer properties. Even with
a specific dendrimer chemistry, the dendrimer properties vary with generation and the
solvent conditions.\textsuperscript{(24,25)} Since their introduction in 1985 by Tomalia \textit{et al.},\textsuperscript{(26)} PAMAM
dendrimers have been studied for a variety of applications using experiments\textsuperscript{(19,27,28)} and
molecular simulations.\textsuperscript{(29–32)} PAMAM dendrimers are comprised of amidoamine branches
with amine terminal groups.\textsuperscript{(26)} Though the structure of the molecule would normally be
considered hydrophilic, the inner regions of the molecule are protected from the aqueous
environment, leading some to consider the interior a hydrophobic environment.\textsuperscript{(33)} Several
researchers have explored PAMAM dendrimers for guest-host applications.\textsuperscript{(30,34,35)} We
hope to use PAMAM dendrimers to partition aromatic pollutants out of the aqueous
phase.

Graphene is a layer of sp\textsuperscript{2} hybridized carbon atoms arranged in a honeycomb struc-
ture with the thickness of one atom. Graphene oxide refers to oxidized GRA.\textsuperscript{(36)} GrO
is oxidized primarily with epoxide, alcohol, and carboxylic acids.\textsuperscript{(37)} GrO has recently
emerged as a promising new material for potential applications, from electronics,\textsuperscript{(38)} to
biomedicine\textsuperscript{(39)} and water remediation \textsuperscript{(40–43).} Graphene is aromatic leading to \(\pi-\pi\)
stacking with aromatic hydrocarbons. Though the aromatic regions in GrO are disrupted by
oxidized groups, recent work shows GRA and GrO nanosheets adsorb PAHs.\textsuperscript{(21,44)} We
expect that there are still aromatic regions on GrO where NPH molecules will associate.

In this paper we investigate the association of NPH with PAMAM dendrimers and
GrO. We use a combination of experiments and all atom explicit water molecular dynamics
(MD) simulations to probe how dendrimer generation and the level of oxidation on GrO
sheets affects dendrimer–NPH and GrO–NPH association. NPH is chosen as a model
hydrocarbon since it is a small PAH which can provide insights into the association
of aromatic pollutants with PAMAM dendrimers and GrO, while keeping the system
sizes computationally accessible for all atom explicit water MD simulations. Our goal
is to elucidate mechanistic details of the association of aromatic contaminants on these materials. We believe the insights gained from this work will help develop design principles to engineer dendrimers and GRA materials for water purification.

Methods

We performed experimental and simulation studies to investigate the potential of PAMAM dendrimers and GrO sheets as materials for removing aromatic contaminants from water.

Experimental Methods

Experiments were performed in order to quantify NPH adsorption by each material. NPH (C\textsubscript{10}H\textsubscript{8}, MW 128) was acquired from Sigma-Aldrich. Stock G3-G5 PAMAM dendrimers were obtained from Dendritech Inc (Midland, MI) and stock GrO from Sigma Aldrich (St. Louis, MO), both in water solvent. The molecular weights of G3, G4, G5, and G6 PAMAM dendrimers are 6.9, 14.2, 28.8, and 58.0 kDa, respectively. Each stock solution was diluted in DI water (18 M\text{\textOmega}-cm) to a final mass concentration of 100 \( \mu \text{g/mL} \) and the pH adjusted to 8.0 using 1.0 N NaCl and NaOH. To each was added 2 mg NPH and the solutions were gently rotated on a rotator for 2 h to reach a saturated equilibrium, with any excess NPH settling out from the solution on standing without rotating. The quantity of NPH in each solution was then quantified from the supernatant solution using the 276 nm absorption peak of NPH (Cary-300 Bio spectrometer, Thermo Electric Corp.) and compared to pure water solution controls. This provides a measure of the maximum adsorbing capacity of the dendrimers and GrO. Each experiment was performed in triplicate and the average and standard deviation calculated.

