

# Article

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

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#### Abstract

2	We present results from experiments and atomistic molecular dynamics simula-
3	tions on the remediation of naphthalene by polyamidoamine (PAMAM) dendrimers
4	and graphene oxide (GrO). Specifically, we investigate $3^{rd}$ - $6^{th}$ generation (G3-G6)
5	PAMAM dendrimers and GrO with different levels of oxidation. The work is mo-
6	tivated by the potential applications of these emerging nanomaterials in remov-
7	ing polycyclic aromatic hydrocarbon contaminants from water. Our experimental
8	results indicate that GrO outperforms dendrimers in removing naphthalene from
9	water. Molecular dynamics simulations suggest that the prominent factors driving
10	naphthalene association to these seemingly disparate materials are similar. Interest-
11	ingly, we find that cooperative interactions between the naphthalene molecules play
12	a significant role in enhancing their association to the dendrimers and GrO. Our
13	findings highlight that while selection of appropriate materials is important, the in-
14	teractions between the contaminants themselves can also be important in governing
15	the effectiveness of a given material. The combined use of experiments and molecu-
16	lar dynamics simulations allows us to comment on the possible factors resulting in
17	better performance of GrO in removing polyaromatic contaminants from water.
18	$Keywords: \ Dendrimers, \ polyaromatic \ hydrocarbons, \ remediation, \ graphene, \ molecture and \ remediation.$
19	ular simulations

Page 3 of 29

# 20 Introduction

Economical and effective water purification is recognized as a top  $21^{st}$  century challenge.<sup>(1)</sup> 21 Applications of water purification to environmental clean-up and removal of contaminants 22 from drinking water will become ever more important as a growing world population places 23 greater stress on the environment and potable water sources. Polycyclic aromatic hydro-24 carbons (PAHs) and other organic compounds with aromatic groups constitute a group of 25 environmental pollutants that represent a threat to  $ecosystems^{(2)}$  and drinking water.<sup>(3,4)</sup> 26 Many PAHs including naphthalene (NPH), phenanthrene, anthracene, and pyrene are 27 found on the US EPA's list of priority pollutants.<sup>(5)</sup> Other priority pollutants, such as 28 dichlorobenzene, benzidine, and diethyl phthalate, contain aromatic groups as well. PAHs 29 and other aromatic organic compounds accumulate in the environment from sources in-30 cluding incomplete combustion,<sup>(6)</sup> industrial effluents,<sup>(7)</sup> and large scale chemical spills 31 such as the Deepwater Horizon accident.<sup>(8)</sup> 32

Prior studies have investigated methods and materials for removing PAHs from the 33 environment<sup>(9)</sup> and point sources of pollution.<sup>(10,11)</sup> A variety of materials such as poly-34 mer nanofibre networks,<sup>(12)</sup> soybean stalk-based activated carbon,<sup>(13)</sup> dendrimers,<sup>(14-16)</sup> 35 and graphene (GRA) materials<sup>(17,18)</sup> have been explored for removing aromatic hydro-36 carbons from water. Our work focuses on two promising materials - polyamidoamine 37 (PAMAM) dendrimers and graphene oxide (GrO). PAMAM dendrimer - aromatic hydro-38 carbon interactions have been studied previously for the purposes of oil dispersion.<sup>(19,20)</sup> 39 GrO is well-dispersed in water, yet retains some of the aromatic structure of GRA, which 40 should enable  $\pi - \pi$  interactions with aromatic pollutants. Recent work by Chen *et al.* 41 has explored using GrO and GRA nanosheets to remove PAHs from water.<sup>(21)</sup> Our work 42 highlights the molecular mechanisms involved in the PAMAM dendrimer-NPH and GrO-43 NPH interactions and compares the respective materials' potential for water purification 44 applications. 45

46 Dendrimers are polymeric materials with a symmetric dendritic structure comprising

a core from which branches emanate.<sup>(22,23)</sup> The dendrimer generation is determined from 47 the number of branch iterations. In addition to varying core and branch chemistries, the 48 terminal groups on the branches can be modified to alter dendrimer properties. Even with 49 a specific dendrimer chemistry, the dendrimer properties vary with generation and the 50 solvent conditions.<sup>(24,25)</sup> Since their introduction in 1985 by Tomalia *et al.*,<sup>(26)</sup> PAMAM 51 dendrimers have been studied for a variety of applications using experiments (19,27,28) and 52 molecular simulations.<sup>(29–32)</sup> PAMAM dendrimers are comprised of amidoamine branches 53 with amine terminal groups.<sup>(26)</sup> Though the structure of the molecule would normally be 54 considered hydrophilic, the inner regions of the molecule are protected from the aqueous 55 environment, leading some to consider the interior a hydrophobic environment.<sup>(33)</sup> Several 56 researchers have explored PAMAM dendrimers for guest-host applications.<sup>(30,34,35)</sup> We 57 hope to use PAMAM dendrimers to partition aromatic pollutants out of the aqueous 58 phase. 59

