Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Understanding the pH-Dependent Adsorption of Ionizable Compounds on Graphene Oxide Using Molecular Dynamics Simulations

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SI1 XPS Characterization of Graphene Oxide

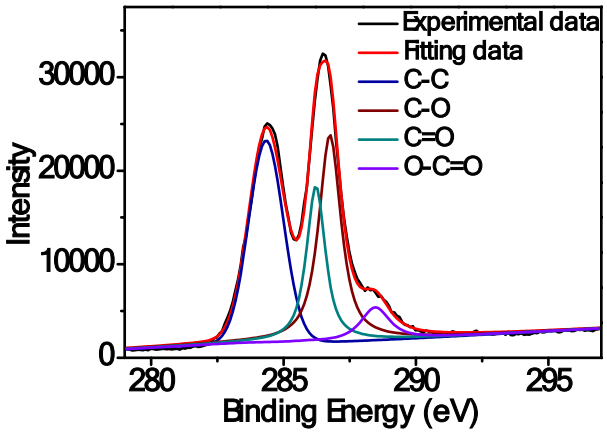


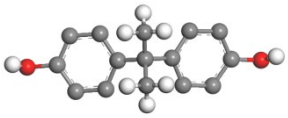
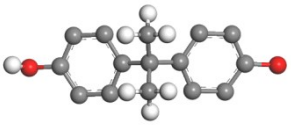
Fig. S1 XPS spectra of GO.

Table S1. XPS data and the models of GO

Sample	O:C	% C-C	% C-O	% C=O	% O-C=O
GO	1:2.083	37±2.85	34±3.62	22±2.47	7±1.36

SI2 Structure of BPA in different pH conditions

Table S2 Structure of BPA in different pH conditions

pH	System	BPA	Structure
5.0~ 6.6	G1	$C_{15}H_{16}O_2$	
6.6~ 8.0	G2	$C_{15}H_{15}O_2$	
8.0~ 9.0	G3	$C_{15}H_{14}O_2$	

SI3 Minimization and Equilibration Results

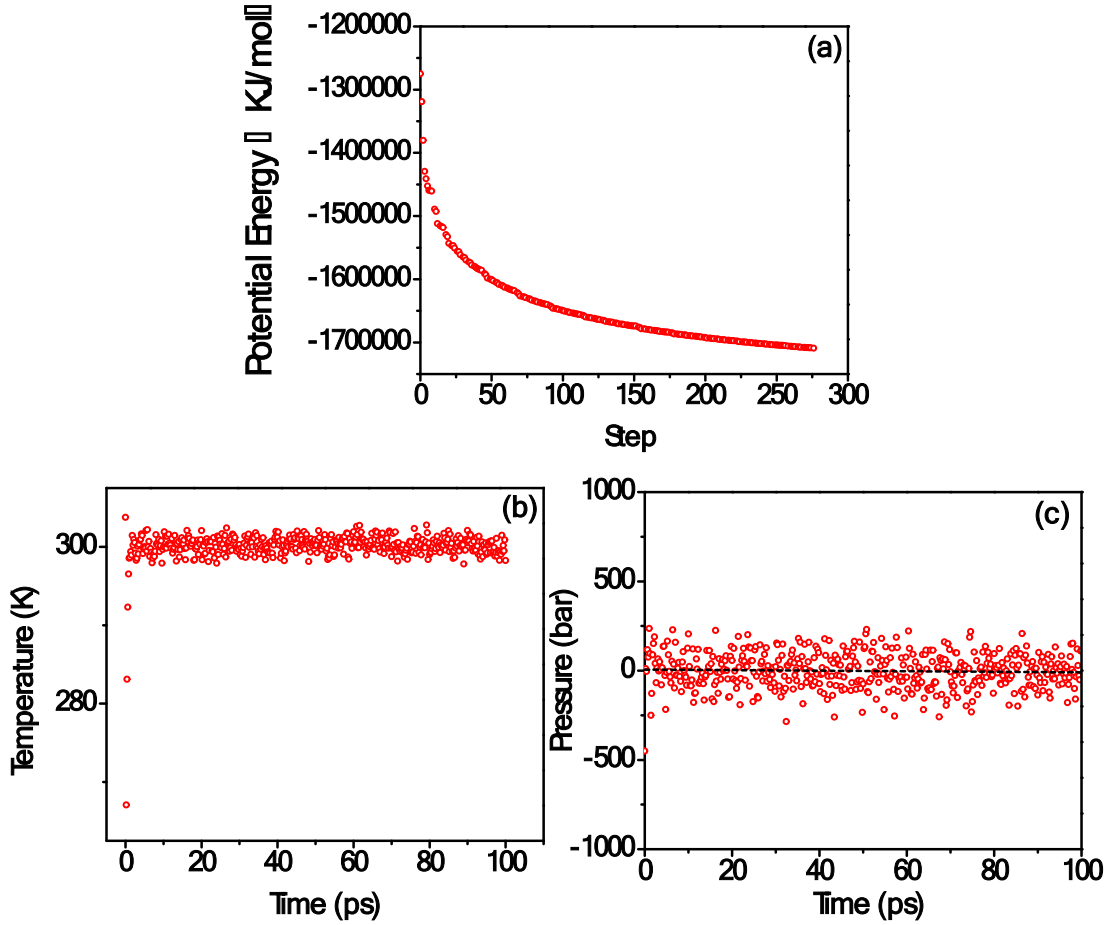


Fig. S2. (a) Energy minimization of the simulation system. After the system is at an energy minimum, we can begin real dynamics. Energy minimization ensured that we have a reasonable starting structure, in terms of geometry and solvent orientation. (b) Temperature equilibration of the simulation system. From the plot, it is clear that the temperature of the system quickly reaches the target value (300 K), and remains stable over the remainder of the equilibration. (c) Pressure equilibration of the simulation system. The pressure value fluctuates widely over the course of the 100-ps equilibration phase, but this behavior is not unexpected. The running average of these data are plotted as the black dashed line in the plot. Over the course of the equilibration, the average value of the pressure is 1.05 bar.