Dendrimer System Setup and Simulations

MD simulations of dendrimers in explicit water were performed. The starting PAMAM structures for the simulations were taken from Maiti \textit{et al.} \cite{45} A hydrogen atom was
added to each primary amine group to mimic the protonated state of the dendrimer at neutral pH conditions. (46) The OPLS-AA (47) force field was used to describe the bonded and non-bonded parameters for the dendrimers. OPLS/AA force field has been used successfully to describe several organic systems in previous studies. (48) More details can be found in Table S1 and Figure S1. The dendrimer structures were energy minimized and the minimized structure was solvated in TIP3P water. (49) Counter ions (Cl\(^-\)) were added to make the system neutral. The dendrimer-water system was simulated for 25 ns in the isothermal-isobaric (NpT) ensemble. The simulations of the dendrimer-water-NPH systems were started using the structure of the dendrimer obtained after the 25 ns simulation of the dendrimer-water system. NPH molecules were added to the system such that all NPH molecules were at least 2.0 nm away from the surface of the dendrimer. The system was solvated in TIP3P water and counter ions (Cl\(^-\)) were added to make the system neutral. The number of water molecules in the system increased with increasing generation of the dendrimer. The number of NPH molecules also was changed to keep the ratio of NPH:water molecules similar in all systems. The G3 system had 10 NPH and 23767 water molecules, G4 system had 10 NPH and 23336 water molecules, G5 system had 11 NPH and 25240 water systems, and the G6 system had 17 NPH and 40591 water molecules. The production MD simulations were performed for 50 ns in the NpT ensemble.

**Graphene Oxide System Setup and Simulations**

To build our GrO sheet, we began with GRA and randomly selected carbon atoms to oxidize. The carbon atoms were oxidized either by attaching an epoxide group between the initial carbon and a randomly selected neighboring carbon, or by attaching an alcohol group to the initial carbon. Oxidizing groups were added to both sides of the GrO sheet. The level of oxidation is reported as the ratio of oxygen atoms to carbon atoms in the system. In both GrO systems the number of epoxide groups was equal to the number of alcohol groups. We did not add any carboxylic acid groups on the edges of the sheet.
since they are considered to be present in low quantities\(^{(36)}\) and we believe the GrO–NPH association will be primarily driven by the chemistry of the “flat” surface of the sheets studied here. Once the surface groups had been added to the sheet, the valency of each carbon was analyzed. First, the remaining aromatic regions were identified, then double bonds were placed where possible, and finally a hydrogen atom was added to any carbon with an unsatisfied valency. Mkhoyvan et al. reports 40% sp\(^3\) bonds for GrO with an oxygen to carbon ratio of 5:1.\(^{(50)}\) Our 15% oxidized GrO system has 35% sp\(^3\) carbons, suggesting our structure contains the correct distribution of carbon atom types. We recalculated the partial charges on GrO using \textit{ab-initio} methods since OPLS-AA partial charges were obtained for liquid hydrocarbons while GrO is a highly aromatic planar solid. We found that for most atom types the partial charges from our calculations and those reported for OPLS force field were similar. The partial charges determined from our quantum calculations were scaled for the MD simulations to make the GrO sheets neutral (i.e. total charge on the sheet was zero). Further details are provided in Table S2.

To study the effect of oxidation level on the association of NPH to GrO, we simulated GRA, GrO with a oxygen to carbon ratio of 15% (GrO\(_{15}\)) and GrO with an oxygen to carbon ratio of 30% (GrO\(_{30}\)). 8 nm x 8 nm GRA and GrO sheets were generated with the methods described above. Experiments indicate that GrO is not perfectly planar, and has a thickness of 1.6 nm.\(^{(50)}\) Therefore, we first energy minimized the GrO sheets allowing the sheet to deform and providing a more realistic structure of GrO. The GrO sheets from the minimizations were held rigid for the production MD simulations. NPH molecules were added around the GrO sheets and the system was solvated with TIP3P water. The final systems comprised one GRA or GrO sheet, ten NPH and 22,795-23,053 water molecules. The ratio of NPH:water molecules was similar to the NPH–dendrimer–water simulations. Each system was energy minimized and simulated for 50 ns in the NpT ensemble.
Simulation Details

