Supporting Information for

Combined Molecular Dynamics and Density Functional Theory Study of Azobenzene-Graphene Interfaces

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Contents:

1. Molecule-graphene Surface Contact Area

The molecule-graphene surface contact area, SCA, is estimated using the solvent accessible surface area (SASA) concept.[1-3]

The SCA is obtained by subtracting the SASA of the graphene when the molecules are adsorbed on it from the SASA of the bare graphene sheet.

SASAs are calculated with the g_sas GROMACS utility using 0.14 nm as probe diameter and 50 as number of points per sphere.

2. Surface coverage and energy analysis

The total SASA for the bare graphene sheet is 231.58 nm^2 and, since graphene is a 2D material with a negligible thickness, the SASA of a bare face of the graphene sheetis 115.89 nm^2, half of the total surface area.

The coverage is obtained as the percentage of the SCA divided by the half of the total surface area of the graphene layer.

Table S1. Summary of structural and energetic characterizations of dense *trans* fluorinated azobenzene monolayers.

# Molecules N	<SCA> nm^2	% Coverage	$\langle E_{vdW} \rangle$ / N (kJ mol^{-1} $molecule^{-1}$)	E_{bin} / N (kJ mol^{-1} $molecule^{-1}$)
60	2.12	94.3	-139.9	-40.8
64	2.09	96.5	-138.3	-43.6

Table S2. Summary of structural and energetic characterizations of dense *cis* fluorinated azobenzene monolayers.

# Molecules N	<SCA> nm^2	% Coverage	$\langle E_{vdW} \rangle$ / N (kJ mol^{-1} $molecule^{-1}$)	E_{bin} / N (kJ mol^{-1} $molecule^{-1}$)
64	1.72	82.1	-114.3	-36.1
72	1.73	96.1	-119.8	-46.1
80	1.66	96.0	-109.4	-41.9

3. Final MD configuration

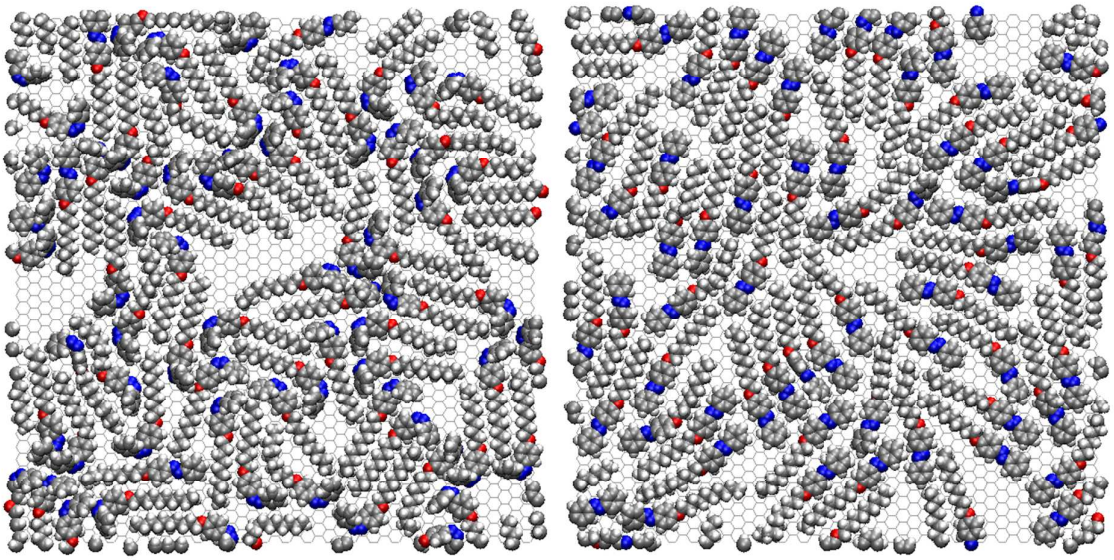


Figure S1. Top view of the *cis* (left) and *trans* (right) monolayer of the non-fluorinated azobenzene assembly on graphene. The images refer to the last snapshot of the MD simulations. Carbon atoms are in grey, hydrogen white, oxygen red and nitrogen blue.

