Supporting Information

for

Covalent functionalization of graphene with PAMAM dendrimer and its implications on graphene's dispersion and cytotoxicity

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Definition of the grafting approaches used: grafting-from and grafting-to.

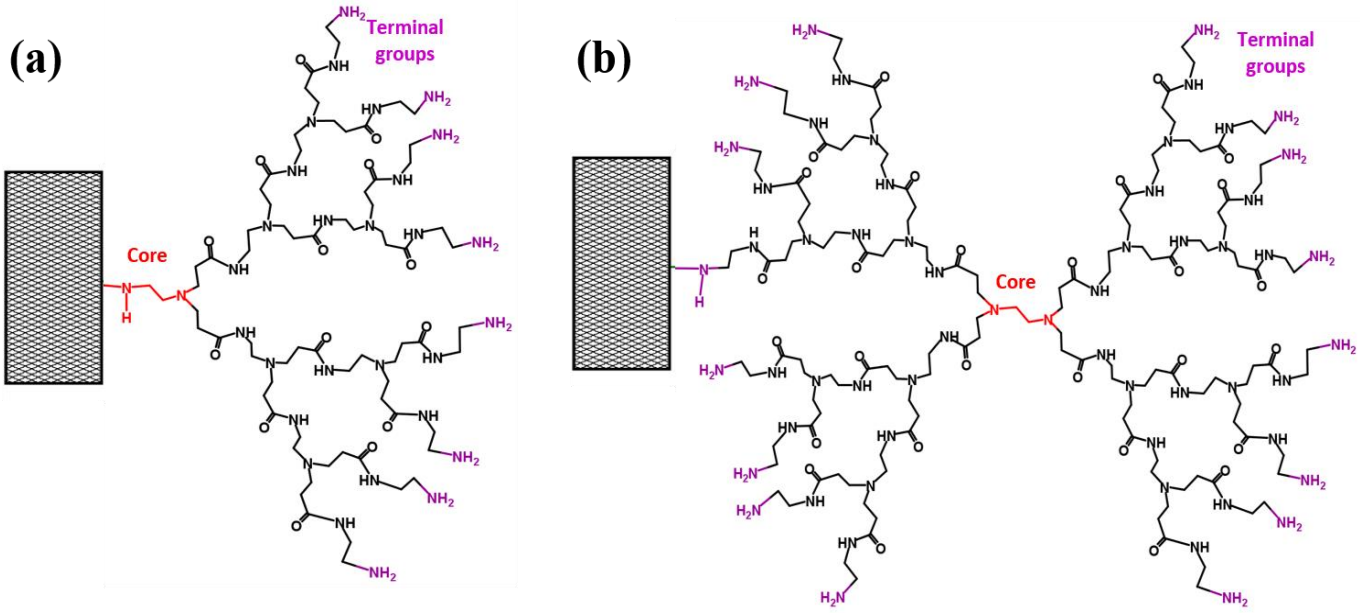

Figure S1: Schematic representation of two types of grafting approaches of covalent functionalization of graphene with dendrimer: (a) *grafting-from* and (b) *grafting-to*. The core part and the terminal groups of the dendrimer are colored in red and purple respectively. Gray color checked rectangle is a schematic of graphene sheet.