MD simulations were performed in GROMACS v4.5.5. TIP3P water model was used in all MD simulations described. Unless otherwise specified, the production runs were performed for 50 ns at 1 bar and 300 K in the NpT ensemble with the Nosé-Hoover thermostat (τ = 0.5 ps) and Parrinello-Rahman barostat (τ = 1.0 ps). Pressure coupling was isotropic with a compressibility of $4.5 \times 10^{-5}$ bar$^{-1}$. The leap-frog integrator was used with a timestep of 2 fs, and center of mass translation was removed every 10 steps. A cutoff value of 1 nm was used for both Lennard-Jones and Coulombic interactions. The dendrimer and water–NPH solution were thermostated to two separate Nosé-Hoover thermostats. Bonds involving hydrogen atoms were constrained using the P-LINCS algorithm, and the particle mesh Ewald method as implemented in GROMACS was used to treat the long-range electrostatic interactions.

Results and Discussion

Experimental studies were performed to investigate the association of NPH with dendrimers and GrO. The dendrimers and GrO were kept at a constant mass concentration of 100 µg/mL for all experiments. Note that this will mean decreasing molar concentrations of PAMAM dendrimers in solution with increasing dendrimer generation. In Figure 1a, the total associated NPH for the different materials is reported. We see that G3 has the least associated NPH, G4 and G5 behave statistically identically on this basis, and G6 has the most associated NPH. GrO has more than 100% greater amount of associated NPH than any of the dendrimers when used in equal mass concentration. At first glance this is a surprising result. We expected that the 3-D structure of the dendrimer would provide more surface area for association and therefore increased association of NPH. The surface area per unit mass is higher for dendrimers than GrO based on our calculations of solvent accessible surface area of the structures used in our simulations. However, the area for association is more readily accessible in case of the flat and exposed GrO sur-
faces, and the aromatic structure of GrO facilitates $\pi$-$\pi$ stacking between GrO sheet and NPH molecules. In contrast, the dendrimer branches need to rearrange cooperatively to accommodate the NPH molecules and provide a surface for association. We hypothesize that this hinders the NPH association to the dendrimer relative to GrO resulting in the better performance of GrO observed in experiments.

We further examined the NPH association to the G3-G6 dendrimers as shown in Figure 1b. The number of NPH molecules associated to each dendrimer molecule shows a linear increase with molecular weight of the dendrimer from G3 to G5. The number of associated NPH molecules increased from $\sim$2 NPH molecules for the G3 dendrimer to approximately 8 NPH molecules for the G5 dendrimer. However, the G6 dendrimer associates more than 1.5 times greater NPH than predicted from the linear trend for the G3-G5 dendrimers. Our experiments indicate that 27 NPH molecules are associated with G6 dendrimer instead of the expected $\sim$16 NPH molecules based on the linear trend. To understand these observations better we performed MD simulations of dendrimer-NPH-water and GrO-NPH-water systems. The molecular insights may help explain the better performance of GrO as well as the non-linear increase in the associated NPH molecules with dendrimer molecular weight.

Simulations of the dendrimers from G3 to G6 generation were performed in pure water and in NPH-water solutions. The size of the dendrimers as indicated by the radius of gyration, $R_g$ equilibrated quickly in both cases. The $R_g$ values obtained from our simulations were in good agreement with those determined using SAXS and SANS experiments\(^{(56–58)}\) and those reported in previous simulation studies.\(^{(46,56–59)}\) A summary of the $R_g$ values for the dendrimers obtained from our simulations and those reported in previous studies are given in Table S3. We also calculated the overall and individual generation densities for the dendrimers. These were found to be in good agreement with previous studies indicating that OPLS force field does well in representing dendrimers. For more detailed analysis the readers are referred to the work by DeFever \textit{et al.}\(^{(60)}\)