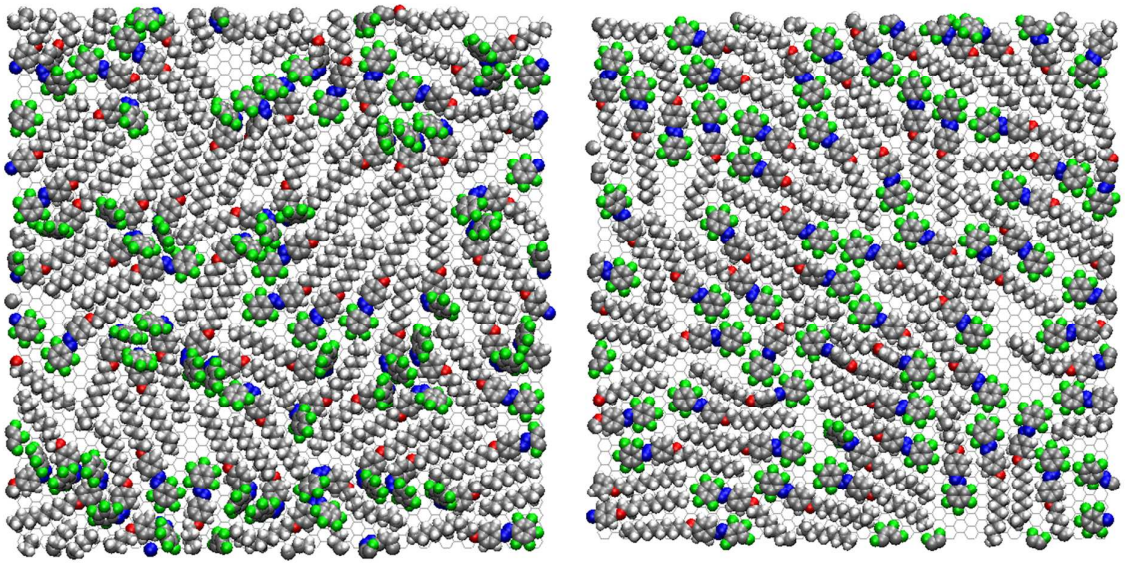


Figure S2. Top view of the *cis* (left) and *trans* (right) monolayer of the fluorinated azobenzene assembly on graphene. The images refer to the last snapshot of the MD simulations. Carbon atoms are in grey, hydrogen white, oxygen red, nitrogen blue and fluorine green.

4. Correlation between MD/DFT dipoles

Table S3. Normal (to the graphene sheet) molecular dipole moment component obtained by DFT (gray background) and FF/MD (white background) for 8 randomly extracted molecules (rows) in 10 frames (columns) for the *trans* azobenzene isomer. All values are in Debye.