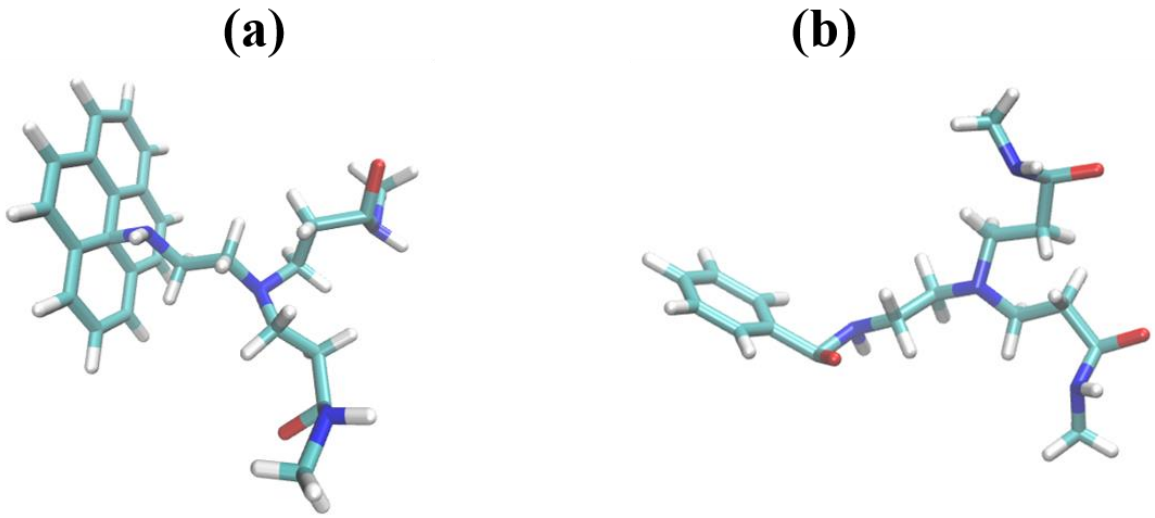

Figure S2: Parts of the graphene-dendrimer composite for which charge equilibration was performed (a) grafting-from top and (b) grafting-from edge. Color code: Carbon in cyan, hydrogen in white, oxygen in red and nitrogen in blue.

Table S1: Partial atomic charges and its GAFF atom types are presented here for core branch atoms of grafting from method at two different binding locations (top and edge) (Fig. S2).

Grafting from					
Core branch atoms at Top Binding			Core branch atoms at Edge Binding		
Atom	GAFF atom type	Charge	Atom	GAFF atom type	Charge
			C	c	0.6051
			O	o	-0.5556
N	n	-0.7064	N	n	-0.7993
H	hn	0.3996	H	hn	0.3739
C	c3	-0.1676	C	c3	0.2014
H	h1	0.2626	H	h1	0.1153
H	h1	0.2626	H	h1	0.1153
C	c3	0.4234	C	c3	0.2547
H	h1	-0.0273	H	h1	0.0201
H	h1	-0.0273	H	h1	0.0201
N	n3	-0.9506	N	n3	-0.8904
C	c3	0.4671	C	c3	0.0599
H	h1	-0.0350	H	h1	0.0822
H	h1	-0.0350	H	h1	0.0822
C	c3	0.4671	C	c3	0.0599
H	h1	-0.0350	H	h1	0.0822
H	h1	-0.0350	H	h1	0.0822
C	c3	-0.4672	C	c3	-0.0440
H	hc	0.1912	H	hc	0.1111
H	hc	0.1912	H	hc	0.1111
C	c3	-0.4672	C	c3	-0.0440
H	hc	0.1912	H	hc	0.1111
H	hc	0.1912	H	hc	0.1111
C	c	0.5372	C	c	0.3764
C	c	0.5372	C	c	0.3764
O	o	-0.5750	O	o	-0.5091
O	o	-0.5750	O	o	-0.5091

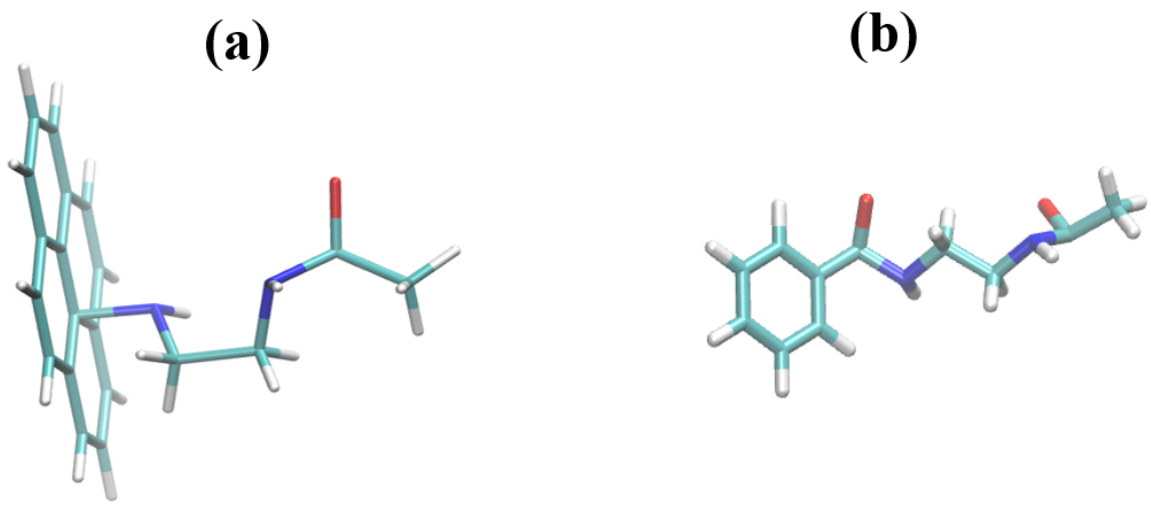

Figure S3: Parts of the graphene-dendrimer composite for which charge equilibration was performed (a) grafting-to top and (b) grafting-to edge. Color code: Carbon in cyan, hydrogen in white, oxygen in red and nitrogen in blue.