SI4 Structures for π-π inreraction.

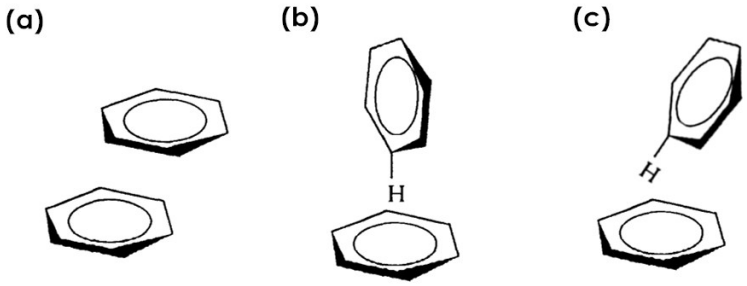


Fig. S3 (a) offset face-to-face (sometimes referred to as parallel displaced). (b) T-shaped edge-to-face. (c) tilted-T structure. [1]

SI5 DFT Calculation Results of BPA and GO

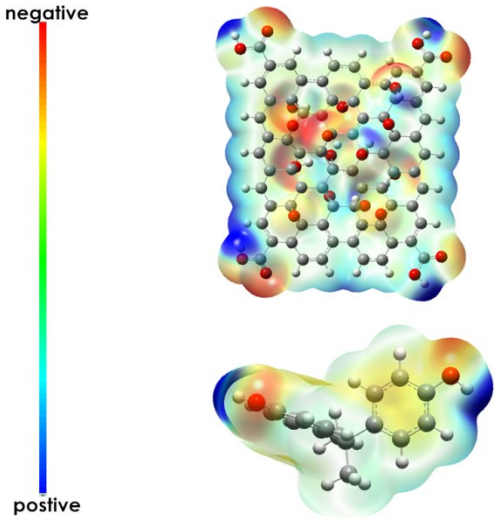
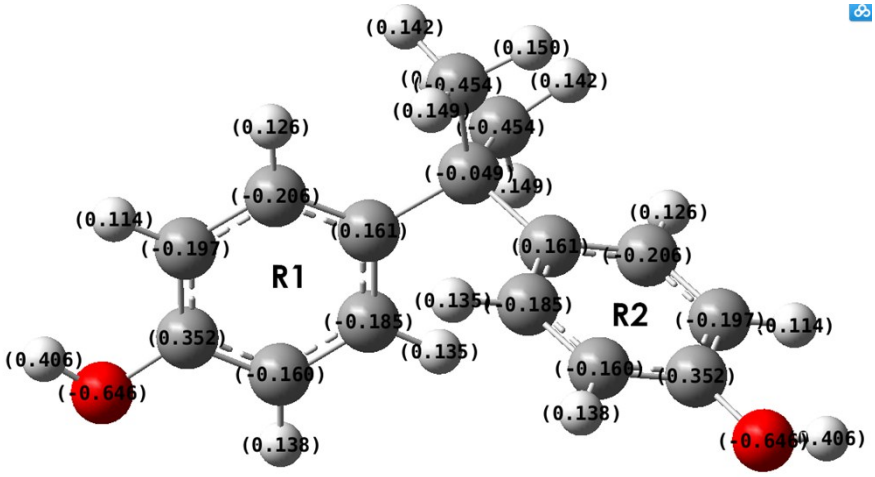


Fig. S4 Surface electrostatic potentials of GO and BPA.

