Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary data

Synthesis, DFT, molecular dynamics, and Monte Carlo simulation of novel thiourea derivative with extraordinary inhibitive properties for mild steel in 0.5 M sulphuric acid

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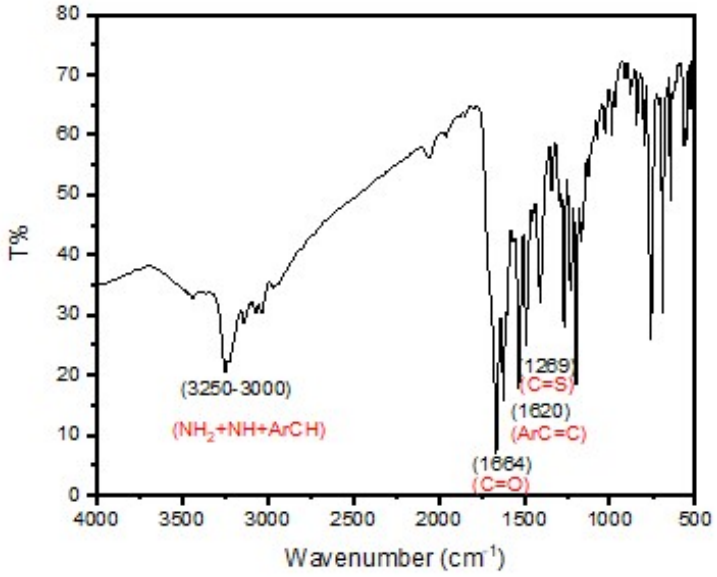

Fig. S1 FT-IR spectrum of inhibitor 2-amino-*N*-(phenylcarbamothioyl) benzamide.