Graphene is a layer of  $sp^2$  hybridized carbon atoms arranged in a honeycomb struc-60 ture with the thickness of one atom. Graphene oxide refers to oxidized GRA.<sup>(36)</sup> GrO 61 is oxidized primarily with epoxide, alcohol, and carboxylic acids.<sup>(37)</sup> GrO has recently 62 emerged as a promising new material for potential applications, from electronics,<sup>(38)</sup> to 63 biomedicine<sup>(39)</sup> and water remediation <sup>(40–43)</sup>. Graphene is aromatic leading to  $\pi$ - $\pi$  stack-64 ing with aromatic hydrocarbons. Though the aromatic regions in GrO are disrupted by 65 oxidized groups, recent work shows GRA and GrO nanosheets adsorb PAHs.<sup>(21,44)</sup> We 66 expect that there are still aromatic regions on GrO where NPH molecules will associate. 67 In this paper we investigate the association of NPH with PAMAM dendrimers and 68 GrO. We use a combination of experiments and all atom explicit water molecular dynamics 69 (MD) simulations to probe how dendrimer generation and the level of oxidation on GrO 70 sheets affects dendrimer–NPH and GrO–NPH association. NPH is chosen as a model 71 hydrocarbon since it is a small PAH which can provide insights into the association 72 of aromatic pollutants with PAMAM dendrimers and GrO, while keeping the system 73 sizes computationally accessible for all atom explicit water MD simulations. Our goal 74

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.

# 78 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.

### 81 Experimental Methods

Experiments were performed in order to quantify NPH adsorption by each material. NPH 82 (C<sub>10</sub>H<sub>8</sub>, MW 128) was acquired from Sigma-Aldrich. Stock G3-G5 PAMAM dendrimers 83 were obtained from Dendritech Inc (Midland, MI) and stock GrO from Sigma Aldrich (St. 84 Louis, MO), both in water solvent. The molecular weights of G3, G4, G5, and G6 PAMAM 85 dendrimers are 6.9, 14.2, 28.8, and 58.0 kDa, respectively. Each stock solution was diluted 86 in DI water (18 M $\Omega$ -cm) to a final mass concentration of 100  $\mu$ g/mL and the pH adjusted 87 to 8.0 using 1.0 N NaCl and NaOH. To each was added 2 mg NPH and the solutions were 88 gently rotated on a rotator for 2 h to reach a saturated equilibrium, with any excess NPH 89 settling out from the solution on standing without rotating. The quantity of NPH in each 90 solution was then quantified from the supernatant solution using the 276 nm absorption 91 peak of NPH (Cary-300 Bio spectrometer, Thermo Electric Corp.) and compared to pure 92 water solution controls. This provides a measure of the maximum adsorbing capacity of 93 the dendrimers and GrO. Each experiment was performed in triplicate and the average 94 and standard deviation calculated. 95

## <sup>96</sup> 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 *et al.*<sup>(45)</sup> A hydrogen atom was

added to each primary amine group to mimic the protonated state of the dendrimer at 99 neutral pH conditions.<sup>(46)</sup> The OPLS-AA<sup>(47)</sup> force field was used to describe the bonded 100 and non-bonded parameters for the dendrimers. OPLS/AA force field has been used 101 successfully to describe several organic systems in previous studies.<sup>(48)</sup> More details can 102 be found in Table S1 and Figure S1. The dendrimer structures were energy minimized 103 and the minimized structure was solvated in TIP3P water.<sup>(49)</sup> Counter ions (Cl<sup>-</sup>) were 104 added to make the system neutral. The dendrimer-water system was simulated for 25 105 ns in the isothermal-isobaric (NpT) ensemble. The simulations of the dendrimer-water-106 NPH systems were started using the structure of the dendrimer obtained after the 25 107 ns simulation of the dendrimer-water system. NPH molecules were added to the system 108 such that all NPH molecules were at least 2.0 nm away from the surface of the dendrimer. 109 The system was solvated in TIP3P water and counter ions  $(Cl^{-})$  were added to make the 110 system neutral. The number of water molecules in the system increased with increasing 111 generation of the dendrimer. The number of NPH molecules also was changed to keep 112 the ratio of NPH:water molecules similar in all systems. The G3 system had 10 NPH and 113 23767 water molecules, G4 system had 10 NPH and 23336 water molecules, G5 system 114 had 11 NPH and 25240 water systems, and the G6 system had 17 NPH and 40591 water 115 molecules. The production MD simulations were performed for 50 ns in the NpT ensemble. 116