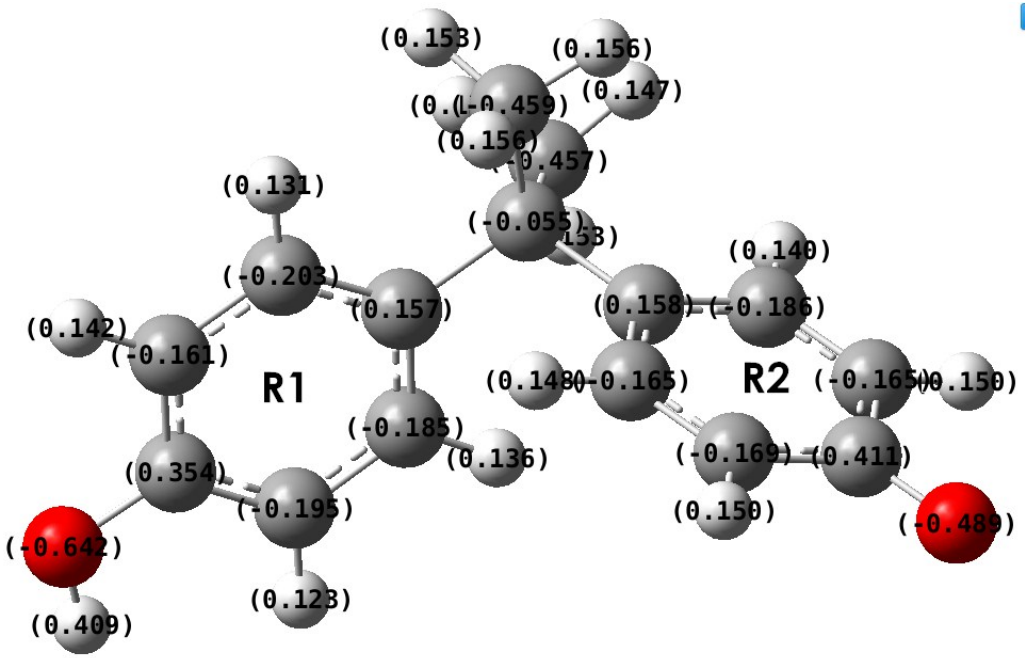
SI6 Mulliken electrons of BPA

System G1



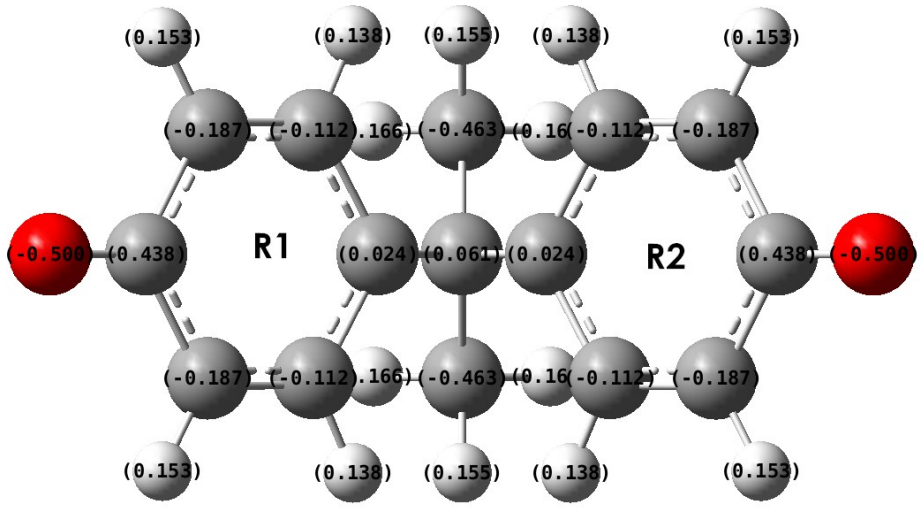
The total Mulliken electrons on benzene ring R1 and R2 of neutral BPA are the same as -0.235 e.

System G2



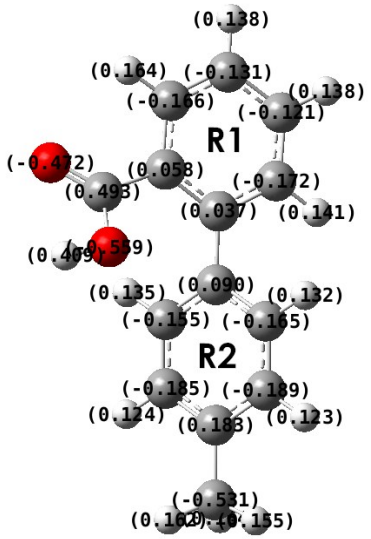
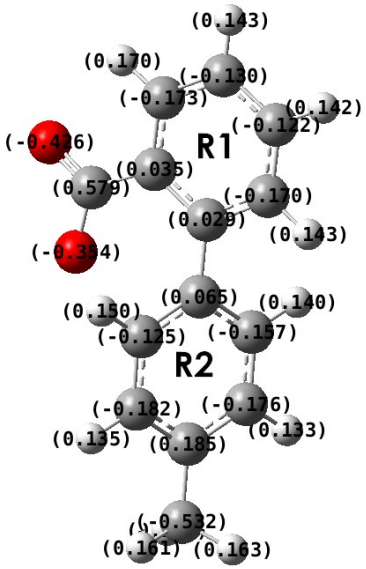
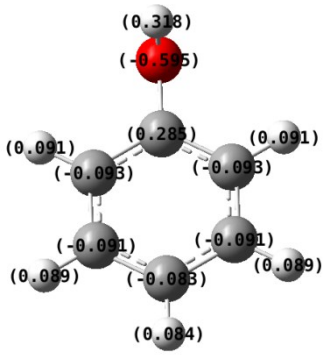
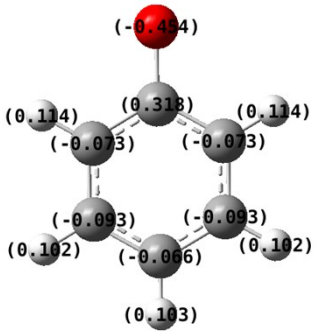
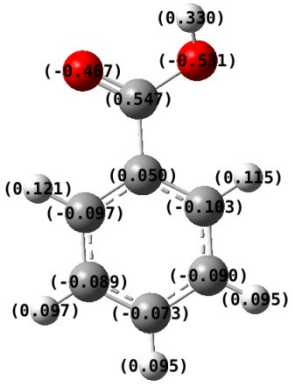
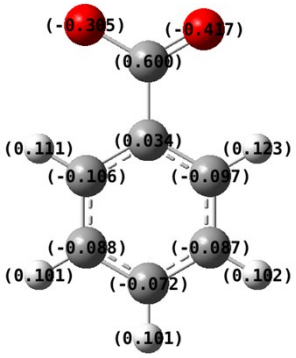
The total Mulliken electrons on benzene ring R1 and R2 of BPA with one ionized hydroxy are -0.233 e and -0.116 e.