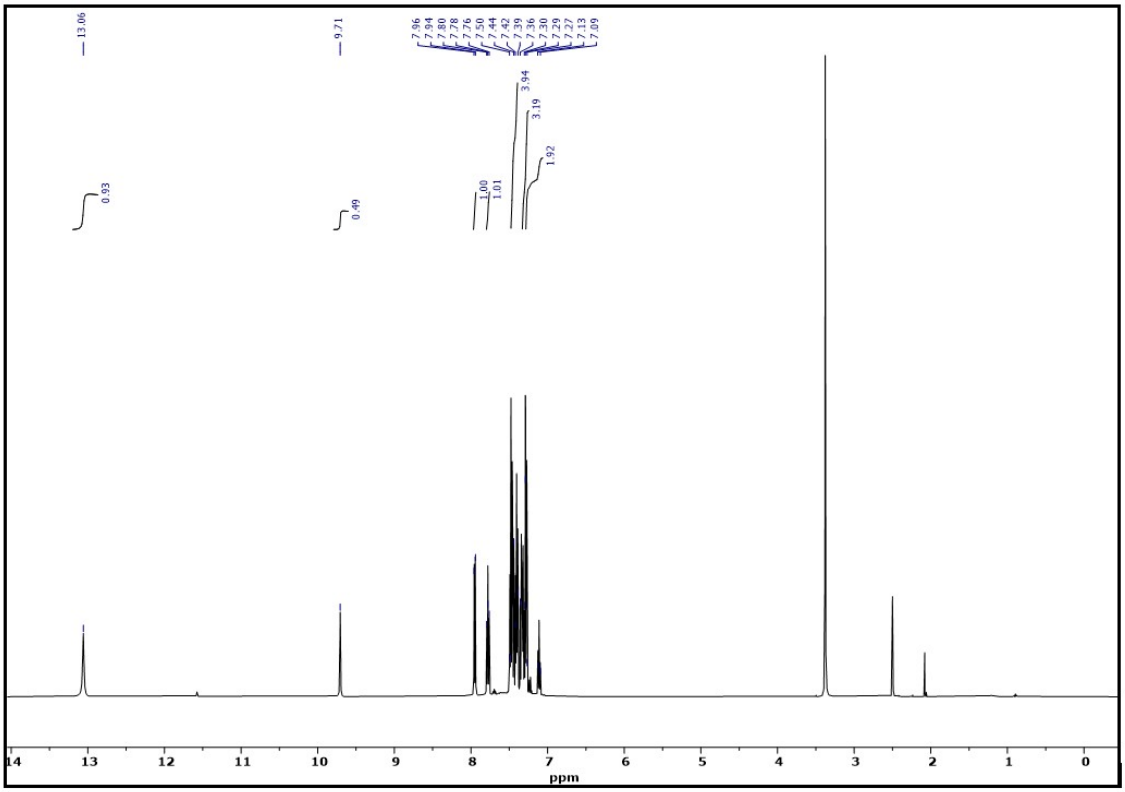

Fig. S2 ^{1}H-NMR (DMSO-d_6) spectrum of 2-amino-*N*-(phenylcarbamothioyl)benzamide.