We examined the effect of dendrimer generation on NPH association with PAMAM
dendrimers. The different generation dendrimer systems started with a similar initial concentration (~ 3 g/L) of NPH present in the simulation box. Note the initial concentration of NPH was approximately two orders of magnitude above the experimental solubility of NPH in water (35.4 mg/L\textsuperscript{(61)}) to observe association behavior in reasonable computational time. The percent of NPH molecules associated to the dendrimers during the 50 ns production runs is reported in Figure 2. For the purposes of this discussion, we consider a NPH molecule to be associated with the dendrimer when there are more than four instances of a heavy NPH atom and a heavy dendrimer atom within 0.4 nm of one another. Due to the open and dynamic structure of the dendrimers, we found that measures such as the number of NPH within the dendrimer R\textsubscript{g} were inadequate in identifying associated NPH molecules. In the 50 ns of the simulations, ~80% of the NPH molecules in the system associated to the dendrimer in case of the G4, G5, and G6 dendrimers. The percent of NPH associated to the G3 dendrimer appeared to stabilize around 40-60\%, but at points in the simulation the percent associated reached 70\%. The G3 dendrimer is more dynamic than other structures and the branches can rearrange to accommodate large clusters of NPH molecules. These clusters grew up to 4 NPH molecules in the simulations when the highest percent of associated NPH molecules were observed in the G3 system. However, these were relatively short lived. It appears that while the G3 dendrimer branches can readily rearrange to accommodate such large clusters, the resultant configurations are unfavorable. The absolute number of NPH molecules associated increases with increasing dendrimer size, following the trend seen in experiments. Quantitatively our simulations show more NPH molecules associating with the G3-G4 dendrimers, and fewer NPH molecules associating with the G6 dendrimer when compared with experiments. The concentration differences between the experimental and simulation conditions (amount of available NPH, and relative amount of NPH per dendrimer) may account for the quantitative differences, and we are currently investigating these effects through MD studies of concentration dependence of NPH association to dendrimers.

What are the factors that drive the NPH molecules to associate with the dendrimer
molecules? It has been suggested that dendrimers present hydrophobic interiors that drive the hydrophobic aromatic molecules to penetrate the dendrimer interiors.\(^{(33,62)}\) Simulations of the dendrimer–NPH–water solutions reveal that is only part of the picture. Visual inspection of the simulation trajectories suggest that in case of the smaller dendrimers, cooperative effects between the NPH molecules contribute to the association of NPH molecules to the dendrimer. Figure 3 shows a snapshot of NPH associating with the G3 dendrimer in which there are two examples of NPH molecules associating in close proximity to each other. This suggests that NPH–NPH interactions have a role in driving NPH molecules to associate with dendrimers. From the trajectories, it appears that one associated NPH molecule will sometimes interact with a nearby un-associated NPH, keeping the molecule near the dendrimer, and increasing its chances at finding a favorable site for associating with the dendrimer. In other instances, two or more already associated NPH molecules interact with each other (as shown in the Figure 3), perhaps stabilizing the association. When NPH associates to the larger dendrimers, there appear to be fewer instances where NPH molecules interact with each other. We believe the increased surface area of the larger dendrimers provides more available sites for association of single NPH molecule, thereby reducing the chances that two NPH molecules will be close to one another. In addition, unlike the smaller dendrimers which have more readily accessible internal voids and can rearrange to facilitate the NPH–NPH interactions, the larger dendrimers are less dynamic and have decreased accessibility of internal voids.

The NPH–NPH interactions that occur during association can be quantified through the density of NPH as a function of the radial distance from an NPH molecule already associated to the dendrimer (Figure 4). One would expect this density to be higher close to an associated NPH molecule in case of strong NPH–NPH interactions. Figure 4 shows a peak in the NPH density at 0.8-0.9 nm from an associated NPH molecule. The radial NPH–NPH density in a NPH–water solution (Figure 4 inset) shows that the peaks seen in the dendrimer systems are near the maximum distance of the (first) peak in the NPH–NPH density in water. The first peak height in the density curves is similar in magnitude
for G3 and G4 dendrimer systems (nearly double NPH–water) and decreases for the G5 and G6 dendrimers. This suggests that cooperative effects play a stronger role in the association of NPH with G3 and G4 systems compared to the G5 and G6 dendrimers. The systems also exhibit a small second peak in the NPH density at ∼1.1 nm. The second peak is likely derived from two NPH molecules associated on opposite sides of a dendrimer branch. Therefore, in addition to hydrophobic interactions between the dendrimer and NPH, NPH–NPH interactions play a significant role in NPH–dendrimer association. We suspect that at higher NPH concentrations this cooperative effect of NPH association governed by the NPH–NPH interactions will also increase. This suggests that at higher concentrations we would see increased cooperative effects for the larger dendrimers as well. This may contribute to the large number of NPH molecules associated to the G6 dendrimer observed in experiments.