## <sup>117</sup> 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<sup>(36)</sup> and we believe the GrO–NPH 125 association will be primarily driven by the chemistry of the "flat" surface of the sheets 126 studied here. Once the surface groups had been added to the sheet, the valency of each 127 carbon was analyzed. First, the remaining aromatic regions were identified, then double 128 bonds were placed where possible, and finally a hydrogen atom was added to any carbon 129 with an unsatisfied valency. Mkhoyvan *et al.* reports 40% sp<sup>3</sup> bonds for GrO with an 130 oxygen to carbon ratio of 5:1.<sup>(50)</sup> Our 15% oxidized GrO system has 35% sp<sup>3</sup> carbons, 131 suggesting our structure contains the correct distribution of carbon atom types. We 132 recalculated the partial charges on GrO using *ab-initio* methods since OPLS-AA partial 133 charges were obtained for liquid hydrocarbons while GrO is a highly aromatic planar 134 solid. We found that for most atom types the partial charges from our calculations and 135 those reported for OPLS force field were similar. The partial charges determined from 136 our quantum calculations were scaled for the MD simulations to make the GrO sheets 137 neutral (i.e. total charge on the sheet was zero). Further details are provided in Table 138 S2. 139

To study the effect of oxidation level on the association of NPH to GrO, we simulated 140 GRA, GrO with a oxygen to carbon ratio of 15% (GrO<sub>15</sub>) and GrO with an oxygen to 141 carbon ratio of 30% (GrO<sub>30</sub>). 8 nm x 8 nm GRA and GrO sheets were generated with the 142 methods described above. Experiments indicate that GrO is not perfectly planar, and has 143 a thickness of 1.6 nm.<sup>(50)</sup> Therefore, we first energy minimized the GrO sheets allowing the 144 sheet to deform and providing a more realistic structure of GrO. The GrO sheets from the 145 minimizations were held rigid for the production MD simulations. NPH molecules were 146 added around the GrO sheets and the system was solvated with TIP3P water. The final 147 systems comprised one GRA or GrO sheet, ten NPH and 22,795-23,053 water molecules. 148 The ratio of NPH:water molecules was similar to the NPH-dendrimer-water simulations. 149 Each system was energy minimized and simulated for 50 ns in the NpT ensemble. 150

#### 151 Simulation Details

MD simulations were performed in GROMACS v4.5.5.<sup>(51)</sup> TIP3P water model<sup>(49)</sup> was 152 used in all MD simulations described. Unless otherwise specified, the production runs 153 were performed for 50 ns at 1 bar and 300 K in the NpT ensemble with the Nosé-Hoover 154 thermostat<sup>(52)</sup> ( $\tau = 0.5$  ps) and Parrinello-Rahman barostat<sup>(53)</sup> ( $\tau = 1.0$  ps). Pressure 155 coupling was isotropic with a compressibility of  $4.5 \times 10^{-5} \text{ bar}^{-1}$ . The leap-frog inte-156 grator was used with a timestep of 2 fs, and center of mass translation was removed 157 every 10 steps. A cutoff value of 1 nm was used for both Lennard-Jones and Coulombic 158 interactions. The dendrimer and water-NPH solution were thermostated to two sepa-159 rate Nosé-Hoover thermostats. Bonds involving hydrogen atoms were constrained using 160 the P-LINCS algorithm,<sup>(54)</sup> and the particle mesh Ewald method<sup>(55)</sup> as implemented in 161 GROMACS was used to treat the long-range electrostatic interactions. 162