Table S2: Partial atomic charges and its GAFF atom types are presented here for terminal branch atoms of grafting to method at two different binding locations (edge and top) (Fig. S3).

Grafting To					
Terminal branch atoms at Top Binding			**Terminal branch atoms at Edge Binding**		
Atom	**GAFF atom type**	**Charge**	**Atom**	**GAFF atom type**	**Charge**
			C	c	0.4005
			O	o	-0.4120
N	n	-0.4661	N	n	-0.6055
H	hn	0.3994	H	hn	0.3413
C	c3	-0.2295	C	c3	0.3413
H	h1	0.1567	H	h1	0.1109
H	h1	0.1567	H	h1	0.1109
C	c3	0.1239	C	c3	0.0813
H	h1	0.0292	H	h1	0.0450
H	h1	0.0292	H	h1	0.0450
N	n	-0.6102	N	n	-0.6025
H	hn	0.4169	H	hn	0.3678

Table S3: Details of the systems simulated. The graphene-dendrimer complex used in the DMPC + GPDD system corresponds to the grafting-to edge binding case with GP size 6 × 3 nm^2 (TE-6x3). DMPC + GP 6×3 and DMPC + GPDD correspond to the DMPC-bare graphene (Fig. 8 (a)) and DMPC-functionalized graphene (Fig. 8 (c)) systems, respectively.

Case	No. of atoms						Box Dimensions Å × Å × Å
	DMPC	Graphene (GP)	Dendrimer	Counterions	Water	Total	
DMPC + GP 6×3	60416	800	0	0	179928	241144	146 × 144 × 166
DMPC + GPDD	60416	784	1060	30	182916	245206	146 × 144 × 168

Wrapping nature of multiple top-binding dendrimers (grafting-from):

To see the brush like structure we have simulated with maximum number of dendrimers coated on graphene sheets of size of 6×3 nm^2 by both grafting approaches. The simulation study on two dendrimers coated on the top from the grafting-to method already shown a brush like structure (Fig. 3 (b)). For grafting-from method, six dendrimers can be coated on the graphene top surface. The equilibrated structures are shown in Fig. S4. In consequence, in the grafting-to method the graphene surface can accommodate three dendrimers whereas six dendrimers can be coated on the graphene surface by grafting-from method. These results suggest that grafting-from method exhibits more grafting density than that of grafting-to method.

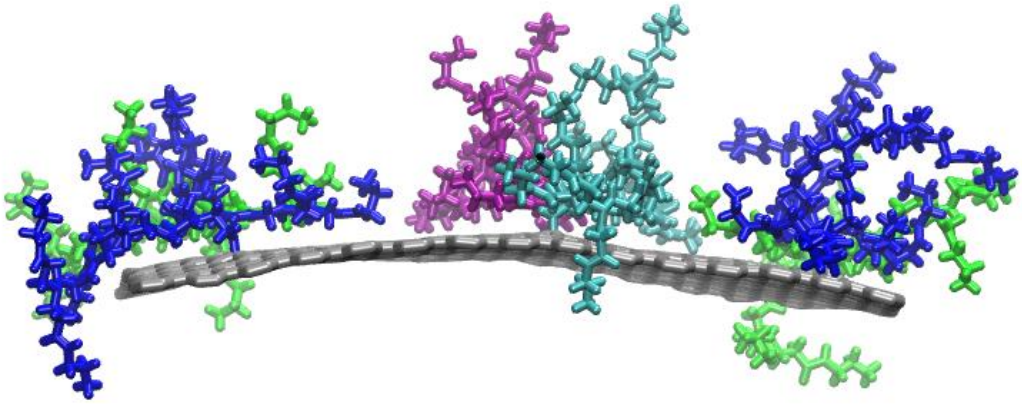

Figure S4: Equilibrated structure of grafting from method of the case of top binding with 6 half dendrimers. To differentiate the multiple dendrimers, we have used different colors.