	26	**28**	**29**	**48**	**51**	**57**	**58**	**62**
4	5.30E-01	5.84E-01	1.27E-01	-3.35E-01	4.74E-01	-1.40E+00	7.49E-01	2.17E-01
	5.61E-01	1.35E+00	6.44E-02	-5.13E-01	6.61E-01	-2.40E+00	4.58E-01	7.75E-01
20	5.24E-01	3.16E-01	5.25E-01	-1.24E-01	2.56E-01	4.06E-01	-3.28E-01	1.66E-01
	6.83E-01	6.18E-01	3.22E-01	1.74E-01	3.81E-01	4.90E-01	-2.38E-01	2.58E-01
170	2.23E-01	-1.72E-01	-3.41E-01	1.96E-01	2.60E-01	-3.30E-01	4.03E-01	9.60E-03
	4.87E-01	-1.56E-01	3.85E-01	4.57E-01	2.79E-01	-1.66E-01	7.37E-02	4.83E-02
188	-2.28E-02	3.23E-01	6.60E-01	6.37E-01	5.56E-01	8.42E-01	2.58E-01	6.53E-01
	3.63E-01	8.77E-02	2.64E-01	8.51E-01	7.09E-01	2.18E-01	3.99E-01	4.65E-01
278	2.41E-01	5.91E-02	2.57E-01	3.89E-01	4.02E-01	7.51E-02	5.30E-02	-1.63E-01
	4.98E-01	-1.14E-01	8.50E-02	4.30E-01	7.17E-01	-1.95E-01	-8.41E-03	-5.57E-01
311	4.00E-01	1.57E-01	-1.81E-01	5.96E-01	3.26E-01	1.72E-01	3.11E-01	-2.01E-01
	2.69E-01	-1.16E-01	-1.07E+00	4.46E-01	4.92E-01	-1.14E-01	2.14E-01	-1.38E-01
334	-2.11E-01	4.26E-02	3.09E-01	3.74E-01	9.56E-02	2.14E-01	-2.63E-01	3.81E-01
	1.33E-01	-7.95E-02	-1.67E-01	-1.72E-01	1.19E-01	3.43E-01	2.47E-01	6.72E-01
451	3.80E-02	-2.24E-01	3.78E-01	-5.96E-02	-2.68E-02	-3.45E-01	2.25E-01	9.31E-02
	-1.41E-01	-7.20E-03	4.29E-01	3.78E-01	-3.19E-02	-4.87E-01	3.37E-01	2.41E-01
471	0.1167	4.04E-01	5.23E-01	1.45E-01	0.5415	-7.68E-02	5.44E-01	6.95E-02
	6.63E-02	1.40E-01	1.80E-01	3.57E-01	7.97E-01	-3.03E-01	1.19E+00	1.42E-01
480	8.84E-02	5.82E-01	3.98E-01	1.16E-01	-3.93E-01	3.45E-01	8.32E-01	-3.04E-01
	-4.64E-02	3.85E-01	5.30E-01	-1.02E-01	1.71E-01	2.68E-01	8.24E-01	-4.55E-01

Table S4. Normal (to the graphene sheet) molecular dipole moment component obtained by DFT (gray background) and FF/MD (white background) calculations for randomly extracted 8 molecules (rows) in 10 frames (columns) for the *cis* azobenzene isomer. All values are in Debye.

	6	**17**	**28**	**33**	**49**	**54**	**67**	**68**
44	3.70E-01	5.09E-01	7.61E-01	3.22E-01	3.28E-01	6.44E-02	-4.13E-01	7.66E-02
	3.70E-01	5.09E-01	7.61E-01	3.22E-01	3.28E-01	6.44E-02	-4.13E-01	7.66E-02
157	-1.26E+00	6.50E-01	-6.18E-01	5.00E-02	6.56E-01	-3.43E-02	-3.47E-01	5.19E-01
	-1.26E+00	6.50E-01	-6.18E-01	5.00E-02	6.56E-01	-3.43E-02	-3.47E-01	5.19E-01
199	-5.52E-01	3.27E-01	3.73E-01	-1.69E-01	2.15E-01	6.05E-01	-4.39E-01	-2.55E-02
	-5.52E-01	3.27E-01	3.73E-01	-1.69E-01	2.15E-01	6.05E-01	-4.39E-01	-2.55E-02
204	-1.07E+00	2.82E-01	2.39E-01	4.64E-01	1.51E-01	-2.87E-01	3.34E-01	-1.10E-01
	-1.07E+00	2.82E-01	2.39E-01	4.64E-01	1.51E-01	-2.87E-01	3.34E-01	-1.10E-01
225	-9.66E-01	1.14E+00	9.48E-01	1.20E+00	6.00E-01	5.74E-01	2.06E-01	4.08E-01
	-9.66E-01	1.14E+00	9.48E-01	1.20E+00	6.00E-01	5.74E-01	2.06E-01	4.08E-01
366	-2.49E-01	2.40E-01	-3.34E-02	1.50E-01	2.23E-01	9.21E-01	-3.77E-02	1.75E-01
	-2.49E-01	2.40E-01	-3.34E-02	1.50E-01	2.23E-01	9.21E-01	-3.77E-02	1.75E-01
369	4.68E-01	2.09E-01	2.00E-01	4.52E-02	1.12E-01	2.59E-01	2.11E-01	2.65E-01
	4.68E-01	2.09E-01	2.00E-01	4.52E-02	1.12E-01	2.59E-01	2.11E-01	2.65E-01
373	1.56E+00	-9.65E-02	2.56E-01	3.89E-01	3.07E-01	8.73E-01	4.00E-01	-8.50E-02
	1.56E+00	-9.65E-02	2.56E-01	3.89E-01	3.07E-01	8.73E-01	4.00E-01	-8.50E-02
421	5.74E-02	6.17E-02	1.81E-01	1.48E-01	5.85E-01	-6.27E-01	-1.45E-01	1.52E-01
	5.74E-02	6.17E-02	1.81E-01	1.48E-01	5.85E-01	-6.27E-01	-1.45E-01	1.52E-01
442	-2.70E-01	6.74E-01	5.77E-01	2.02E-01	3.91E-01	-2.97E-01	4.52E-01	2.90E-01
	-2.70E-01	6.74E-01	5.77E-01	2.02E-01	3.91E-01	-2.97E-01	4.52E-01	2.90E-01