# 163 Results and Discussion

Experimental studies were performed to investigate the association of NPH with den-164 drimers and GrO. The dendrimers and GrO were kept at a constant mass concentration 165 of 100  $\mu$ g/mL for all experiments. Note that this will mean decreasing molar concentra-166 tions of PAMAM dendrimers in solution with increasing dendrimer generation. In Figure 167 1a, the total associated NPH for the different materials is reported. We see that G3 has 168 the least associated NPH, G4 and G5 behave statistically identically on this basis, and 169 G6 has the most associated NPH. GrO has more than 100% greater amount of associated 170 NPH than any of the dendrimers when used in equal mass concentration. At first glance 171 this is a surprising result. We expected that the 3-D structure of the dendrimer would 172 provide more surface area for association and therefore increased association of NPH. The 173 surface area per unit mass is higher for dendrimers than GrO based on our calculations 174 of solvent accessible surface area of the structures used in our simulations. However, the 175 area for association is more readily accessible in case of the flat and exposed GrO sur-176

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 182 Figure 1b. The number of NPH molecules associated to each dendrimer molecule shows 183 a linear increase with molecular weight of the dendrimer from G3 to G5. The number 184 of associated NPH molecules increased from  $\sim 2$  NPH molecules for the G3 dendrimer 185 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 187 G3-G5 dendrimers. Our experiments indicate that 27 NPH molecules are associated with 188 G6 dendrimer instead of the expected  $\sim$ 16 NPH molecules based on the linear trend. To 189 understand these observations better we performed MD simulations of dendrimer-NPH-190 water and GrO-NPH-water systems. The molecular insights may help explain the better 191 performance of GrO as well as the non-linear increase in the associated NPH molecules 192 with dendrimer molecular weight. 193

Simulations of the dendrimers from G3 to G6 generation were performed in pure water 194 and in NPH-water solutions. The size of the dendrimers as indicated by the radius of gy-195 ration,  $R_g$  equilibrated quickly in both cases. The  $R_g$  values obtained from our simulations 196 were in good agreement with those determined using SAXS and SANS experiments<sup>(56–58)</sup> 197 and those reported in previous simulation studies.<sup>(46,56–59)</sup> A summary of the  $R_g$  values 198 for the dendrimers obtained from our simulations and those reported in previous studies 199 are given in Table S3. We also calculated the overall and individual generation densities 200 for the dendrmiers. These were found to be in good agreement with previous studies 201 indicating that OPLS force field does well in representing dendrimers. For more detailed 202 analysis the readers are referred to the work by DeFever *et al.*<sup>(60)</sup></sup> 203

204 We examined the effect of dendrimer generation on NPH association with PAMAM

dendrimers. The different generation dendrimer systems started with a similar initial 205 concentration ( $\sim 3 \text{ g/L}$ ) of NPH present in the simulation box. Note the initial con-206 centration of NPH was approximately two orders of magnitude above the experimental 207 solubility of NPH in water  $(35.4 \text{ mg/L}^{(61)})$  to observe association behavior in reasonable 208 computational time. The percent of NPH molecules associated to the dendrimers during 209 the 50 ns production runs is reported in Figure 2. For the purposes of this discussion, 210 we consider a NPH molecule to be associated with the dendrimer when there are more 211 than four instances of a heavy NPH atom and a heavy dendrimer atom within 0.4 nm 212 of one another. Due to the open and dynamic structure of the dendrimers, we found 213 that measures such as the number of NPH within the dendrimer  $R_q$  were inadequate 214 in identifying associated NPH molecules. In the 50 ns of the simulations,  $\sim 80\%$  of the 215 NPH molecules in the system associated to the dendrimer in case of the G4, G5, and G6 216 dendrimers. The percent of NPH associated to the G3 dendrimer appeared to stabilize 217 around 40-60%, but at points in the simulation the percent associated reached 70\%. The 218 G3 dendrimer is more dynamic than other structures and the branches can rearrange to 219 accommodate large clusters of NPH molecules. These clusters grew up to 4 NPH molecules 220 in the simulations when the highest percent of associated NPH molecules were observed 221 in the G3 system. However, these were relatively short lived. It appears that while the 222 G3 dendrimer branches can readily rearrange to accommodate such large clusters, the 223 resultant configurations are unfavorable. The absolute number of NPH molecules asso-224 ciated increases with increasing dendrimer size, following the trend seen in experiments. 225 Quantitatively our simulations show more NPH molecules associating with the G3-G4 226 dendrimers, and fewer NPH molecules associating with the G6 dendrimer when compared 227 with experiments. The concentration differences between the experimental and simulation 228 conditions (amount of available NPH, and relative amount of NPH per dendrimer) may 229 account for the quantitative differences, and we are currently investigating these effects 230 through MD studies of concentration dependence of NPH association to dendrimers. 231 What are the factors that drive the NPH molecules to associate with the dendrimer 232

