

Molecular Dynamics Insights into the Structural and Water Transport Properties of a Forward Osmosis Polyamide Thin-Film Nanocomposite Membrane Modified with Graphene

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1 **Molecular Dynamics Insights into the Structural and Water**
2 **Transport Properties of a Forward Osmosis Polyamide Thin Film**
3 **Nanocomposite Membrane Modified with Graphene Quantum Dots**

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24
25 **Abstract**

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26 An approach combining molecular dynamics simulations and laboratory experiments was
27 applied to provide new theoretical insights into the chemical structure of polyamide (PA) thin-
28 film composite (TFC) membranes modified with graphene quantum dots (GQDs). The
29 interaction energies, fractional free-volumes, mean-square displacements, densities, and water
30 diffusion coefficients were computed for PA and four likely chemical structures of the GQDs-
31 embedded PA membranes. These theoretical results aided with experimentally-measured water
32 fluxes allowed for determining the most likely structure of the GQD-PA membrane. The
33 compatibility of the GQDs and PA chains was found to be due to the formation of hydrogen and
34 covalent bonds to m-phenylenediamine units. The modified membrane has a higher water
35 diffusivity but a lower overall free volume, compared to the pristine PA membrane. MD
36 simulations in concert with laboratory experiments were found to provide a good understanding
37 of the relationship between microscopic characteristics and macroscopic transport properties of
38 TFC membranes.

39

40 **1. Introduction**

41 Due to their excellent chemical stability as well as high rejection of salts and other
42 dissolved contaminants,¹ polyamide (PA) thin-film composite (TFC) membranes are applied
43 widely in desalination and forward osmosis (FO) processes.^{2,3} The performance of these
44 membranes depends strongly on their structure and physiochemical properties.^{4,5} Extensive
45 experimental studies have been carried out to fabricate PA FO membranes with a high water flux
46 and a high salt rejection.⁶⁻⁸ To improve and tailor the membrane properties, numerous types of
47 nanomaterials have been incorporated into the PA selective layer.^{9,10} However, this
48 incorporation leads to improved complexity of the membrane structure of the membranes, which
49 often prevents a rationalization of their final performance.

50 The physical properties of a PA layer that influence water and salt permeabilities include
51 polymer composition,¹¹ molecular structure,¹² fractional free-volume (FFV),¹³ and surface
52 electric potential.¹⁴ The functional groups of a PA membrane also have a significant effect on
53 the water transport.^{15,16} For example, hydroxyl and carboxyl functional groups have affinity to
54 water molecules, and increasing the density of these moieties improve the water adsorption
55 capacity of the membrane.^{2,17} When a nanocomposite membrane is fabricated by incorporating
56 nanomaterials into the membrane selective layer, the interfacial regions between PA chains and
57 the filler affect the transport properties of the resulting membrane, especially the modifying
58 materials have high density of surface functional groups.

59 Graphene quantum dots (GQDs) have appealing characteristics for membrane
60 functionalization, such as large surface area and tunable surface grafting thanks to the presence
61 of functional surface groups.¹⁸⁻²⁰ Specifically, the presence of hydroxyl and carboxyl functional
62 groups on the surface of GQDs improves their compatibility with various polymeric,

63 organic/inorganic, and biological species.²¹⁻²³ Due to the presence of oxygen-containing
64 moieties, the incorporation of GQDs into the PA matrix alters its physiochemical structure, and
65 thus its water transport mechanisms. To develop nanocomposite PA membranes with suitable
66 performance, better understandings of the microscopic structure of the membranes and of the
67 interactions between PA chains and nanomaterials are needed.² As current experimental
68 methods are largely inadequate to provide insights into how the transport properties of PA
69 membranes are related to their microscopic structure, robust theoretical methods such as
70 molecular dynamics (MD) are appealing.²⁴

71 MD studies have shown that the incorporation of nanoparticles into PA changes the
72 cross-linking degree of the PA network, significantly altering the water flux of the resulting
73 membranes.^{25,26} It has been reported that MD can reliably predict the interfacial interactions
74 between fillers and the polymer matrix at the molecular level.²⁷⁻²⁹ MD can also be applied to
75 elucidate the function of the filler functional groups and has provided a deeper insight into the
76 transport of water molecules through the structure of traditional PA membranes.²⁵ Overall, MD
77 simulation provides an improved understanding of the relationship between macroscopic
78 membrane transport properties and microscopic membrane properties, such as polymer
79 configuration and free volume distribution.^{30,31} Previous MD studies have focused on the water
80 transport within PA membranes,^{32,33} but they have not evaluated the effect of filler-polymer
81 interactions on membranes transport properties. Experimentally, it has been shown that
82 functionalization of carbon nanotubes (CNTs) can enhance their compatibility with polymeric
83 matrix,³⁴ and that embedding CNTs into PAs alters the performance of the resulting
84 nanocomposite membranes.^{35,36} There have been a few MD studies on the effects of
85 incorporating CNTs into PA. These include investigations on the structure and hydration

86 properties of a CNTs/PA-TFC membrane, ³⁷ the effect of interfaces on the structural and
87 dynamical properties of CNTs/PA-66, ³⁸ and the effect CNTs functionalization on the
88 mechanical properties of the CNTs/chitosan nanocomposites. ³⁹

89 In this study, MD is applied to understand how the incorporation of GQDs into the PA
90 matrix affect the molecular-scale interactions and to evaluate their effects on the water flux
91 behavior of the resulting PA-GQDs membranes. To this end, the PA and GQDs structures are
92 first constructed and they then placed in a cubic amorphous cell. Afterwards, the potential sites
93 for the formation of covalent and hydrogen bonds on the PA chain are identified, and full MD
94 simulations are conducted by binding GQDs to these sites. Considering the possible sites,
95 different structures of the PA-GQDs membranes are created and then investigated. For all the PA
96 and PA-GQDs structures, the interaction energies, density, fractional free-volume, mean square
97 displacement, and water diffusivity coefficients are calculated. Based on these predictions and
98 water flux data obtained from experiments, the most probable structure of the final
99 nanocomposite matrix is determined, providing insights into the rationalization of the transport
100 properties as a function of the nanoscale membrane structure.

101

102 **2. Materials and Methods**

103 ***2.1. Fabrication of the membranes***

104 The PES membrane substrates were fabricated by the conventional phase inversion
105 technique. ^{40,41} The casting solution containing polyethersulfone beads (PES 14 wt.%, Ultrason
106 E6020P, $M_w = 58,000$ g/mol), polyvinylpyrrolidone (PVP 1 wt%, $M_w = 25,000$ g/mol, Merck),
107 and Triton X-100 (2 wt%, Merck) was stirred in N,N-dimethylformamide (DMF, 99.5%,
108 Scharlau) for at least 10 h to form a completely homogenous solution. After keeping the solution

109 stagnant for 6 h to eliminate entrapped bubbles, it was casted on a glass plate using a casting
110 knife set at a gate height of 90 μm . The casted film was then immersed into a coagulation bath of
111 deionized water (DI) and 1 wt/v % SDS.