	trans		cis	
#mol	**LDA**	**MP2**	**LDA**	**MP2**
1	0.7506	1.1816	2.5867	2.8764
2	0.6129	0.8610	2.055	2.3694
3	0.4833	0.6361	1.2186	1.6715
4	0.5429	0.6221	0.5659	0.7311
5	0.2177	0.3701	0.4383	0.6606
6	0.1690	0.0755	0.2846	0.4336
7	-0.1791	-0.3289	-0.0967	-0.126
8	-0.1756	-0.3693	-0.3554	-0.311
9	-0.3273	-0.3493	-1.1973	-1.3397
10	-0.3331	-0.3980	-1.777	-2.0821

Table S5. Molecular dipole moment (calculated along the normal to the graphene sheet) obtained by DFT/LDA and MP2 calculations for randomly extracted 8 molecules for the *trans* (left) and *cis* (right) azobenzene isomer. All values in Debye.

5. Conformation of the Azobenzene forming the SAM

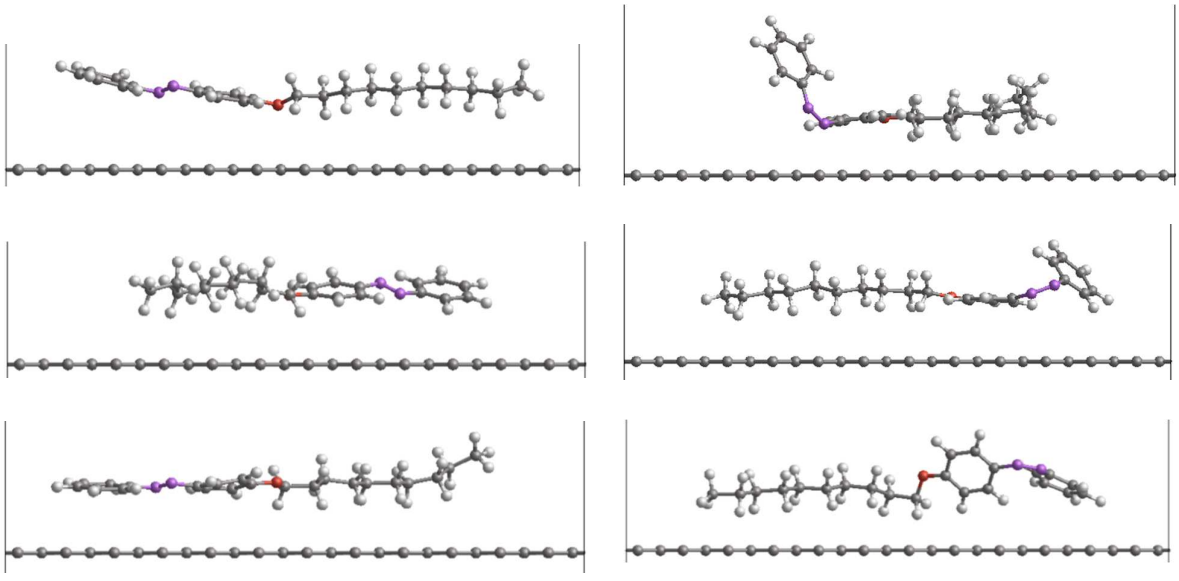


Figure S3. Representative conformations for the *trans* (left) and *cis* (right) azobenene isomers physisorbed on graphene. The conformations refer to different molecules extracted from different frames along the MD simulations.