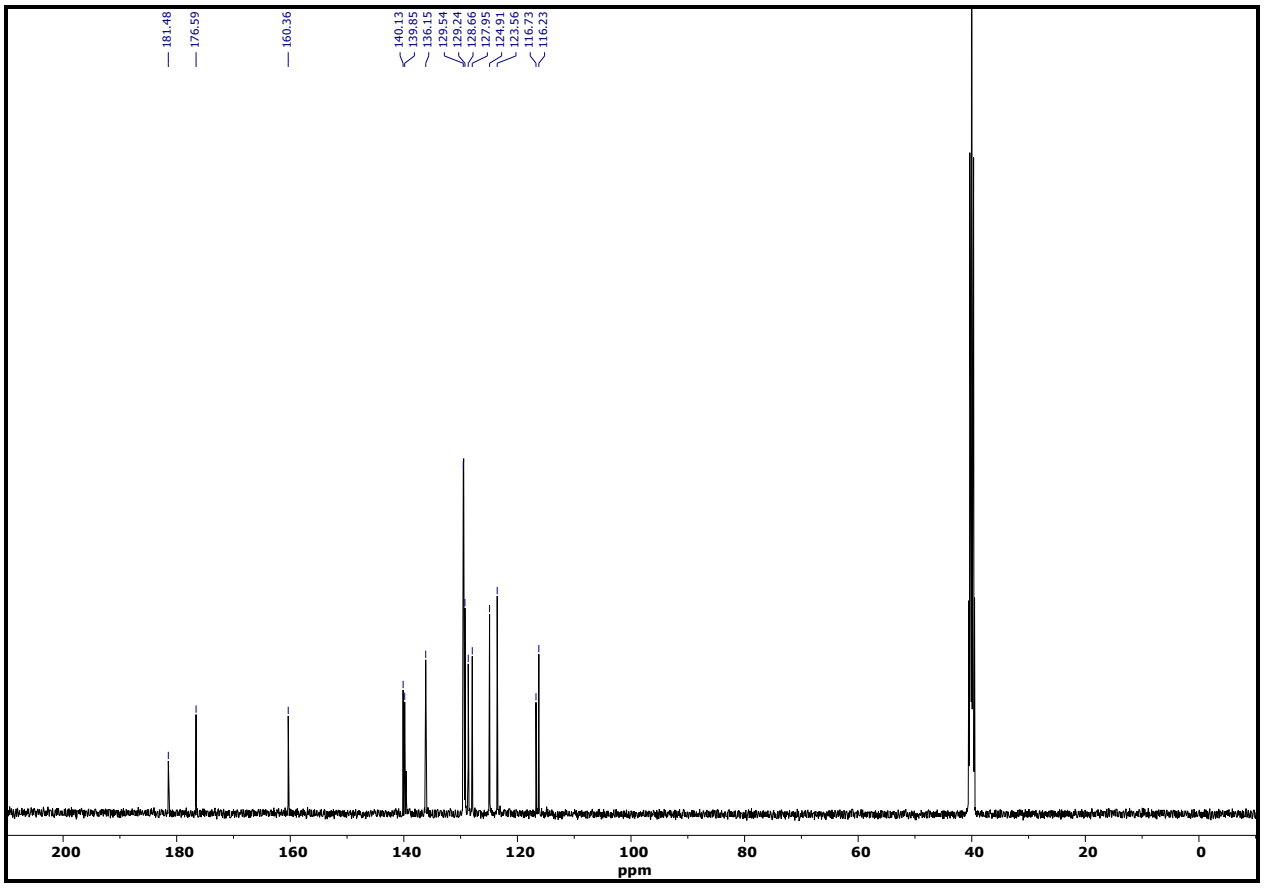

Fig. S3 ^{13}C-NMR (DMSO-d_6) spectrum of 2-amino-*N*-(phenylcarbamothioyl)benzamide.