We also investigated the association of NPH molecules on GRA and GrO sheets. We studied two levels of GrO oxidation, 15% (GrO$_{15}$) and 30% (GrO$_{30}$). All three systems studied (GRA, GrO$_{15}$, GrO$_{30}$) have the similar values of the ratio of NPH:water molecules. We use the same definition of association as used for the dendrimer systems. All ten NPH molecules present in the system associate with GRA within 8 ns and one molecule occasionally dissociates (Figure 5). Though it may appear that 90% of the NPH molecules are associated instead of 100%, the average number of associated NPH molecules over the last 15 ns of the simulation rounds to 10.0. GrO$_{15}$ associates nearly as many NPH molecules as GRA, though it takes longer (∼10 ns) (Figure 5a). There is a much larger decrease in the percent of NPH associated going from the GrO$_{15}$ to GrO$_{30}$ than from GRA to GrO$_{15}$. The GrO$_{30}$ associates a maximum of 80% NPH molecules, but the percent associated fluctuates between 30% to 50% for a larger portion of the simulation. This suggests that GrO performs very well at removing aromatic constituents from water until it reaches a certain level of oxidation, at which point it’s ability to remove aromatic pollutants from a water solution is greatly degraded. This appears to be between 15 and 30% oxidation based on our simulations.
Hydrophobic interactions and the $\pi$-$\pi$ stacking between the aromatic rings of the GRA or GrO sheet and NPH molecules likely drive association of NPH to GRA and GrO. As seen in Figure 5b, associated NPH molecules orient parallel to the GRA sheet. As the carbons on GRA sheets are oxidized, the aromaticity of the sheet is broken and the number of aromatic regions of the GrO which are larger than a single NPH molecule decreases. For GrO$_{15}$, there are still many aromatic regions across the sheet larger than a single NPH molecule, however those regions decrease in number for GrO$_{30}$ (see Figure 6). This decreases availability of regions where NPH can associate planar to the GrO sheet, reducing the $\pi$-$\pi$ interactions between the NPH molecules and GrO sheets. Further, increased oxidation reduces the hydrophobicity of GrO, also resulting in decreased NPH–GrO interaction strength. These effects are manifested in a decrease in associated NPH molecules that are oriented parallel to the GrO sheet as seen in Figure 5b. The decreased strength of interactions between the sheets and NPH molecules leads to less stable NPH association. This is seen prominently in case of GrO$_{30}$ sheets (Figure 5a), where the number of associated NPH fluctuates much more than in the case of GRA or GrO$_{15}$. Density profiles of NPH as a function of the distance from the GRA or GrO sheet show a single peak in the vicinity of the GRA sheet indicating that NPH molecules do not form multiple layers at this concentration (Figure 5c). The density profile of NPH molecules are broader near GrO surfaces compared to GRA sheets (Figure 5c), confirming that the NPH molecules do not associate as parallel to the GrO sheets compared with GRA sheets.

Analogous to the dendrimer systems, the NPH density from an already associated NPH molecule was calculated to determine if cooperative effects help drive NPH association to GRA and GrO. The GRA system displayed a large density peak at about 1 nm. This peak comes from associated NPH molecules touching end-to-end (i.e. lying next to each other rather than being stacked on top of each other) and provides further evidence that NPH molecules are not stacked at these concentrations, and that $\pi$-$\pi$ interactions based NPH–NPH interactions are not prominent in this system. Such arrangement of NPH molecules on GRA sheets have been hypothesized in previous experimental studies.$^{(21)}$
For the GrO$_{30}$ system, there is a peak in the NPH density at $\sim$0.7 nm. This peak could be due to NPH–NPH interactions similar to those seen in bulk water and in case of dendrimers. Since the NPH molecules are less likely to find an association site on the GrO$_{30}$ sheet, they may instead interact with an already associated molecule of NPH. In this manner NPH–NPH interactions may promote association for the GrO$_{30}$ system by keeping the un-associated NPH molecule closer to the sheet for a longer period of time, giving it a better opportunity to associate to the sheet.