112 GQDs were prepared by direct pyrolysis of citric acid (CA, Merck) according to the
113 procedure previously reported in Ref.^{42,43} The pristine and the GQDs-functionalized TFC
114 membranes were prepared based on the procedure reported in our previous paper.⁴¹ Briefly,
115 polyamide layers of all neat TFC and thin-film nanocomposite (TFN) membranes were
116 fabricated by interfacial polymerization (IP) between 3-phenylenediamine (MPD, Merck) (2 min)
117 and trimesoylchloride (TMC, Merck) TMC (30 s) solutions on the PES substrate. The aqueous
118 solution contained 2 wt% MPD, 2 wt% Camphorsulfonic acid (CSA, Merck) and 1 wt%
119 Triethylamine (TEA, Merck), while the organic solution included 0.1 wt/v% TMC in n-hexane
120 (96%, scharlau). After sequential immersion into aqueous and organic solutions, the polyamide
121 membrane was subjected to post-treatment in an oven at 80 $^{\circ}\text{C}$ for 5 min to ensure complete
122 cross-linking between monomers.⁴⁴ The TFN membranes were fabricated via incorporating
123 GQDs (0.05, 0.1, 0.3 and 0.5 wt.%) into the aqueous solution during the IP process, in which the
124 GQDs were distributed in the MPD solution using ultra-sonication.

125 It is worth mentioning that as this study focused on the characteristics of the selective
126 layer of polyamide membranes, the support layer was not considered during simulations.
127 Hereafter, the resulting membranes are denoted as thin-film nanocomposite (TFN)-0.05, TFN-
128 0.1, TFN-0.3 and TFN-0.5, respectively.

129 **2.2. Membrane water flux measurement**

130 The water flux (J_w) of the TFC and TFN membranes were determined by a lab-scale
131 cross-flow FO unit with an active area of 30 cm^2 and an active layer in the feed side. A closed-

132 loop configuration with the aid of two gear pumps was applied to circulate the feed and draw
133 solutions.⁴⁰ In all experiments, DI water was used as the feed, and sodium chloride (NaCl,
134 99.5% Merck) with a concentration of 0.5 M NaCl was used as the draw solution. Each
135 experiment was conducted for 30 min and was repeated three times. Conductivities of the feed
136 and draw solutions were measured online using a bench-scale conductivity meter (AZ86503).
137 The change of mass in feed solution was determined by a digital balance (AND EK6000I)
138 connected to a computer. The FO water flux (J_w) was then calculated via the following equation:

$$J_w = -\frac{\Delta(m_{fs} \times y_w)}{\Delta t} \times \frac{1}{\rho_w A_m} \quad (1)$$

139
140 where m_{fs} , ρ_w , and y_w are the mass of the feed solution, the pure-water density, and the mass
141 fraction of water in the feed solution, respectively. A_m is the effective membrane area. $\Delta(m_{fs} \times$
142 $y_w)$ is the change in term $(m_{fs} \times y_w)$ over a time interval of Δt .

143

144 **2.2. Simulation methodology**

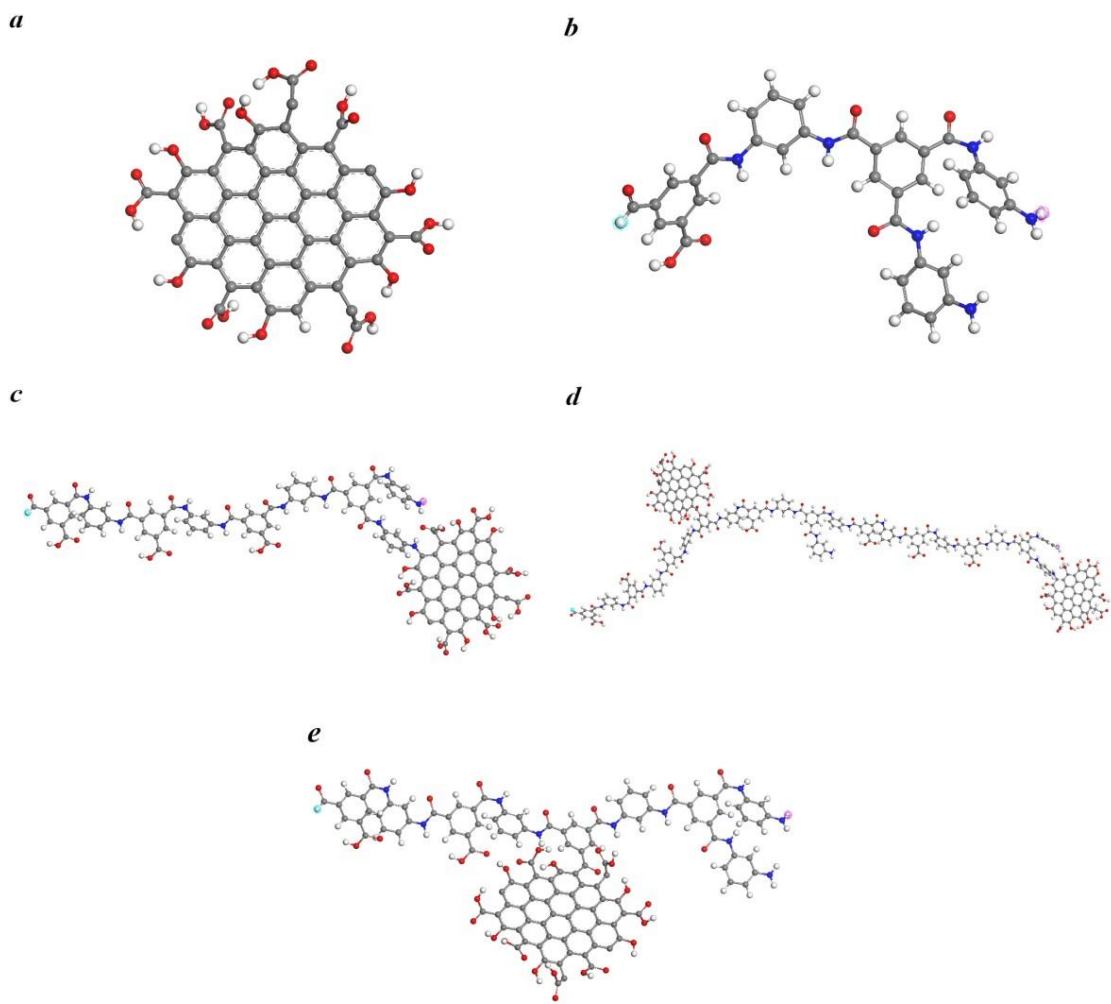
145 All the molecular dynamics (MD) simulations were performed with Materials Studio 6
146 (MS) software (Accelrys Inc., San Diego). To simulate likely interactions of hydroxyl- and
147 carboxyl-functionalized GQDs with polyamide chains, the following five different structures
148 were considered:

- 149 • P1: A neat polyamide chain formed by the reaction of TMC and MPD.
- 150 • P1-GQD: A mixture of P1 and three non-bonded GQDs.
- 151 • P2-GQD: A mixture of two non-bonded GQDs and one functionalized P1 with GQDs
152 (one GQD is connected to an MPD unit of the P1 monomer).