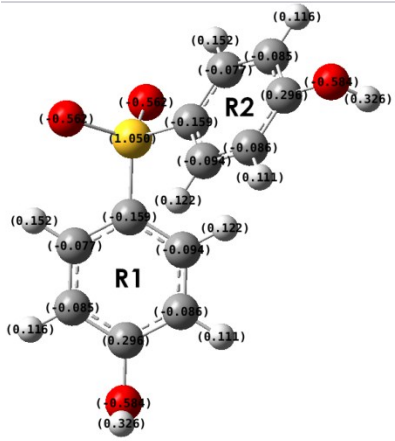
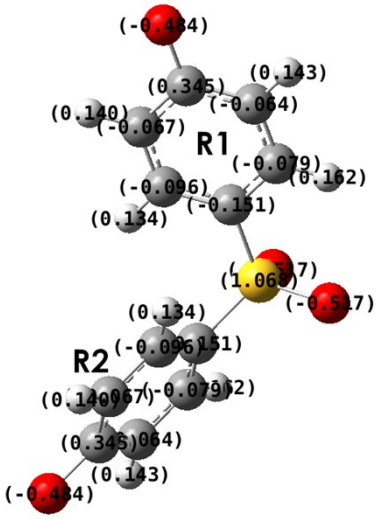
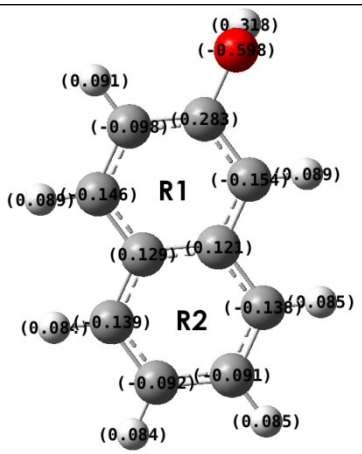
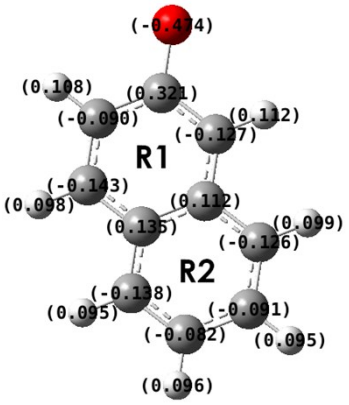
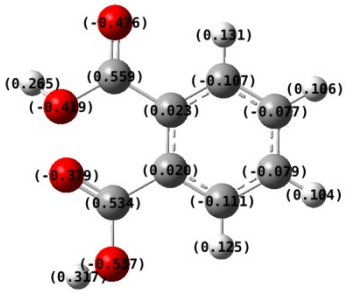
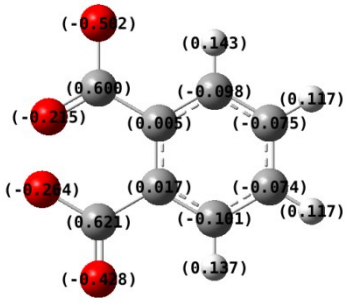
System G3

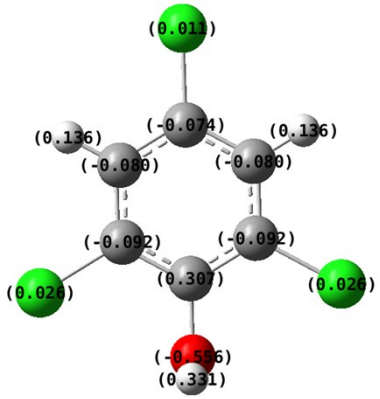
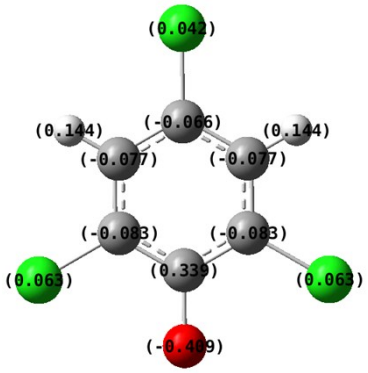
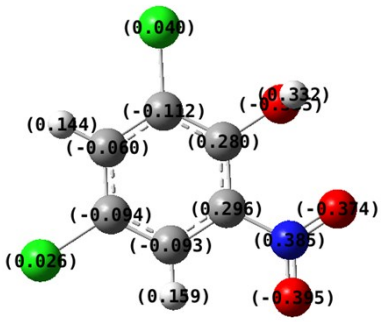
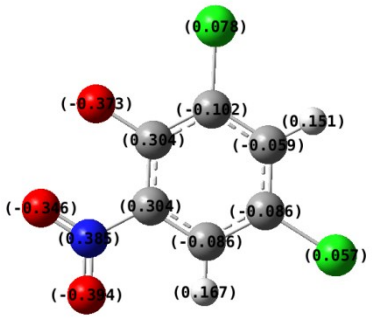


The total Mulliken electrons on benzene ring Ⅰ and Ⅱ of neutral BPA are the same as -0.136 e.