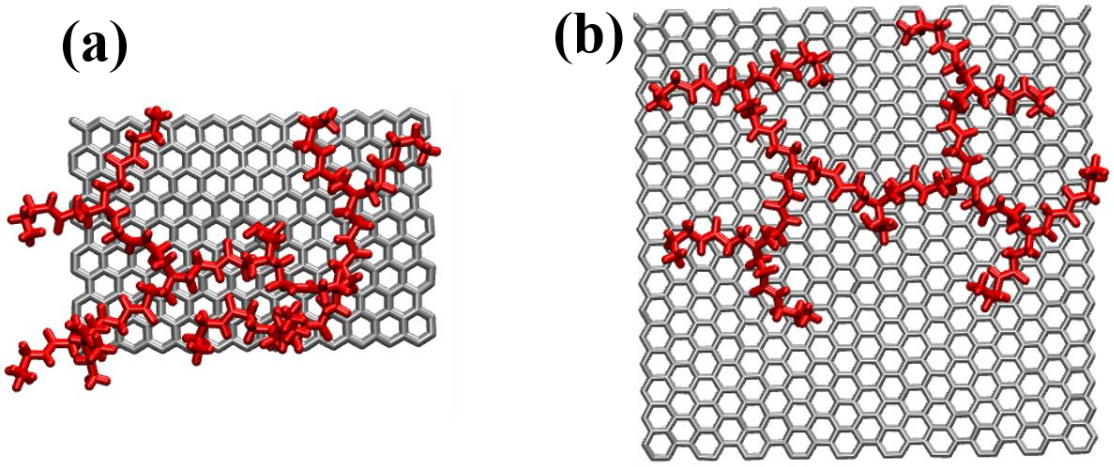

Figure S5: Equilibrated structure of dendrimer-graphene composite in top-view, for (a) FT-3x2 and (b) FT-4x4 cases.