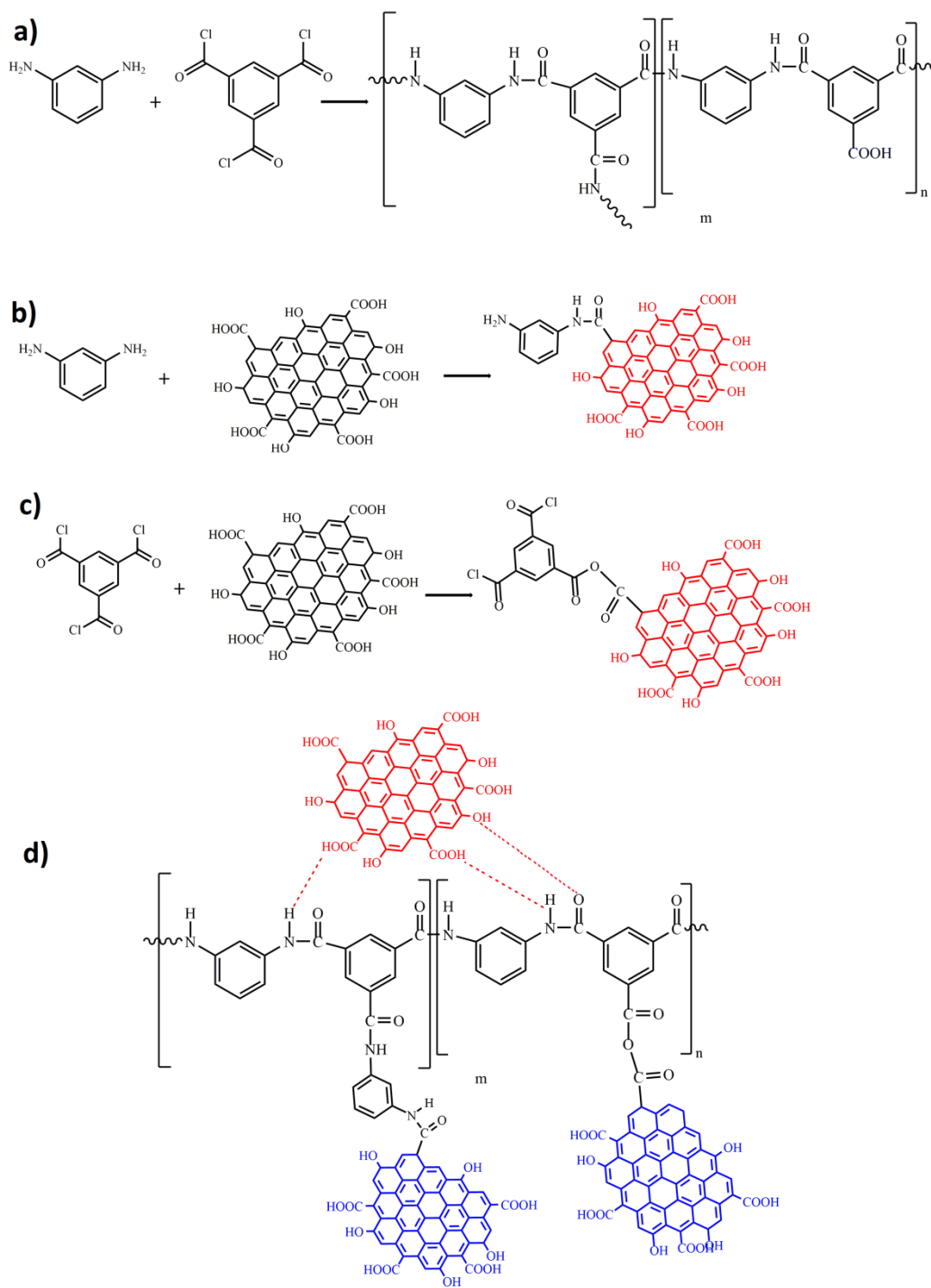
- 153 • P3-GQD: A mixture of two non-bonded GQDs and one functionalized P1 with GQDs
154 (GQDs are connected to several MPD and TMC units of the P1 monomer).
155 • P4-GQD: A mixture of two non-bonded GQDs and a functionalized P1 with GQDs
156 (one GQD is connected to a TMC unit of the P1 monomer).

157 The structures of GQD and the repeat units of P1, P2-GQD, P3-GQD and P4-GQ, are illustrated
158 in Figure 1. 3D atomic models of GQD and the monomers depicted in Fig. 1 are provided in the
159 Supporting Information. The files, GQD, Amid-1, Amid-2, Amid-3, and Amid-4, correspond to
160 the structures provided in Fig. 1a-e, respectively. Moreover, Figure 2 shows the interfacial
161 polymerization reaction of TMC and MPD to form a PA chain, as well as the interaction
162 mechanisms of GQDs with MPD and TMC units proposed in previous studies.^{41,45}

163 Xu et al.⁴⁶ proposed a reaction mechanism, in which the formation of covalent bonds
164 between amine species (polyethylenimine) and GQDs is more probable than the reaction
165 between GQDs and TMC units. In this study, we investigate this mechanism and three more
166 likely ones described above.



167
 168 **Figure 1:** Chemical structures of (a) GQD and the other monomer structures used in (b) P1, (c) P2-GQD,
 169 (d) P3-GQD, and (e) P4-GQD samples, respectively
 170



171

172 **Figure 2.** a) Interfacial polymerization between a TMC and an MPD unit, b) the interaction between a
 173 GQD and an MPD unit, c) the interaction between a GQD and a TMC, and d) the hydrogen bonds
 174 between GQDs and a PA chain and the formed covalent bonds between GQDs and both MPD and TMC
 175 units in a PA chain proposed in previous studies.^{41,45}

176

177 The structures of P1 and GQDs were connected by deploying the ‘Homopolymer Builder
178 Module’. The initial model of the membranes was developed based on the proposed structures
179 constructed under periodic boundary conditions in the "Amorphous Cell" module. The lattice
180 type of the cells was adjusted as cubic and their initial densities were set at 0.1 g/cm^3 . One chain
181 of each proposed structure was included in the simulation cell and its molecular weight was set
182 around 10,000 g/mol. Using the ‘Forcite Module’ and the ‘Smart Minimizer’ function, all the
183 structures were optimized in terms of both geometry and energy.