Table S3 Mulliken electrons of common IOCs under low and high pH conditions

IOC	Low pH	High pH
4'-Methylbiphenyl-2-Carboxylic Acid	 R1: -0.495 e R2: -0.421 e	 R1: -0.531 e R2: -0.390 e
Phenol	 -0.166 e	 -0.732 e
Benzoic Acid	 -0.402 e	 -0.416 e

Bisphenol S	 R1: -0.205 e R2: -0.205 e	 R1: -0.112 e R2: -0.112 e
Naphthol	 R1: 0.135 e R2: -0.210 e	 R1: 0.208 e R2: -0.190 e
Phthalic Acid	 -0.331 e	 -0.326 e

2,4,6-Trichlorophenol	 -0.111 e	 -0.047 e
2,4-Dichloro-6-Nitrophenol	 0.217 e	 0.275 e

SI 7 Mulliken electrons of GO under low and high pH regimes

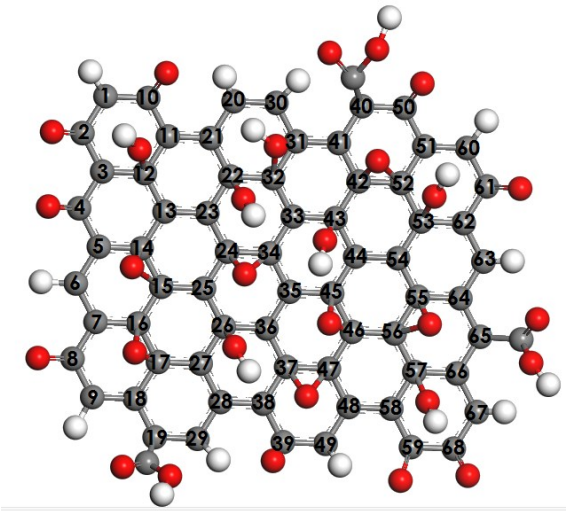


Fig S5. The model of GO and the number of carbon atoms on benzene rings

Table S4 Mulliken Electron Distributions of GO with All Carboxyl Groups Protonated

Number	1-9	10-19	20-29	30-39	40-49	50-59	60-68	
Mulliken Electron (e)	-0.173	0.405	-0.222	-0.126	-0.063	0.382	-0.223	Total Mulliken Electron 5.774e
	0.355	0.009	0.124	0.037	0.157	0.096	0.404	
	-0.012	0.145	0.022	0.126	0.088	0.109	0.010	
	0.326	0.030	0.210	0.074	0.138	0.127	-0.206	
	0.062	0.140	0.145	0.107	0.109	0.132	0.145	
	-0.155	0.140	0.106	0.098	0.054	-0.017	-0.025	
	0.061	0.225	0.145	0.026	0.216	0.290	0.087	
	0.384	-0.003	0.108	0.053	-0.027	0.061	-0.260	
	-0.222	0.120	0.092	-0.029	0.094	0.076	0.387	
		0.031	-0.247	0.489	-0.151	0.376		

Table S5 Mulliken Electron Distributions of GO with One Carboxyl Groups Deprotonated

Number	1-9	10-19	20-29	30-39	40-49	50-59	60-68	
Mulliken Electron (e)	-0.182	0.411	-0.208	-0.126	-0.064	0.383	-0.226	Total Mulliken Electron 5.825e
	0.355	-0.010	0.111	0.032	0.160	0.097	0.404	
	-0.013	0.153	0.048	0.129	0.087	0.108	0.012	
	0.334	0.033	0.208	0.079	0.142	0.129	-0.209	
	0.090	0.139	0.139	0.110	0.110	0.131	0.146	
	-0.161	0.135	0.120	0.099	0.050	-0.019	-0.024	
	0.082	0.227	0.141	0.014	0.226	0.298	0.086	
	0.387	-0.003	0.110	0.059	-0.022	0.052	-0.258	
	-0.229	0.132	0.092	-0.022	0.099	0.098	0.388	
		0.013	-0.241	0.489	-0.205	0.372		

Table S6 Mulliken Electron Distributions of GO with Two Carboxyl Groups Deprotonated

Number	1-9	10-19	20-29	30-39	40-49	50-59	60-68	
Mulliken Electron (e)	-0.170	0.410	-0.180	-0.141	-0.051	0.384	-0.218	Total Mulliken Electron 5.955e
	0.355	0.010	0.116	0.054	0.154	0.093	0.406	
	-0.010	0.144	0.026	0.119	0.089	0.107	0.009	
	0.331	0.038	0.210	0.074	0.140	0.128	-0.196	
	0.068	0.141	0.145	0.109	0.106	0.137	0.139	
	-0.153	0.140	0.106	0.101	0.056	-0.015	-0.021	
	0.068	0.223	0.144	0.024	0.217	0.288	0.078	
	0.386	-0.001	0.109	0.057	-0.022	0.056	-0.221	
	-0.218	0.120	0.095	-0.026	0.097	0.092	0.388	
		0.032	-0.245	0.492	-0.149	0.383		

Table S7 Mulliken Electron Distributions of GO with All Carboxyl Groups Protonated

Mulliken Electron Distributions of GO with All Carboxyl Groups Protonated								
Number	**1-9**	**10-19**	**20-29**	**30-39**	**40-49**	**50-59**	**60-68**	
Mulliken Electron (e)	-0.179	0.413	-0.205	-0.150	-0.037	0.384	-0.222	Total Mulliken Electron 5.898e
	0.355	-0.011	0.113	0.069	0.142	0.096	0.406	
	-0.012	0.153	0.050	0.123	0.091	0.107	0.015	
	0.335	0.033	0.208	0.077	0.142	0.127	-0.207	
	0.093	0.138	0.140	0.111	0.110	0.132	0.153	
	-0.160	0.135	0.121	0.098	0.050	-0.019	-0.045	
	0.084	0.226	0.141	0.013	0.226	0.297	0.108	
	0.388	-0.002	0.111	0.059	-0.019	0.050	-0.269	
	-0.227	0.132	0.092	-0.020	0.099	0.101	0.397	
		0.014	-0.241	0.491	-0.204	0.378		