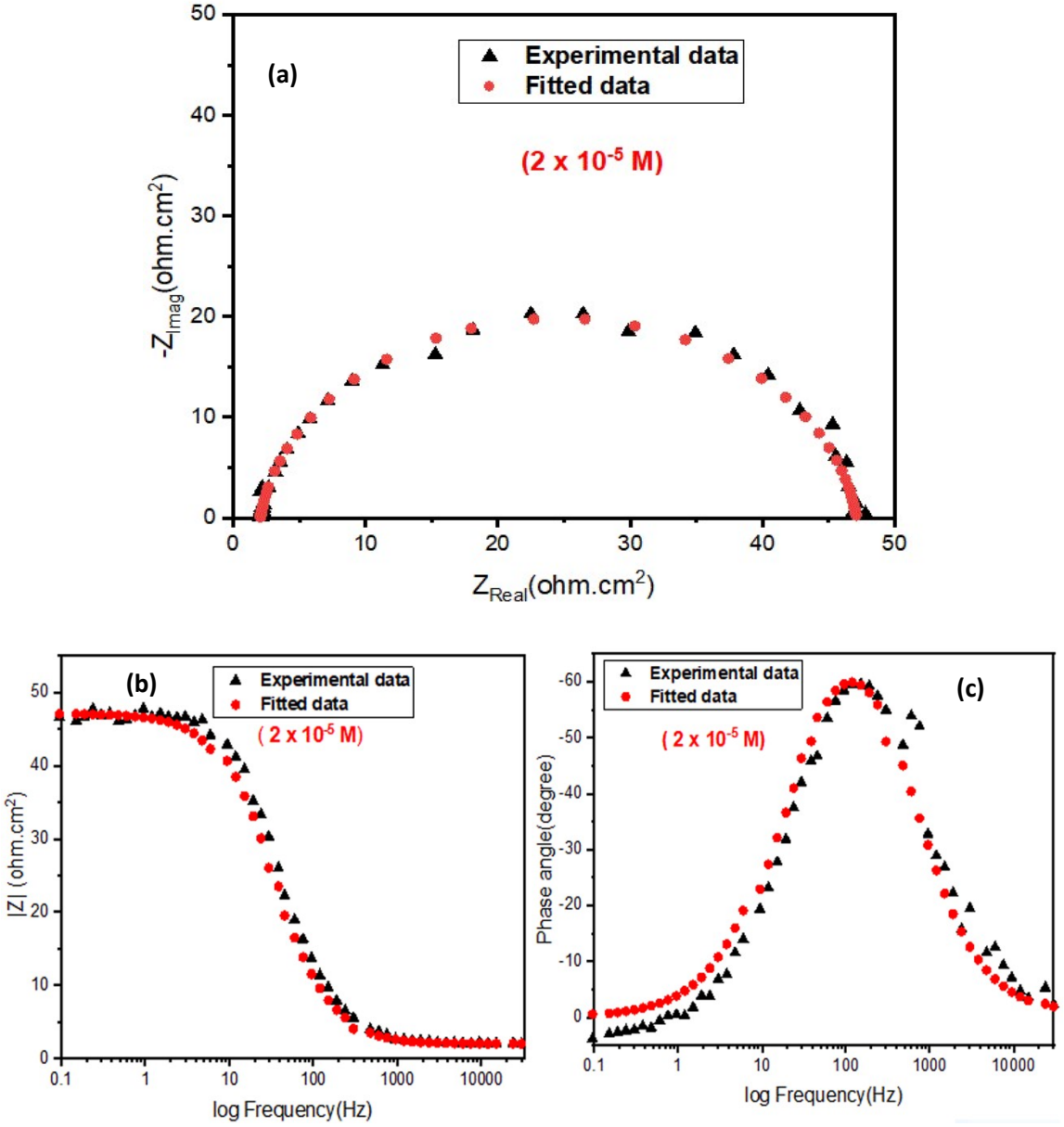

Fig.S4 (a) Experimental and fitted Nyquist plots for MS in the presence of 2 x 10^{-5} M of APCB**. (b)** Experimental and fitted Bode plots for MS in the presence of 2 x 10^{-5} M of APCB**. (c)** Experimental and fitted phase angle plots for MS in the presence of 2 x 10^{-5} M of APCB

$$\log\left(\frac{\theta}{1-\theta}\right) = logk^{/} + y.logC \qquad k_{ads} = k^{/\frac{1}{y}} \qquad \textbf{(Eq.S1)}$$

$$\log\left(\frac{\theta}{C}\right) = logx.k_{ads} + xlog(1-\theta) \qquad \textbf{(Eq.S2)}$$

$$\theta = \frac{1}{f}lnk_{ads} + \frac{1}{f}lnC \qquad \textbf{(Eq.S3)}$$

Table S1. Langmuir adsorption isotherm parameters.

T (K)	K_{ads}	$-\Delta G^{0}_{ads}$ (kJ/mol)	R^2
303	115207	39.45	0.9983
313	253807	42.81	0.9999
323	277777	44.42	0.9997
333	306654	46.70	0.9998

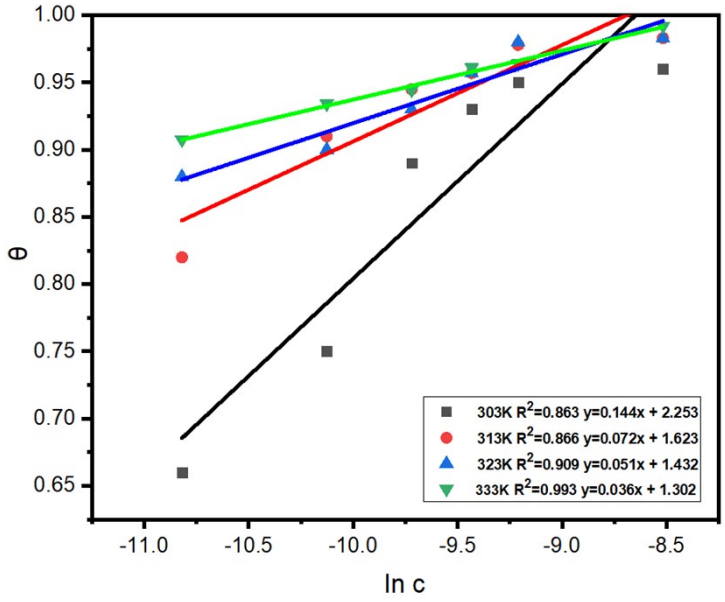

Fig. S5 Temkin isotherm for adsorption of APCB on MS in 0.5M H_2SO_4.