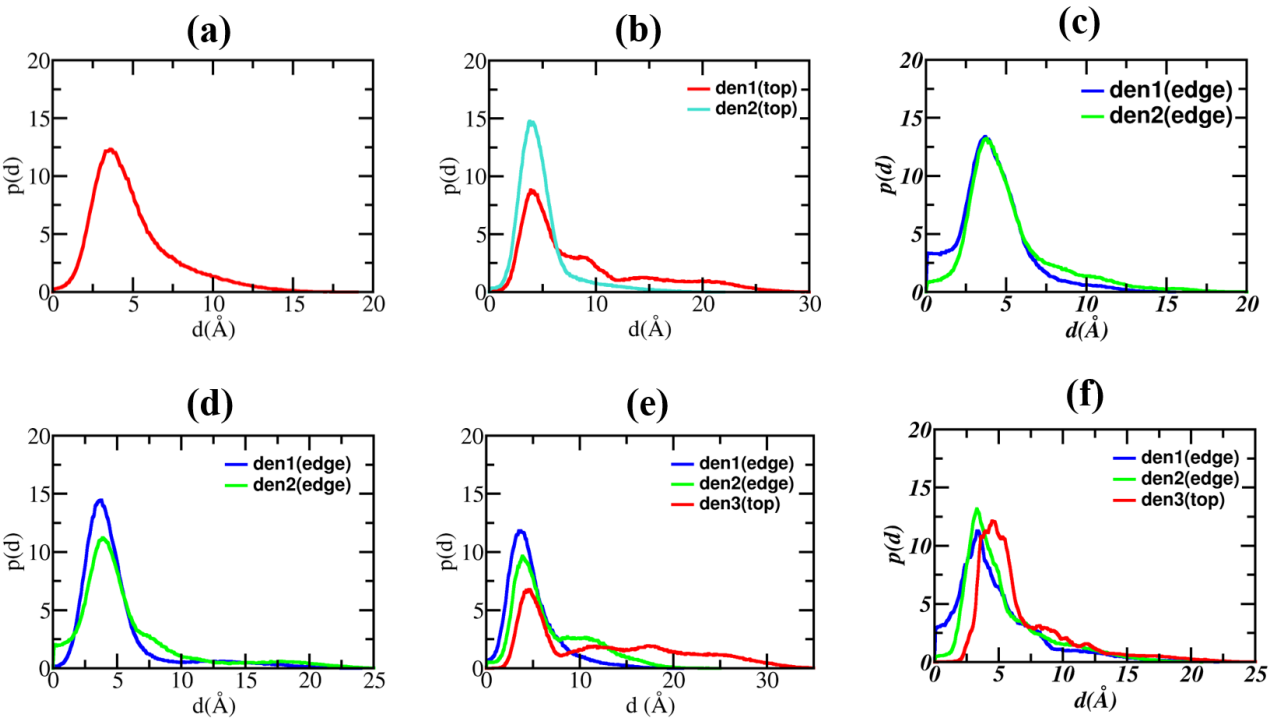

Figure S6. Thickness distribution profiles of the functionalized graphene for *grafting-to* case at top binding with (a) one dendrimer (TT-6x3-1), (b) two dendrimers (TT-6x3-2). Similarly, (c) and (d) correspond to TE-4x3 and TE-6x3 cases, respectively. Finally, (e) and (f) belong to the top-edge binding cases *i.e.*, TTE-6x3 and TTE-10x3 cases, respectively. The color code used for the curves (red, cyan: top-binding and blue, green: edge-binding dendrimers) is consistent with that in Fig. 3.

Table S4: Average number of close contacts between graphene and dendrimer for all the cases.

	Grafting from Approach					
Case	**FT-3x2**	**FT-4x4**	**FE-3x2**	**FE-4x3**	**FTE-4x3**	**FTE-6x3**
No. of close contacts	27.1 ± 3.2	36.3 ± 3.5	62.9 ± 4.7	69.2 ± 5.1	85.3 ± 5.7	81.2 ± 5.6
	Grafting to Approach					
Case	**TT-6x3-1**	**TT-6x3-2**	**TE-4x3**	**TE-6x3**	**TTE-6x3**	**TTE-10x3**
No. of close contacts	49.7 ± 4.2	94.0 ± 6.2	96.1 ± 6.2	104.5 ± 6.3	128.7 ± 7.1	130.5 ± 7.0

Table S5: Average number of close contacts between graphene and dendrimer of grafting from approach of edge and top-edge binding. D1 and D2 are the edge-binding dendrimers colored in blue and green, respectively (Fig. 2 (c) – (f)). D3 is the top-binding dendrimer (colored in red) in Figs. 2 (e), (f).

	Edge				**Top-edge**					
Sheet size	**FE-3x2**		**FE-4x3**		**FTE-4x3**			**FTE-6x3**		
	D1(edge)	**D2(edge)**	**D1(edge)**	**D2(edge)**	**D1(edge)**	**D2(edge)**	**D3(top)**	**D1(edge)**	**D2(edge)**	**D3(top)**
$<N_c>$	31.9 ± 3.6	31.0 ± 3.1	37.7 ± 3.6	31.5 ± 3.5	23.5 ± 3.3	33.7 ± 3.5	28.1 ± 3.1	32.3 ± 3.3	28.5 ± 3.6	20.4 ± 2.9

Table S6: Average number of close contacts between graphene and dendrimer of grafting-to approach of all the three binding locations with more than one dendrimer cases. D1 and D2 are the edge-binding dendrimers colored in blue and green, respectively (Figs. 3 (c) – (f)). D3 is the top-binding dendrimer (colored in red) in Figs. 3 (e), (f). D1T and D2T are the top-binding dendrimers colored in red and cyan, respectively, in Fig. 3 (b).

	Top		**Edge**				**Top-edge**					
Sheet size	**TT-6x3-2**		**TE-4x3**		**TE-6x3**		**TTE-6x3**			**TTE-10x3**		
	D1T (top)	**D2T (top)**	**D1 (edge)**	**D2 (edge)**	**D1 (edge)**	**D2 (edge)**	**D1 (edge)**	**D2 (edge)**	**D3 (top)**	**D1 (edge)**	**D2 (edge)**	**D3 (top)**
$<N_c>$	33.7 ± 3.3	60.3 ± 4.9	48.3 ± 4.3	47.9 ± 4.4	53.9 ± 4.4	50.5 ± 4.5	49.8 ± 4.3	39.4 ± 4.1	39.7 ± 4.1	39.0 ± 4.1	46.7 ± 4.1	44.9 ± 4.1

Solvent Coverage Area of Graphene:

Subtracting the SASA of graphene when it was covered with dendrimer from the SASA of graphene before covering will give the graphene surface coverage area by the dendrimer. An illustration of SASA of bare-graphene and functionalized-graphene is given in Fig. S7 and Fig. S8, respectively.