SI8 Adsorption of 4'-Methylbiphenyl-2-Carboxylic Acid (MCA) on GO

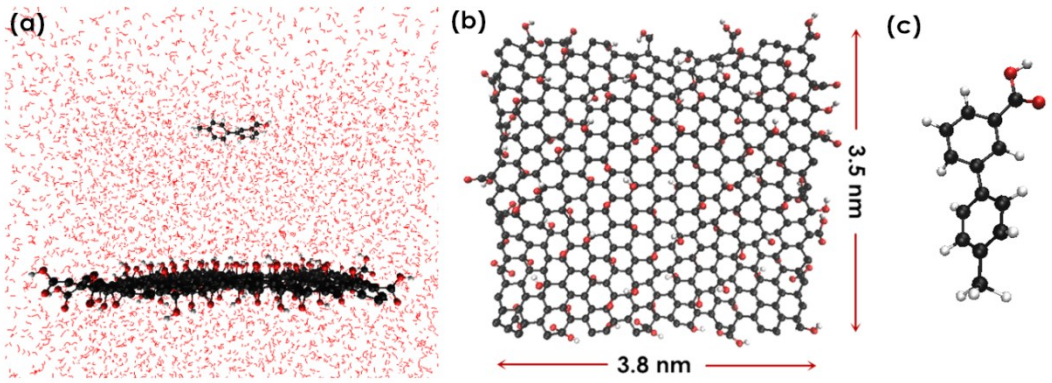


Fig. S5 Setup of the simulation system. (a) The sideview of one example system (H in white, O in red, and C in black). The smaller molecule represents MCA, the larger molecule represents GO, and the tiny redlines represent water molecules. The initial distance between GO and BPA was 2 nm. (b) The dimension of GO. (c) The model of MCA.

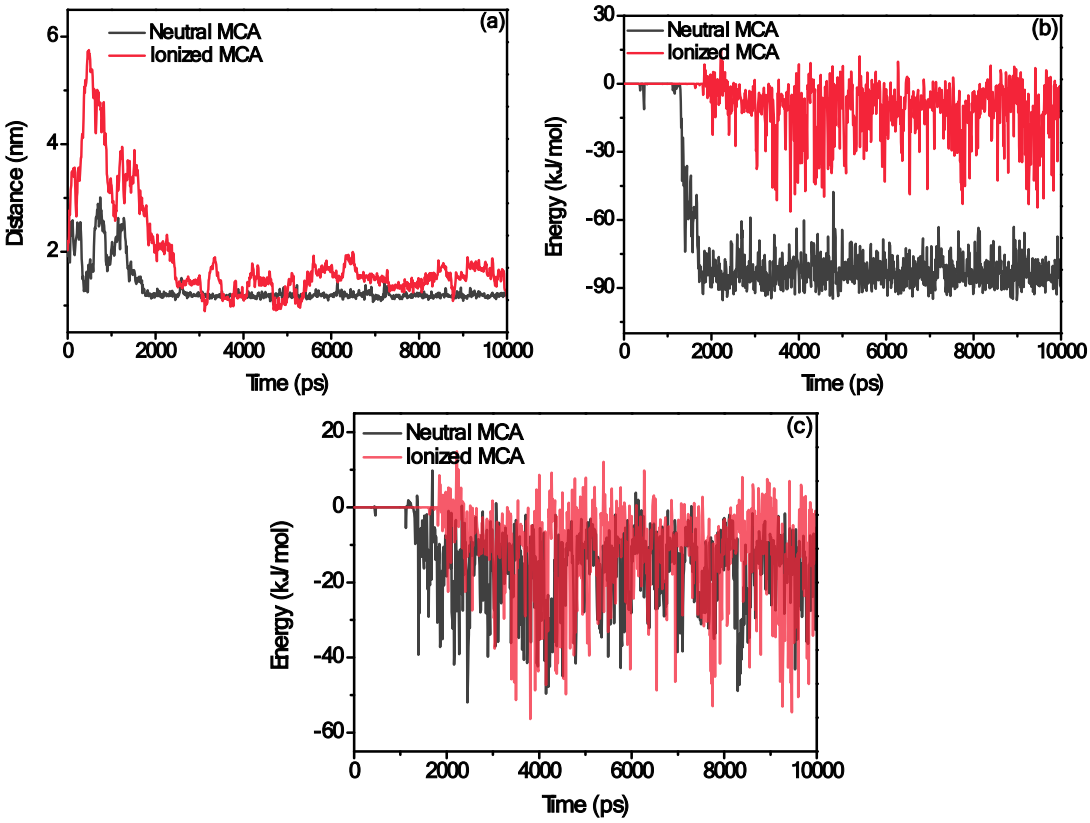


Fig. S6 Molecular dynamics simulation results. (a) Distance between GO and BPA. The initial distance was 2.0 nm. (b) L-J potential energy between GO and MCA. (c) Electrostatic potential energy between GO and MCA. The positive values imply electrostatic repulsions.

The above figures indicated that at high pH, longer time was needed for MCA to adsorbed on GO.