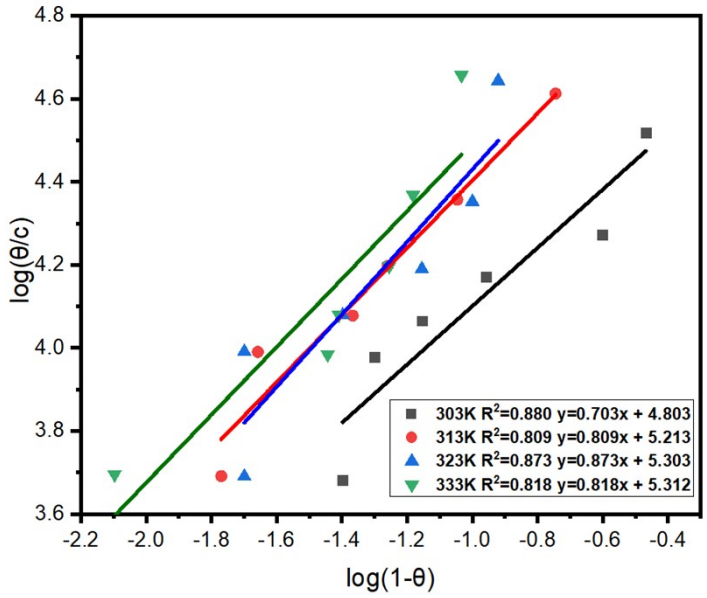

Fig. S6 Flory-Huggins isotherm for adsorption of APCB on steel in 0.5M H_2SO_4.

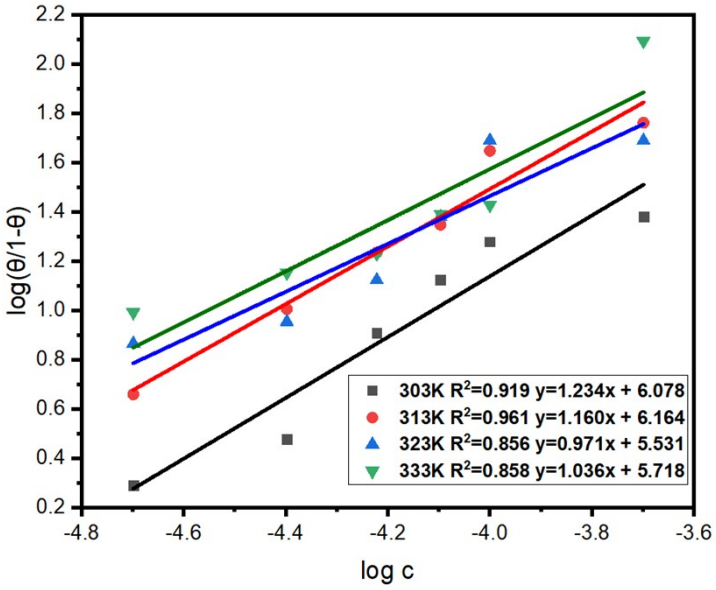

Fig. S7 Kinetic-thermodynamic isotherm for adsorption of APCB on steel in 0.5M H_2SO_4.

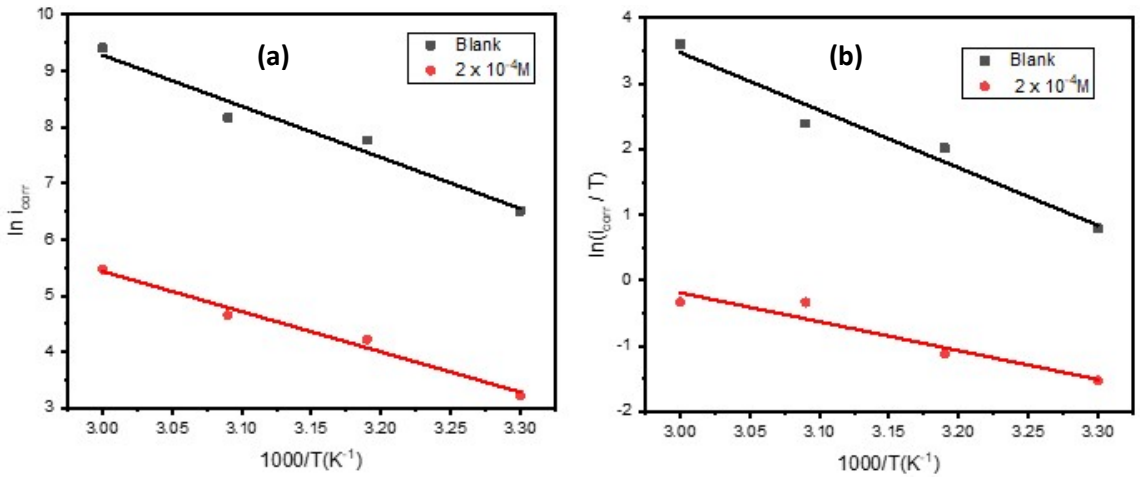

Fig. S8 (a) Arrhenius plot for MS in 0.5M H_2SO_4 in the absence and presence of various concentrations of APCB. **(b)** Eyring plot for MS in 0.5M H_2SO_4 in the absence and presence of various concentrations of APCB.