184 Two sets of simulations were conducted to study the properties of the four different
185 structures. One set investigated the intramolecular interactions between the GQDs and PA chains
186 in terms of covalent and hydrogen bonds, while the second set evaluated the water diffusivity by
187 loading water molecules within the amorphous cells. At each simulation stage, the periodic
188 boundary conditions (PBC) method was implemented to avoid undesirable interactions of the
189 molecules with the walls of the amorphous cell. An energy minimization procedure was applied
190 to find the equilibrated structure with the minimum potential energy for the amorphous cells. To
191 obtain equilibrium structures and true densities, MD simulations were conducted using the NPT
192 ensemble (constant number of molecules, constant pressure and temperature) for a period of
193 2200 ps including several repeat steps at 298.15 K at four pressures (1000 ps at 1 bar, 100 ps at
194 100 bar, 100 ps at 10000 bar, and 1000 ps at 1 bar) by adopting the Dreiding force field.⁴⁷ The
195 compression/relaxation procedure was applied to the low-density model of the membrane to
196 reach the equilibrium state. High pressures (100 bar and 10000 bar) were applied only to the
197 compaction part of that compression/relaxation simulation procedure. Next, the final equilibrated
198 structure was used to calculate the membrane properties such as interaction energies and
199 diffusion coefficients at ambient pressure.⁴⁸⁻⁵⁰ Figure 3 depicts snapshots of the final

200 equilibrated amorphous cells that MD simulations predicted for the proposed structures. The
 201 Crystallographic Information Files (cif) of the equilibrated amorphous cells are provided in the
 202 Supporting Information.

203 The microscopic non-bond interactions can be expressed using the interaction energy,
 204 $E_{\text{interaction}}$. Classical MD predicts this energy using: ^{44,51}

$$205 \quad E_{\text{interaction}} = E_{\text{Mixture}} - (E_{\text{Polyamide}} + E_{\text{GQDs}}) \quad (2)$$

206 where $E_{\text{interaction}}$, E_{Mixture} , $E_{\text{Polyamide}}$ and E_{GQDs} are the interaction energy, the total energy of the
 207 GQDs and the PA mixture, the total energy of the polyamide, and the total energy of GQDs,
 208 respectively.

209 Insights into the mechanism of water transport in each of the proposed structures were
 210 obtained from diffusion coefficients calculated from the mean squared displacement (MSD)
 211 using: ⁴⁸

$$212 \quad MSD(t) = \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(t_0)]^2 \quad (3)$$

213 where t is the simulation time, N is the number of particles in the system, and $r_i(t_0)$ and $r_i(t)$ are
 214 positions of an atom i at the initial time (t_0) and at time t , respectively. We then determined the
 215 diffusion coefficient, D , using the Einstein's relation for a three-dimensional system: ⁴⁸

$$216 \quad D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d(MSD(t))}{dt} \quad (4)$$

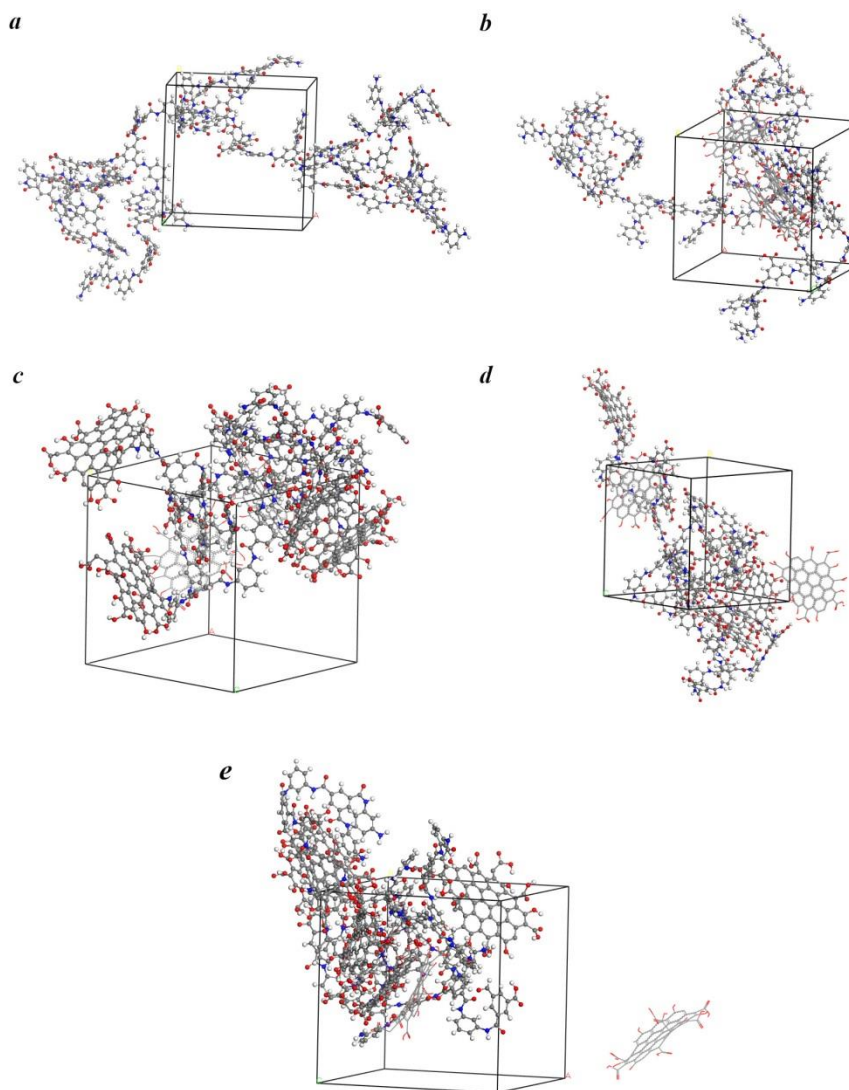
217 The FFV values for the proposed structures (Table 2) were calculated using:

$$218 \quad FFV_{\text{sim}} = \frac{V - V_0}{V} \quad (5)$$

219 where

$$220 \quad V_0 = 1.3 \times V_{vdW} \quad (6)$$

221 V is the volume of the equilibrated simulation cell, V_0 is the occupied volume by polymer, and
222 V_{vdW} is the van der Waals volume of all atoms calculated by the van der Waals surface method.⁵²
223



224
225 **Figure 3:** A snapshot of the final equilibrated 3D amorphous cells for (a) P1, (b) P1-GQD, (c) P2-GQD,
226 (d) P3-GQD, and (e) P4-GQD structures.

227
228 During the simulations, we considered that the thin film polyamide layer is intrinsically
229 porous. The Monte Carlo algorithm was applied to determine the number of water molecules that
230 should be loaded into each simulation cell. The water diffusion coefficient was calculated after

231 an equilibrated structure was reached. The maximum water adsorption capacity of each
232 polyamide thin film was determined based on the Grand Canonical Monte Carlo (GCMC)
233 method.⁵³ In this context, 20 water molecules (a few more than adsorption capacity of each
234 configuration) were loaded into each simulation cell to provide a super saturated state for the
235 proposed structures during simulations. After loading of the water molecules, a 100-ps NPT
236 simulation was conducted at 298.15 K and 1 bar to reach a new equilibrium and obtain the new
237 density. The water diffusivity of each proposed structure was calculated by the mean square
238 displacement (MSD) analysis (a 5000-ps NVT simulation at 298.15 K). The possibility of
239 intermolecular interactions between GQDs and the PA chains was investigated by calculating the
240 total potential energy of the polymeric mixture in each structure. The energy change difference
241 among different configurations was the basis of the calculations.