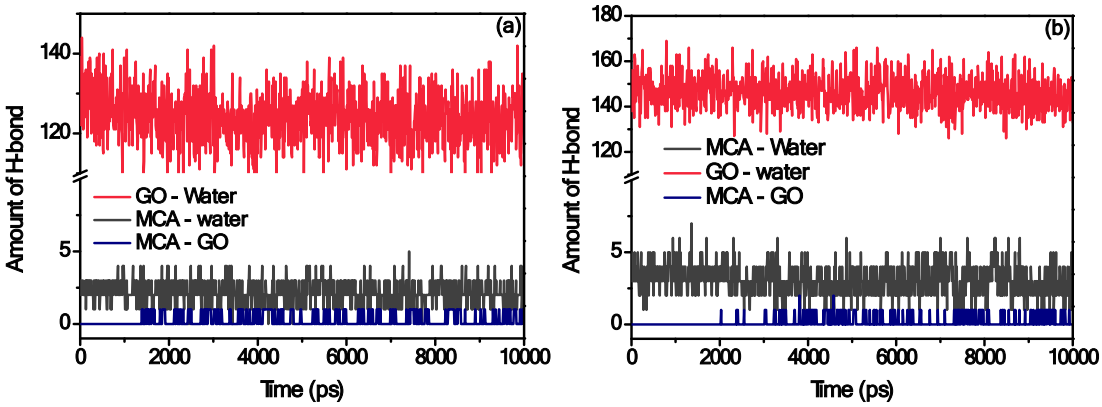


Fig. S7 Amount of different kinds of H-bonds formed under low and high pH conditions. (a) Amount GO…water, MCA…water and MCA…GO H-bond formed under low pH condition. (a) Amount GO…water, MCA…water and MCA…GO H-bond formed under high pH condition.

At high pH, more H-bonds formed between MCA and GO, which decreased the adsorption efficiency. More GO…water and MCA-water H-bonds appeared than that of MCA…GO H-bond, indicating the water mediated H-bond acted as a steering force in the adsorption process.

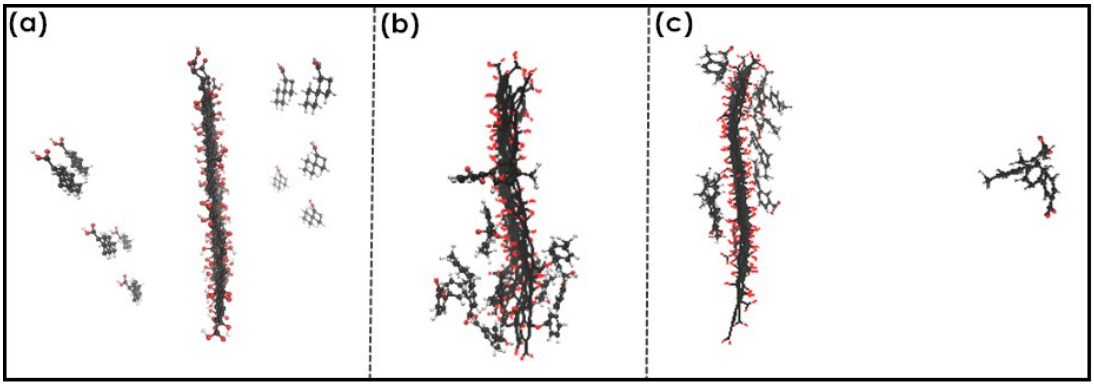


Fig. S8 Amount of MCA adsorbed onto

GO after 20ns. (a) The initial distribution of 10 MCAs around GO. (b) After 20 ns of simulation, 10 MCAs adsorbed on GO at under low pH conditions. (c) After 20 ns of simulation, 8 MCAs adsorbed on GO at under high pH conditions.

The results indicated under high pH, the adsorption capacity of MCA on GO decreased.

SI9 Force Field Parameters

```
[ defaults ]
1                    3                    yes                  0.5       0.5
[ atomtypes ]
CB     6       12.01100       0.000          A      3.55000e-01    2.92880e-01
HA     1        1.00800       0.06           A      2.42000e-01    1.25520e-01
CH     6       12.01100      -0.12           A      3.55000e-01    2.92880e-01
HW     1        1.00800       0.41           A      0.00000e+00    0.00000e+00
OW     8       15.99940      -0.82           A      3.16557e-01    6.50194e-01
CT     6       12.01100       0.140          A      3.50000e-01    2.76144e-01
OS     8       15.99940      -0.280          A      2.90000e-01    5.85760e-01
CF     6       12.01100       0.150          A      3.55000e-01    2.92880e-01
OH     8       15.99940      -0.585          A      3.07000e-01    7.11280e-01
HO     1        1.00800       0.435          A      0.00000e+00    0.00000e+00
C      6       12.01100       0.520          A      3.75000e-01    4.39320e-01
OH2    8       15.99940      -0.530          A      3.00000e-01    7.11280e-01
O_3    8       15.99940      -0.440          A      2.96000e-01    8.78640e-01
HO2    1        1.00800       0.450          A      0.00000e+00    0.00000e+00
 [ bondtypes ]
   CB      CB       1      0.14000     392459.2
   CB      CH       1      0.14000     392459.2
   CH      CH       1      0.14000     392459.2
   CH      HA       1      0.10800     307105.6
   HW      OW       1      0.09572     502080.0
   CB      CT       1      0.15100     265265.6
   CB      C        1      0.14000     392459.2
   CT      OS       1      0.14100     267776.0
   C       O_3      1      0.12290     476976.0
   C       OH2      1      0.13640     376560.0
   HO      OH       1      0.09450     462750.4
   CF      OH       1      0.13640     376560.0
   CF      CB       1      0.14000     392459.2
   CT      CT       1      0.15290     224262.4
   CB      OH       1      0.13640     376560.0
   CT      CF       1      0.15100     265265.6
   CF      CF       1      0.14000     392459.2
   HO2     OH2      1      0.09450     462750.4

[ angletypes ]
   CB      CB      CB       1     120.000      527.184
   CB      CB      CH       1     120.000      527.184
   CH      CH      CB       1     120.000      527.184
   CB      CH      HA       1     120.000      292.880
   CH      CH      HA       1     120.000      292.880
```