molecules? It has been suggested that dendrimers present hydrophobic interiors that drive 233 the hydrophobic aromatic molecules to penetrate the dendrimer interiors.<sup>(33,62)</sup> Simula-234 tions of the dendrimer–NPH–water solutions reveal that is only part of the picture. Visual 235 inspection of the simulation trajectories suggest that in case of the smaller dendrimers, 236 cooperative effects between the NPH molecules contribute to the association of NPH 237 molecules to the dendrimer. Figure 3 shows a snapshot of NPH associating with the G3 238 dendrimer in which there are two examples of NPH molecules associating in close proxim-239 ity to each other. This suggests that NPH–NPH interactions have a role in driving NPH 240 molecules to associate with dendrimers. From the trajectories, it appears that one asso-241 ciated NPH molecule will sometimes interact with a nearby un-associated NPH, keeping 242 the molecule near the dendrimer, and increasing its chances at finding a favorable site 243 for associating with the dendrimer. In other instances, two or more already associated 244 NPH molecules interact with each other (as shown in the Figure 3), perhaps stabilizing 245 the association. When NPH associates to the larger dendrimers, there appear to be fewer 246 instances where NPH molecules interact with each other. We believe the increased sur-247 face area of the larger dendrimers provides more available sites for association of single 248 NPH molecule, thereby reducing the chances that two NPH molecules will be close to 249 one another. In addition, unlike the smaller dendrimers which have more readily accessi-250 ble internal voids and can rearrange to facilitate the NPH-NPH interactions, the larger 251 dendrimers are less dynamic and have decreased accessibility of internal voids. 252

The NPH–NPH interactions that occur during association can be quantified through 253 the density of NPH as a function of the radial distance from an NPH molecule already 254 associated to the dendrimer (Figure 4). One would expect this density to be higher close 255 to an associated NPH molecule in case of strong NPH–NPH interactions. Figure 4 shows 256 a peak in the NPH density at 0.8-0.9 nm from an associated NPH molecule. The radial 257 NPH–NPH density in a NPH–water solution (Figure 4 inset) shows that the peaks seen 258 in the dendrimer systems are near the maximum distance of the (first) peak in the NPH-259 NPH density in water. The first peak height in the density curves is similar in magnitude 260

for G3 and G4 dendrimer systems (nearly double NPH–water) and decreases for the G5 261 and G6 dendrimers. This suggests that cooperative effects play a stronger role in the 262 association of NPH with G3 and G4 systems compared to the G5 and G6 dendrimers. 263 The systems also exhibit a small second peak in the NPH density at  $\sim 1.1$  nm. The 264 second peak is likely derived from two NPH molecules associated on opposites sides of 265 a dendrimer branch. Therefore, in addition to hydrophobic interactions between the 266 dendrimer and NPH, NPH–NPH interactions play a significant role in NPH–dendrimer 267 association. We suspect at higher NPH concentrations this cooperative effect of NPH 268 association governed by the NPH–NPH interactions will also increase. This suggests 269 that at higher concentrations we would see increased cooperative effects for the larger 270 dendrimers as well. This may contribute to the large number of NPH molecules associated 271 to the G6 dendrimer observed in experiments. 272

We also investigated the association of NPH molecules on GRA and GrO sheets. We 273 studied two levels of GrO oxidation, 15% (GrO<sub>15</sub>) and 30% (GrO<sub>30</sub>). All three systems 274 studied (GRA, GrO<sub>15</sub>, GrO<sub>30</sub>) have the similar values of the ratio of NPH:water molecules. 275 We use the same definition of association as used for the dendrimer systems. All ten 276 NPH molecules present in the system associate with GRA within 8 ns and one molecule 277 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 279 the last 15 ns of the simulation rounds to 10.0.  $GrO_{15}$  associates nearly as many NPH 280 molecules as GRA, though it takes longer ( $\sim 10$  ns) (Figure 5a). There is a much larger 281 decrease in the percent of NPH associated going from the  $GrO_{15}$  to  $GrO_{30}$  than from 282 GRA to  $GrO_{15}$ . The  $GrO_{30}$  associates a maximum of 80% NPH molecules, but the 283 percent associated fluctuates between 30% to 50% for a larger portion of the simulation. 284 This suggests that GrO performs very well at removing aromatic constituents from water 285 until it reaches a certain level of oxidation, at which point it's ability to remove aromatic 286 pollutants from a water solution is greatly degraded. This appears to be between 15 and 287 30% oxidation based on our simulations. 288