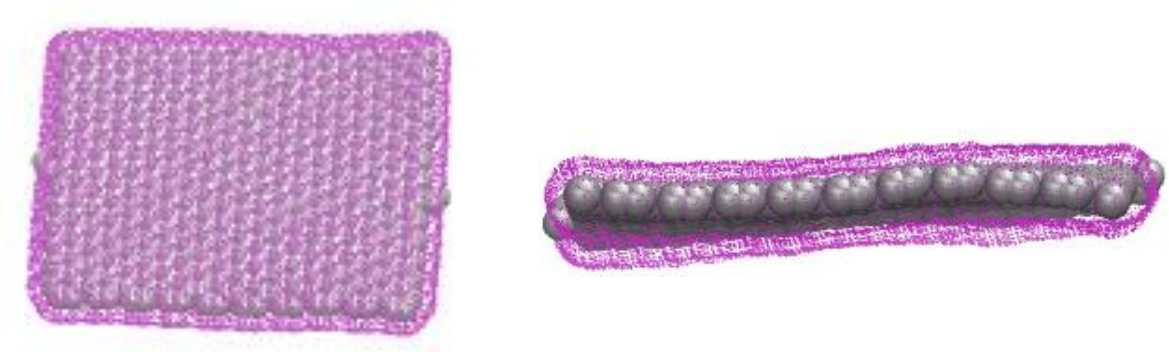

Figure S7: Top and Side views of the solvent accessible surface area of graphene before functionalization.

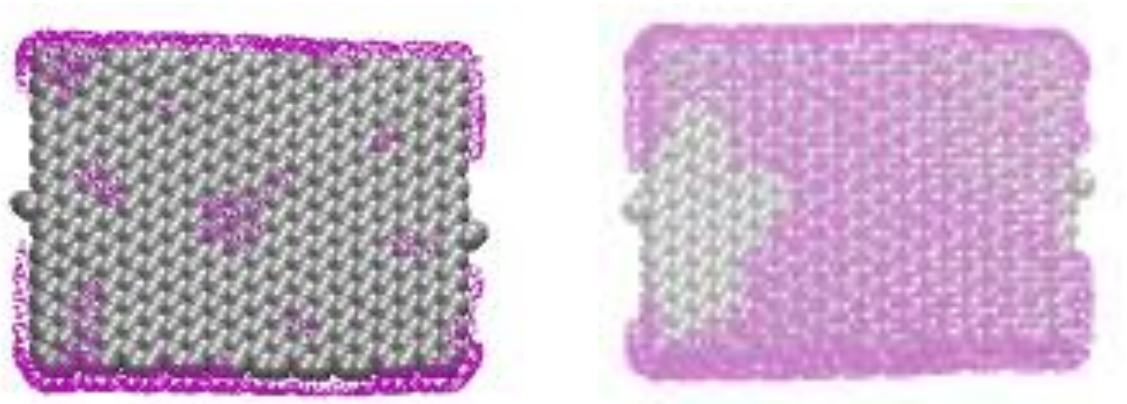

Figure S8: Top and side views of the solvent accessible surface area of graphene after functionalization, calculated with "restrict" option in VMD.

Table S7: Average number of amine-water hydrogen bond per amine. We consider the hydrogen bonds between (i) primary amines and water molecules, (ii) secondary amines and water molecules and (iii) tertiary amines and water molecules, (iv) carbonyl group and water molecules, for the all cases.

	Grafting from Approach						**Grafting to Approach**					
	Top (FT-)		**Edge (FE-)**		**top-edge (FTE-)**		**Top (TT-)**		**Edge (TE-)**		**top-edge (TTE-)**	
Sheet size (nm^2)	**3×2**	**4×4**	**3×2**	**4×3**	**4×3**	**6×3**	**6×3(1den)**	**6×3(2den)**	**4×3**	**6×3**	**6×3**	**10×3**
Primary amine	1.51 ± 0.01	1.56 ± 0.01	1.51 ± 0.01	1.56 ± 0.01	1.55 ± 0.01	1.53 ± 0.01	1.45 ± 0.01	1.46 ± 0.01	1.39 ± 0.01	1.42 ± 0.01	1.49 ± 0.01	1.42 ± 0.01
Secondary amine	0.37 ± 0.01	0.43 ± 0.01	0.41 ± 0.01	0.45 ± 0.01	0.41 ± 0.01	0.44 ± 0.01	0.38 ± 0.01	0.39 ± 0.01	0.38 ± 0.01	0.41 ± 0.01	0.39 ± 0.01	0.36 ± 0.01
Tertiary amine	0.20 ± 0.01	0.18 ± 0.01	0.20 ± 0.01	0.27 ± 0.01	0.24 ± 0.01	0.26 ± 0.01	0.11 ± 0.01	0.13 ± 0.01	0.13 ± 0.01	0.09 ± 0.01	0.13 ± 0.01	0.13 ± 0.01
Carbonyl	1.07 ± 0.01	1.14 ± 0.01	1.02 ± 0.01	1.11 ± 0.01	1.22 ± 0.01	1.22 ± 0.01	1.02 ± 0.01	1.07 ± 0.01	1.07 ± 0.01	1.11 ± 0.01	1.10 ± 0.01	1.04 ± 0.01