242

243 **3. Results and Discussion**

244 ***3.1. Molecular interactions of GQDs with a PA chain***

245 A previously-proposed mechanism for the reaction of GQDs with a polyamide chain
246 during the interfacial polymerization between MPD and TMC monomers^{41,45} is presented in
247 Figure 2. Based on our observation, during the synthesis of the TFN membranes, after addition
248 of GQDs to the MPD solution a color change from transparent to dark green and finally to black
249 occurred during the first few hours. The color change might be ascribed to reaction of several
250 amine functional groups of the MPD monomers with GQDs forming new covalent bonds during
251 ultra-sonication of the GQDs-MPD suspension.⁵⁴ After reaction with MPD or TMC monomers,
252 GQDs can be incorporated to the PA structure.^{55,56} In addition, several hydrogen bonds
253 involving the oxygen containing functional groups of GQDs and primary and secondary amines

254 of the polyamide chains can be formed. Moreover, covalent bonds between GQDs and the
255 carboxyl groups in the linear fraction of the polyamide can be produced through the
256 condensation reaction. This observation is in well agreement with what reported in the literature
257 for a similar scenario.⁴⁵ In their study, a color change occurred after the addition of graphene
258 oxide (GO) to the MPD solution.⁴⁵ This observation was rationalized as several amine
259 functional groups of the MPD monomers reacted with GO and formed covalent bonds.
260 Furthermore, it has been reported that GO reacts with the acyl chloride groups of TMC to form
261 anhydride and ester linkages.⁵⁴ As the MPD aqueous solution is alkalic (pH>7)⁵⁷, the
262 dissociation of -OH from carboxyl group of GQDs does not occur, and thus the most probable
263 reaction sites for the functionalization are the aromatic carbon of GQDs, as shown by Liu et al.⁵⁸
264 and Vacchi et al.⁵⁹ Moreover, since n-hexane (a non-polar solvent for the TMC solution) cannot
265 deprotonate the carboxyl groups of GQDs, the most probable site for that functionalization is
266 also recognized the aromatic carbon of GQD. Due to the presence of numerous oxygen-
267 containing functional groups, such as hydroxyl and carboxyl groups, on the surface and edges of
268 the GQDs and the existence of amide bonds in the polyamide chain, interactions between the
269 GQDs and PA chains are likely.^{55,56} Strong intermolecular interactions and high-density
270 hydrogen bonds should enhance additive-polymer compatibility and reduce structural defects in
271 polymer composites.

272 MD simulations are applied to determine the interactions between GQDs and the
273 polyamide chains at the molecular level. The predicted energies are presented in Table 1. The
274 more negative is the interaction energy of a structure, the more stable is the structure. Therefore,
275 the more negative total interaction energies of the P1-GQD and P2-GQD suggested the
276 formation of more stable configurations compared to that hypothesized for the P3-GQD and P4-

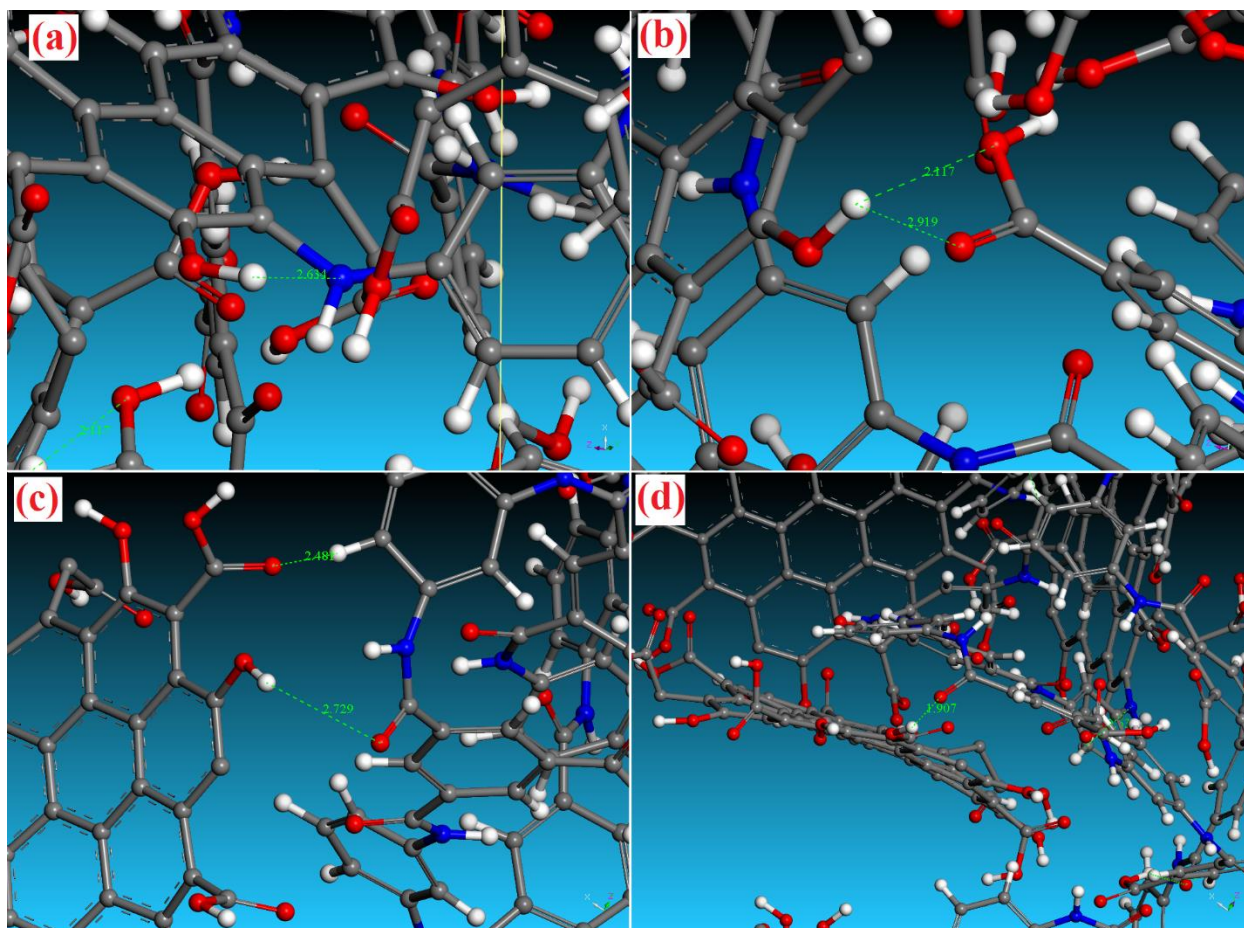
277 GQD structures. Although the functionalization with GQDs increases the steric hindrance, the
 278 uniform arrangement of GQDs around the functional groups of polyamide chain can lead to
 279 enhanced attractive interaction. Furthermore, this higher attractive interaction computed between
 280 GQDs and the functional groups of the polyamide chain suggests the formation of hydrogen
 281 bonds owing to the presence of donor and acceptor groups in the structure of both GQDs and PA,
 282 as depicted in Figure 4. To further verify the presence of hydrogen bonds, radial distances
 283 between hydrogen and nitrogen atoms and between hydrogen and oxygen atoms were calculated.
 284 In this H-bond detection study, the maximum hydrogen-acceptor distance was set to 2.9 Å, and
 285 the minimum donor-hydrogen-acceptor angle to 90°. ^{60,61} A hydrogen-acceptor distance within
 286 2.7–2.8 Å strongly points to the existence of hydrogen bonds in the structures. ⁶⁰ The
 287 representative snapshot of the final structure obtained from the simulations (Figure 4) shows that
 288 the calculated distances between GQDs and the polyamide chain are less than 2.9 Å, which is
 289 indicative of electrostatic interactions, based on Jeffrey’s categorization. ⁶²

290
291

Table 1: Energies calculated by MD simulations (kcal/mol).