Hydrophobic interactions and the  $\pi$ - $\pi$  stacking between the aromatic rings of the 289 GRA or GrO sheet and NPH molecules likely drive association of NPH to GRA and GrO. 290 As seen in Figure 5b, associated NPH molecules orient parallel to the GRA sheet. As 291 the carbons on GRA sheets are oxidized, the aromaticity of the sheet is broken and the 292 number of aromatic regions of the GrO which are larger than a single NPH molecule 293 decreases. For  $GrO_{15}$ , there are still many aromatic regions across the sheet larger than a 294 single NPH molecule, however those regions decrease in number for  $GrO_{30}$  (see Figure 6). 295 This decreases availability of regions where NPH can associate planar to the GrO sheet, 296 reducing the  $\pi$ - $\pi$  interactions between the NPH molecules and GrO sheets. Further, 297 increased oxidation reduces the hydrophobicity of GrO, also resulting in decreased NPH-298 GrO interaction strength. These effects are manifested in a decrease in associated NPH 299 molecules that are oriented parallel to the GrO sheet as seen in Figure 5b. The decreased 300 strength of interactions between the sheets and NPH molecules leads to less stable NPH 301 association. This is seen prominently in case of  $GrO_{30}$  sheets (Figure 5a), where the 302 number of associated NPH fluctuates much more than in the case of GRA or GrO<sub>15</sub>. 303 Density profiles of NPH as a function of the distance from the GRA or GrO sheet show a 304 single peak in the vicinity of the GRA sheet indicating that NPH molecules do not form 305 multiple layers at this concentration (Figure 5c). The density profile of NPH molecules 306 are broader near GrO surfaces compared to GRA sheets (Figure 5c), confirming that the 307 NPH molecules do not associate as parallel to the GrO sheets compared with GRA sheets. 308 Analogous to the dendrimer systems, the NPH density from an already associated NPH 309 molecule was calculated to determine if cooperative effects help drive NPH association to 310 GRA and GrO. The GRA system displayed a large density peak at about 1 nm. This 311 peak comes from associated NPH molecules touching end-to-end (i.e. lying next to each 312 other rather than being stacked on top of each other) and provides further evidence that 313 NPH molecules are not stacked at these concentrations, and that  $\pi$ - $\pi$  interactions based 314 NPH–NPH interactions are not prominent in this system. Such arrangement of NPH 315 molecules on GRA sheets have been hypothesized in previous experimental studies.<sup>(21)</sup> 316

For the  $GrO_{30}$  system, there is a peak in the NPH density at ~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<sub>30</sub> sheet, they may instead interact with an already associated molecule of NPH. In this manner NPH–NPH interactions may promote association for the GrO<sub>30</sub> 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 324 NPH association. In both materials, NPH–NPH interactions play an important role in 325 enhanced NPH association with these materials. We expect that such interactions will be 326 featured in any association process involving aromatic entities. This results in the associ-327 ation being concentration dependent. The increased surface area and reduced NPH–NPH 328 interactions with increasing molecular weight of the dendrimer are two opposing factors 329 affecting NPH-dendrimer association. For lower generations, it appears that NPH-NPH 330 interactions facilitated by the dynamic nature of the dendrimer, contribute significantly 331 to NPH association, while this effect is decreased for larger dendrimers. Experimental 332 studies suggested that GrO outperforms dendrimers in NPH association. On a per unit 333 mass basis (data not shown) we do not observe this in our simulations. This suggests 334 that perhaps phenomena involving multiple GrO sheets such as formation of aggregates 335 of multiple GrO sheets trapping NPH molecules contribute to naphthalene removal from 336 water. Wang et. al. suggest that conformation changes induced in GO and GrO sheets 337 due to association with NPH could also affect the NPH association with these materi-338 als.<sup>(21)</sup> In conclusion, we find that both PAMAM dendrimer and GrO can be used for 339 removal of aromatics from water. The mechanisms of NPH association to these seemingly 340 disparate materials are similar at the molecular level and involve interactions between the 341 NPH molecules themselves. This highlights that for developing materials for removal of 342 polycyclic aromatic contaminants from water we will also need to consider the interactions 343 between the contaminants themselves. 344

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## 350 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%.



533 Keywords: Dendrimers, polyaromatic hydrocarbons, remediation, graphene, molecular

534 simulations