Testing the dependence of the initial structure on the dispersion

To understand whether the results on the dispersibility of the functionalized graphene sheet depend on the initial structure considered, we have repeated the simulations with three different initial structures for FE-3x2 case. As shown in Fig. S9, the COM-COM distance increases and the sheets separate as the simulation progresses, for all the cases. We have shown the initial and final structures of the sheets are also shown in Fig. S9.

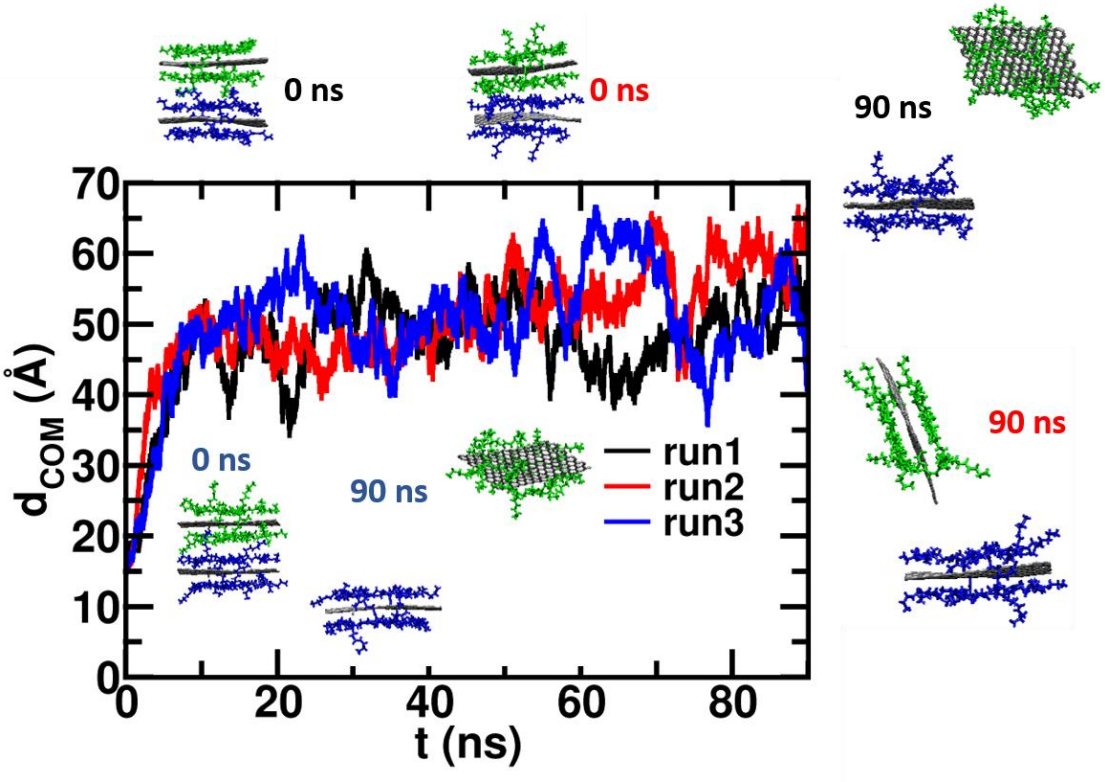

Figure S9: The COM-COM distances as a function of the simulation time for three independent simulations corresponding to FE-3x2 case. The initial and final snapshots of the sheets are also shown. The color of the timestamp on the snapshots is consistent with the color of the run. For all the runs the sheets separate as the simulation progresses.