HW OW HW 1 109.500 627.600
CT OS CT 1 109.500 502.080
CB CB CT 1 120.000 585.760
CB CT CT 1 114.000 527.184
CB CT OS 1 109.500 418.400
CB C O_3 1 120.400 669.440
CB CB C 1 120.000 711.280
CB C OH2 1 120.000 585.760
O_3 C OH2 1 121.000 669.440
CF OH HO 1 113.000 292.880
CB CF OH 1 120.000 585.760
CB CF CB 1 120.000 527.184
CB CB CF 1 120.000 527.184
CB C OH 1 120.000 585.760
CT OH HO 1 113.000 292.880
CF CB CT 1 119.700 585.760
CB CT CB 1 109.500 334.720
CT CT OS 1 109.500 418.400
CB OH HO 1 113.000 292.880
CB CB OH 1 120.000 585.760
CF CB CF 1 120.000 527.184
CT CF OH 1 120.000 585.760
CB CF CT 1 120.000 585.760
CF CT OS 1 109.500 418.400
CF CT CT 1 114.000 527.184
CB CT CF 1 109.500 334.720
CF CF OH 1 120.000 585.760
CF CF CB 1 120.000 527.184
CT CF CF 1 120.000 585.760
CF CB C 1 120.000 711.280
CT CB C 1 119.700 585.760
CT CB CT 1 116.000 585.760
CT CB CB 1 120.000 585.760
CT CF CT 1 120.000 585.760
C OH2 HO2 1 113.000 292.880

[dihedraltypes]

C CB CB CB 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
CH CB CB CH 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
CB CB CB CH 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
CB CH CH CB 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
CB CB CH CH 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
HA CH CH HA 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
HA CH CB CB 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000
HA CH CH CB 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000

CB	CB	CB	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CH	CB	CB	CH	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	CB	CH	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CH	CH	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	CH	CH	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
HA	CH	CH	HA	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
HA	CH	CB	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
HA	CH	CH	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CT	OS	CT	3	1.71544	2.84512	1.04600	-5.60656	0.00000	0.00000
CB	CB	CT	OS	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CB	CT	CT	OS	3	2.87441	0.58158	2.09200	-5.54799	0.00000	0.00000
CB	OS	CT	CT	3	1.71544	2.84512	1.04600	-5.60656	0.00000	0.00000
CB	OS	CT	CB	3	1.71544	2.84512	1.04600	-5.60656	0.00000	0.00000
CB	CB	CB	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CT	CB	CT	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CB	CB	CT	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CB	CT	CT	CB	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CB	C	OH	HO	3	29.28800	-8.36800	-20.92000	0.00000	0.00000	0.00000
HO	OH	C	O_3	3	23.01200	0.00000	-23.01200	0.00000	0.00000	0.00000
CB	CB	C	O_3	3	8.78640	0.00000	-8.78640	0.00000	0.00000	0.00000
CB	CB	C	OH	3	8.78640	0.00000	-8.78640	0.00000	0.00000	0.00000
CB	CB	CB	C	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CF	OH	HO	3	7.03749	0.00000	-7.03749	0.00000	0.00000	0.00000
CB	CB	CB	OH	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	CB	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	CF	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	CT	CB	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CF	CB	CT	CT	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CT	CB	CB	CT	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CF	CB	CT	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CT	CB	CF	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CT	CB	CB	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CF	CB	CB	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	C	OH2	3	8.78640	0.00000	-8.78640	0.00000	0.00000	0.00000
CB	CB	OH	HO	3	7.03749	0.00000	-7.03749	0.00000	0.00000	0.00000
CT	CF	OH	HO	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CT	CF	CB	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000 ;
CT	CF	CB	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000 ;
CB	CT	CF	CB	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CB	CF	CB	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CF	CT	OS	CT	3	1.71544	2.84512	1.04600	-5.60656	0.00000	0.00000
CB	CB	CT	CF	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CF	CT	CT	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CF	CT	CT	3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

CT	CF	CF	CB	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CT	CF	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
CB	CB	CF	CF	3	30.33400	0.00000	-30.33400	0.00000	0.00000	0.00000
C	CB	CF	CB	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CF	CB	C	O_3	3	8.78640	0.00000	-8.78640	0.00000	0.00000	0.00000
CB	CT	CB	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CT	CT	CT	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CT	CT	CB	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CB	CT	CT	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000
CT	CT	OS	CT	3	1.71544	2.84512	1.04600	-5.60656	0.00000	0.00000
CB	C	OH2	HO2	3	29.28800	-8.36800	-20.92000	0.00000	0.00000	0.00000
CB	CT	CF	CT	3	44.97800	0.00000	-44.97800	0.00000	0.00000	0.00000

References

1. Jennings, W. B.; Farrell, B. M.; Malone, J. F., Attractive intramolecular edge-to-face aromatic interactions in flexible organic molecules. *Accounts. Chem. Res.* **2001,***34*, (11), 885-894.