We find that similar mechanisms are at play in both these materials with regards to NPH association. In both materials, NPH–NPH interactions play an important role in enhanced NPH association with these materials. We expect that such interactions will be featured in any association process involving aromatic entities. This results in the association being concentration dependent. The increased surface area and reduced NPH–NPH interactions with increasing molecular weight of the dendrimer are two opposing factors affecting NPH-dendrimer association. For lower generations, it appears that NPH–NPH interactions facilitated by the dynamic nature of the dendrimer, contribute significantly to NPH association, while this effect is decreased for larger dendrimers. Experimental studies suggested that GrO outperforms dendrimers in NPH association. On a per unit mass basis (data not shown) we do not observe this in our simulations. This suggests that perhaps phenomena involving multiple GrO sheets such as formation of aggregates of multiple GrO sheets trapping NPH molecules contribute to naphthalene removal from water. Wang et al. suggest that conformation changes induced in GO and GrO sheets due to association with NPH could also affect the NPH association with these materials.(21) In conclusion, we find that both PAMAM dendrimer and GrO can be used for removal of aromatics from water. The mechanisms of NPH association to these seemingly disparate materials are similar at the molecular level and involve interactions between the NPH molecules themselves. This highlights that for developing materials for removal of polycyclic aromatic contaminants from water we will also need to consider the interactions between the contaminants themselves.
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Supporting Information Available

Details of the force-field parameters are available in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Figure 1: Experimental results: (a) Amount of dendrimer–associated NPH in solution for G3-G6, and GrO-associated NPH. (b) The number of associated NPH molecules per dendrimer in solution as a function of dendrimer molecular weight. The dashed line in (b) is a linear fit to the points for the G3, G4 and G5 dendrimers to highlight the nonlinear increase in the number of NPH molecules associated to the G6 dendrimer.
Figure 2: Percent of NPH molecules associated to the dendrimer over a 50 ns simulation. The NPH:water ratio is kept the same in all simulations. There are 10, 10, 11, and 17 NPH molecules in the G3, G4, G5 and G6 systems, respectively.
Figure 3: Snapshot of two clusters of NPH molecules associating to the G3 dendrimer (red). The bottom left cluster contains four NPH molecules, and the top right cluster contains two NPH molecules. Water molecules are not shown for visual clarity.
Figure 4: Density of NPH as a function of distance from an NPH molecule associated to the dendrimer. G3 (red), G4 (blue), G5 (magenta), G6 (grey). Inset: The NPH–NPH density profile obtained from simulations of NPH–water solution at 300 K. Representative configuration of two interacting NPH molecules corresponding to the peak at \( \sim 0.6 \) nm is shown in green.
Figure 5: Association of NPH molecules with GRA, GrO$_{15}$, and GrO$_{30}$. GRA, GrO$_{15}$, and GrO$_{30}$ systems are shown in grey, red, and blue, respectively. (a) Percent of NPH molecules associated to GRA and GrO over a 50 ns simulation. (b) Snapshots of association to (b1) GRA, (b2) GrO$_{15}$, and (b3) GrO$_{30}$. (c) Density of NPH as a function of the distance from the GRA or GrO sheet. (d) Density of NPH as a function of the distance from an associated molecule of NPH.
Figure 6: Snapshot of the GO$_{15}$ (red) and GO$_{30}$ sheet (blue). The non-carbon atoms on the GrO sheets are shown in white and a single NPH molecule is shown in green to provide a sense of scale. The decrease in the aromatic regions that can accommodate NPH molecules is seen clearly when the oxidation is increased from 15 to 30%.
TOC Graphic:

**Keywords:** Dendrimers, polyaromatic hydrocarbons, remediation, graphene, molecular simulations