Sample	E_{Mixture}	$E_{\text{Polyamide}}$	E_{GQDs}	$E_{\text{interaction}}$
P1-GQD	1086.98	1063.70	499.56	-476.28
P2-GQD	1415.16	1470.28	381.45	-436.57
P3-GQD	1046.06	1007.68	341.53	-303.15
P4-GQD	1285.76	1292.98	344.12	-351.34

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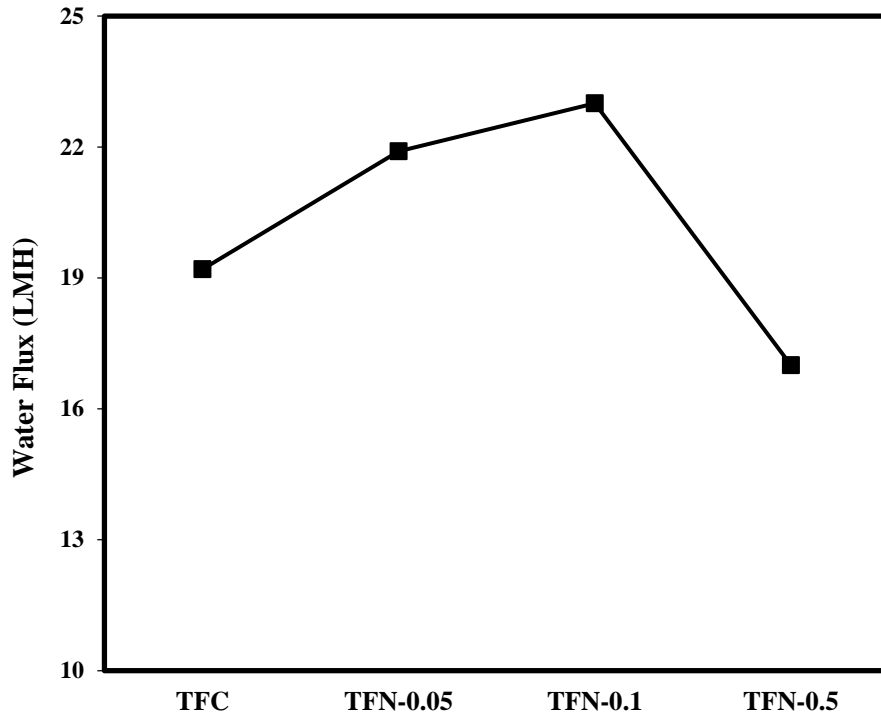


295
 296 **Figure 4:** Snapshots obtained at the end of a simulation of P2-GQD, showing the presence of H-bonds
 297 between each pair of atoms (red balls = oxygen atoms, grey balls = carbon atoms, blue balls = nitrogen
 298 atoms, and white balls = hydrogen atoms).

299
 300 **3.2. Effect of GQDs on the Dynamic Behavior of Water Transport**

301 The predicted interaction energies suggest that the P1-GQD and P2-GQD are the more
 302 stable structures among those investigated. To further elucidate the GQD-PA structure,
 303 diffusivity coefficients were calculated via MD simulation and compared to the water fluxes
 304 obtained from experiments. Figure 5 summarizes the results on the effect of the concentration of
 305 GQDs on the experimental water flux of the TFC membranes.⁴¹ The water flux increased with
 306 increased GQDs concentration until a medium value and then decreased. The decrease in water
 307 flux of the TFN-0.5 was ascribed to GQDs agglomeration and poorer interaction with the

308 polyamide chains. The enhancement at low concentration may instead also be attributed to
309 improved wettability of the GQDs-PA surfaces compared to those of pristine TFC membrane,
310 facilitating water molecules uptake.^{41,44,55} GQDs may also provide extra nano-channels for
311 accelerated transport of water molecules by generating interfacial gaps with the polyamide
312 chains. This phenomenon may concurrently disturb the layer chain packing, which would
313 inevitably increase the free volume of the selective layer and lowers overall selectivity.^{41,63,64}
314 Insights into the mechanism of water transport in each of the proposed structures were obtained
315 from diffusion coefficients calculated using the mean squared displacement (MSD).⁴⁸

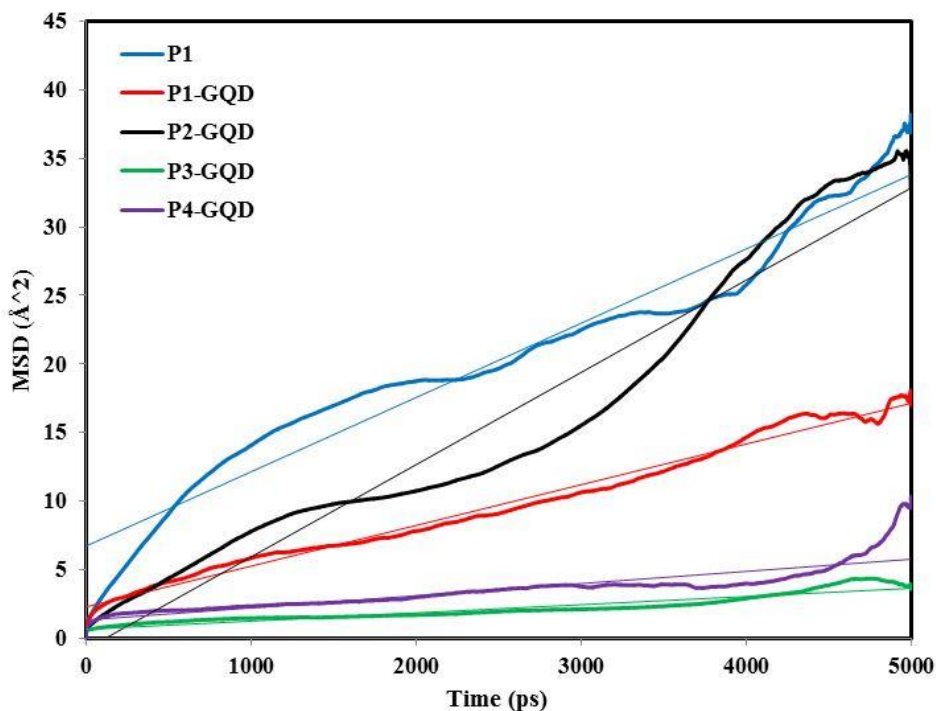


316
317 **Figure 5:** Forward osmosis water flux of the TFC and TFN membranes vs. the concentration of GQDs.