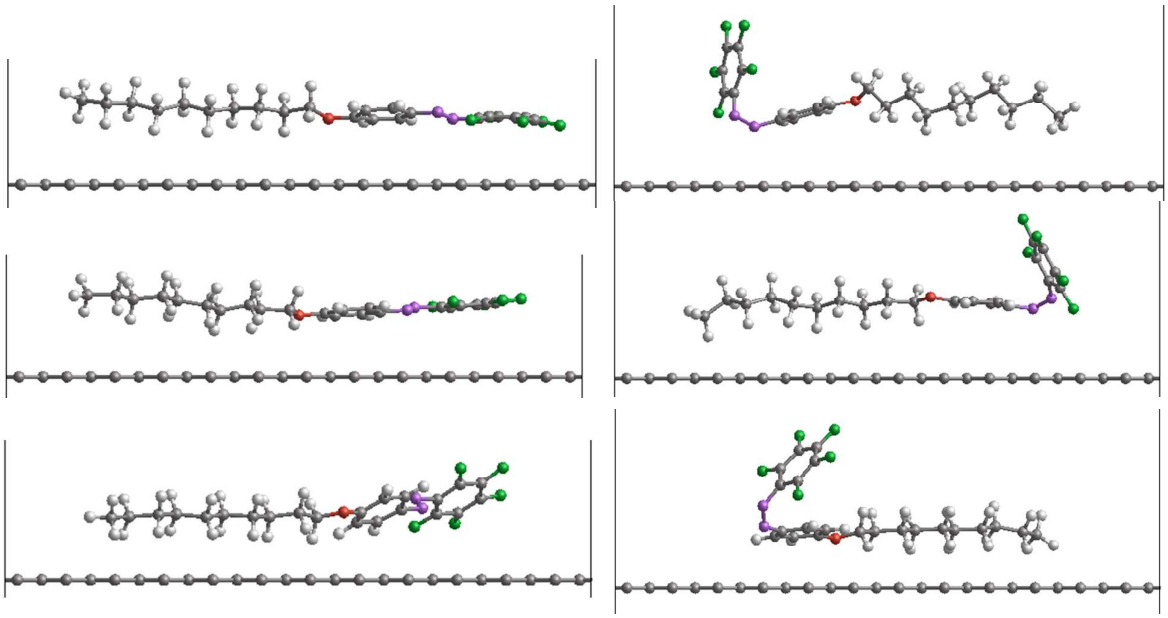
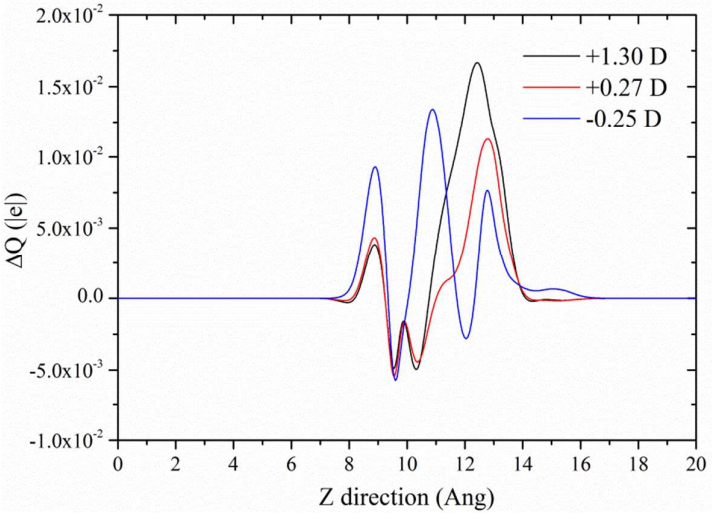


Figure S4. Representative conformations for the fluorinated *trans* (left) and *cis* (right) azobenene isomers physisorbed on graphene. The conformations refer to different molecules extracted from different frames along the MD simulation.