318
319 Figure 6 reports plots of the MSDs of water molecules at 298.15 K vs. time. The MSDs of the P1
320 and P2-GQD structures increased at much faster rate than those of the P1-GQD, P3-GQD and

321 P4-GQD, suggesting that the P1 and P2-GQD structures impose a lower resistance to the passage
322 of water molecules.

323



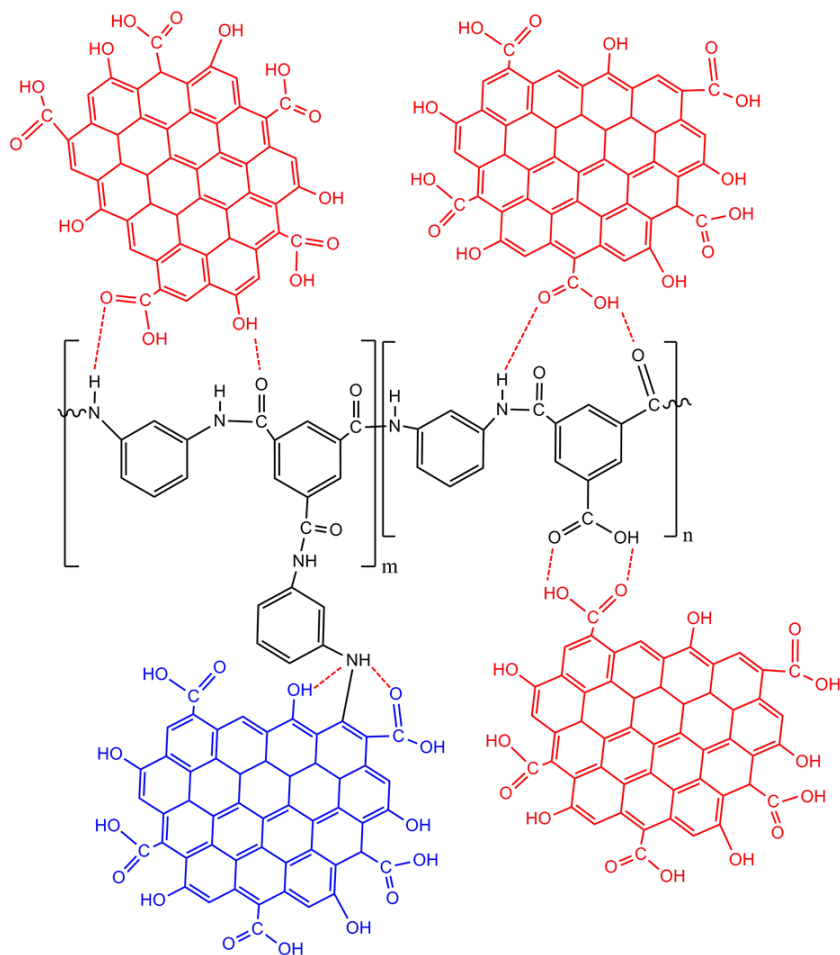
324

325 **Figure 6:** Mean square displacements of water molecules vs. NVT simulation time in the four proposed
326 structures at 298.15 K.

327

328 Chain movement (depending on the presence of functional groups on polymer chains),
329 density, and fractional free-volume (FFV) are the main physical parameters affecting the
330 diffusion through a membrane.⁶⁵ Additionally, the water molecules can be delayed as they are
331 attracted by the hydrophilic terminals (head and tail) inside the narrow channels, a phenomenon
332 that slows down transport. Moreover, the steric hindrance (chain with larger size) and a high-
333 density hydrogen bond distribution also prevent facile transport of water molecules.⁴⁴ To better
334 understand the mechanism of water transport, average molecular weights, densities, fractional
335 free volume, and water diffusion coefficients were calculated for the four proposed structures

336 and presented in Table 2. The first parameter that will be discussed is the diffusion coefficient
337 resulting from the simulations. This parameter follows the following order: P2-GQD > P1 > P1-
338 GQD > P4-GQD > P3-GQD, consistent with the results presented in Figure 6. Also based on the
339 other parameters presented in Table 2 and discussed below, we actually hypothesize that the
340 higher diffusion coefficients of the P2-GQD structure may be explained by the lower density of
341 hydrogen bonds,⁶⁵ lower transport resistance,⁶⁶ and lower affinity to water molecules inside the
342 narrow channels.^{67,68} The enhanced diffusivity coefficient of the P2-GQD structure also agrees
343 well with increased water fluxes obtained from experiments and the low diffusion coefficient
344 computed for P4-GQD structure also confirms the experimental observations suggesting that this
345 configuration is unlikely. The results of interaction energies supported by the computed layer
346 properties and water transport parameters imply that the P2-GQD structure is the most likely
347 structure of the TFN membranes. The strong interaction mechanism of the GQDs with MPD
348 monomers and the weak interaction mechanism of the GQDs with a polyamide chain occurring
349 in this structure are shown in Figure 7. To summarize, the higher water diffusivity of P2-GQD
350 compared to the pristine TFC may be attributed to a larger surface wettability and an overall
351 lower resistance against the passage of water molecules.



352

353 **Figure 7:** The mechanism for the interactions of the GQDs with MPD and TMC units, proposed based on
 354 the MD simulations conducted in this study.

355 To complete the picture of the water transport mechanism across the nanocomposite
 356 layer, the other parameters calculated by the MD simulations are presented in Table 2. The
 357 computed density of the pristine polyamide structure is about 1.186 g/cm^3 , which is consistent
 358 with the reported values of 1.2 and 1.24 g/cm^3 ; ^{26,69} see Table 2. The density of P1-GQD is not
 359 significantly different from this value, while P2-GQD, P3-GQD and P4-GQD densities
 360 surprisingly increased to 1.38 g/cm^3 and 1.35 g/cm^3 with the incorporation of GQDs. Figure 8
 361 shows the simulated morphology of the fractional free volume and its distribution in the
 362 proposed structures. The FFV values for the proposed structures were listed in Table 2. The