6. DFT, Charge analysis



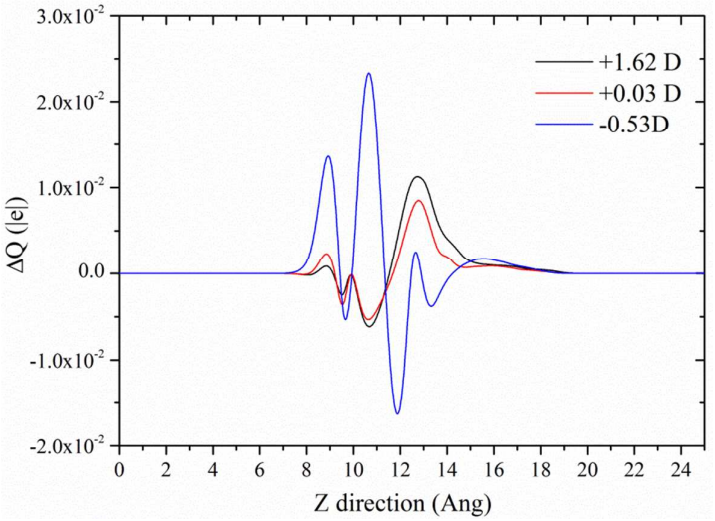


Figure S5. Charge analysis for the *trans* (up) and *cis* (bottom) fluorinated isomers of different conformers selected from the SAM dipole moments distribution, along the z axis of the cell. The gray dotted line points to the graphene sheet.

Figure S5 shows the plane-integrated charge distributions *vs* out-of-plane distance for representative structures of the *trans* and *cis* fluorinated azobenzene isomers. In particular, conformations with negative, medium and large ground-state state molecular dipole moments were selected to check for possible correlation with the interfacial charge reorganization. For the *trans* isomer, a (small) partial positive charge ranging from $0.8 \cdot 10^{-2}$ to $1.7 \cdot 10^{-2}$ |e| is present on the adsorbed molecule and the compensating negative charge on graphene. This thus indicates that the graphene is slightly n-doped, in agreement with the WF analysis. The same analysis for the different conformers of the *cis* isomer leads to the same conclusion, i.e. n-doping of graphene, with a partial charge transfer from the molecule to graphene in the range $0.8 \cdot 10^{-2}$ to $1.1 \cdot 10^{-2}$ |e|.

7. Correlation between WF shift and dipole distribution of fluorinated azobenzene

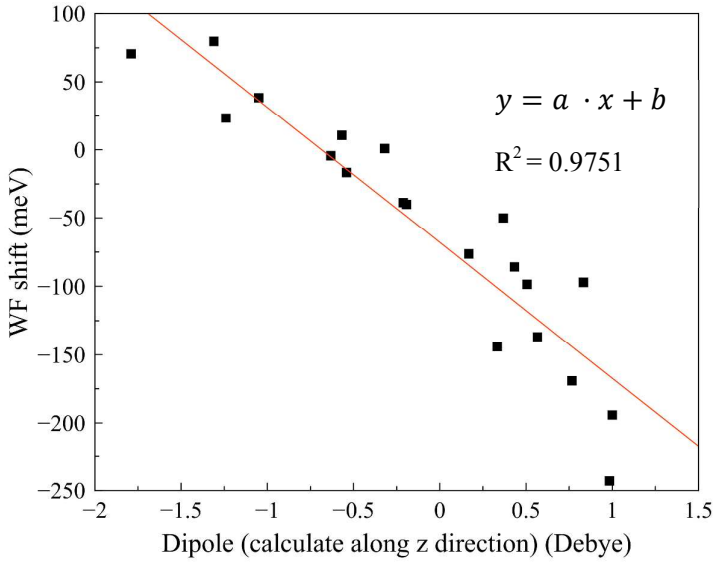


Figure S6. Correlation between WF shift (from DFT) and dipole distribution (obtained by MD simulations). The solid red line is a linear fit; a = -99.29 and b = -67.98.

References

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(2) Shrake, A.; Rupley, J. A. Environment and Exposure to Solvent of Protein Atoms, Lysozyme and Insulin. *J. Mol. Biol.* **1973**, *79*, 351-371.

(3) Connolly, M. L. Solvent-Accessible Surfaces of Proteins and Nucleic-Acids. *Science* **1983**, *221*, 709-713.