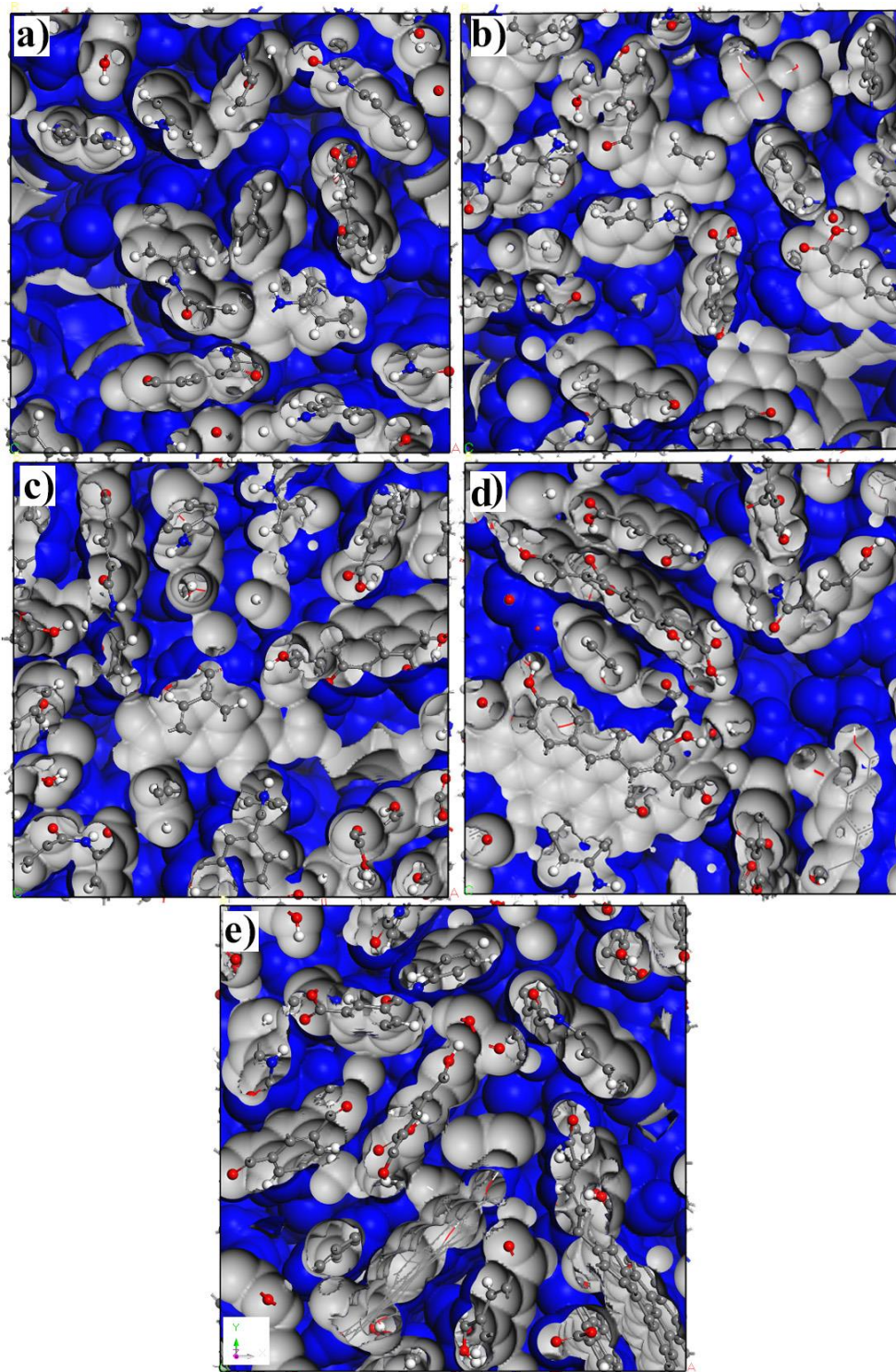
363 fractional accessible volume (FAV) was also calculated based on the diameter of water molecule
 364 (2.75 Å) and according to the solvent excluded surface (Connolly surface) method,⁷⁰ while
 365 ignoring the factor of 1.3 (Table 2).

366 Despite the seemingly reasonable hypothesis that GQDs provide extra nano-channels and
 367 generate more free volume, the incorporation of GQDs into to the amorphous cell seems to
 368 decrease the FFV, due to the overall increased density of the structure and owing to a good
 369 interaction with the polymer chains, thus creating a seamless interface. More connected voids
 370 would provide more water diffusion paths, while smaller and isolated voids in the GQDs-
 371 functionalized polyamide structure are associated with a lower density of effective channels for
 372 water molecules passage.⁷¹ However, as discussed earlier the P2-GQD structure was associated
 373 with higher water diffusion despite its increased density and reduced FFV. As such, the density
 374 and FFV of the selective layer do not seem to be the main factors affecting the overall water
 375 transport characteristics of the membrane. In this case, the presence of shorter paths for transport
 376 of water molecules in the P2-GQD structure may instead be considered as the main features
 377 allowing faster water passage despite higher overall density of the selective layer.⁷²

378 **Table 2:** Predicted average molecular weights of polymer chains, densities of composites, and diffusivity
 379 coefficients of water in the polymeric thin films.

Sample	Molecular Weight (g/mol)	Predicted Density (cm ³ /g)	D × 10 ⁸ (cm ² /s)	FFV (-)	FAV (-)
P1	10476.2	1.19	9.00	0.233	0.172
P1-GQD	10476.2	1.19	5.00	0.253	0.219
P2-GQD	10820.9	1.38	11.17	0.175	0.141
P3-GQD	9766.3	1.38	1.00	0.171	0.127
P4-GQD	10741.0	1.35	1.50	0.193	0.165

380



382

383 **Figure 8.** Morphology of the free volume in (a) P1, (b) P1-GQD, (c) P2-GQD, (d) P3-GQD, and (e) P4-
384 GQD structures (blue areas = free volume).

385

386

387 **4. Conclusion**

388 Several chemical structure models of the polyamide membranes incorporating graphene
389 quantum dots (GQDs) were proposed. Using molecular dynamics (MD), the interaction energies,
390 densities, water diffusion coefficients, mean square displacements, and FFVs were predicted for
391 each of the structures. Experimental data and MD predictions indicated that the chemical
392 structure in which the GQDs form covalent bonds with the amine-containing monomers and
393 which forms hydrogen bonds with the polyamide (PA) chains is the most likely structure for the
394 nanocomposite GQD-PA membrane. The considerably higher water diffusion in such a structure
395 compared to the other hypothesized configurations and to the pristine polyamide was found to be
396 due to a larger surface wettability (because of the presence of GQDs) combined with a lower
397 chance of linkages formed while water molecules move through the layer. This phenomenon
398 seems to overpower the effect provided by a relatively high density and low FFV of the resulting
399 structure. Another critical characteristic allowing an unimpaired nanocomposite selective layer is
400 the high PA-GQDs compatibility, preventing the formation of large interfacial voids that would
401 decrease selectivity and in turn reduce the water transport in forward osmosis. In summary, our
402 simulations suggest that a high-performance nanocomposite layer is one where a relatively low
403 number of fillers interact strongly with the polymer chains to form a seamless structure that
404 maintains selectivity and that, while increasing water uptake by adsorption at the membrane-
405 solution interface, does not hold back water molecules as it reduces the likelihood of water-layer
406 hydrogen bonding. The hierarchical simulation protocol applied in this study may be extended to
407 explore other nanocomposite membranes, and to gain an improved molecular-level
408 understanding with the goal to develop high-performance membranes for a wide range of
409 applications.

410

411 **Supporting information**

412 Crystallographic Information File (CIF) of the equilibrated structure of each simulation cell and
413 the 3D atomic models of GQD and the monomers in the ".mol" format.

414

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