Table S2. Activation parameters obtained from Arrhenius equation and Erying equation.

APCB Concentration(M)	**E_a (kJ/mol)**	**$\Delta H^{\neq}$ (kJ/mol)**	**$\Delta S^{\neq}$ (J/K.mol)**
-	76.00	73.76	53.10
2 x 10^{-4}	57.87	55.20	-19.44

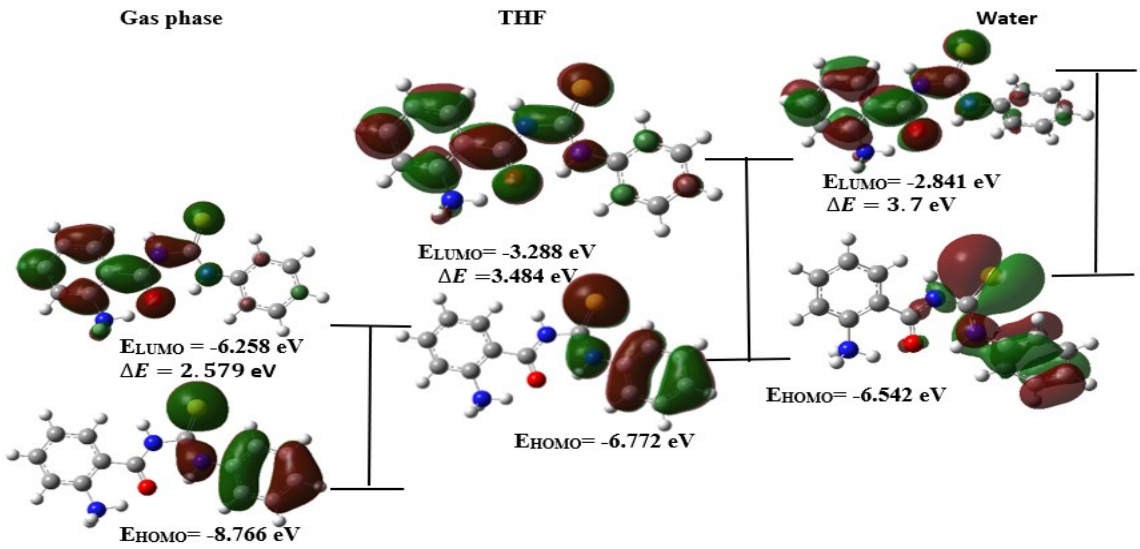

Figure S9. Energies of HOMO and LUMO levels of protonated **APCB** in the gas phase, THF, and water.

Table S3. Mulliken charges and Fukui functions of different atoms in neutral APCB in the gas phase.

Atom	q_{k+1}	q_k	q_{k-1}	f^+_k	f^-_k	Δf
C1	0.857	0.804	0.716	0.052	0.088	-0.035
C2	-0.167	-0.191	-0.243	0.023	0.052	-0.028
C3	-0.242	-0.284	-0.281	0.042	-0.003	0.045
C4	-0.132	-0.139	-0.221	0.007	0.081	-0.073
C5	-0.158	-0.221	-0.295	0.063	0.074	-0.011
C6	-0.560	-0.537	-0.472	-0.022	-0.065	0.042
N11	-0.440	-0.527	-0.565	0.087	0.037	0.049
C14	0.158	0.165	0.133	-0.006	0.031	-0.037
O15	-0.529	-0.549	-0.651	0.020	0.101	-0.081
N16	-0.101	-0.111	-0.122	0.011	0.010	0.001
C18	0.057	0.047	0.058	0.009	-0.010	0.019
N19	-0.161	-0.217	-0.233	0.056	0.015	0.040
S20	0.034	-0.148	-0.369	0.182	0.220	-0.038
C22	-0.154	-0.189	-0.229	0.034	0.040	-0.005
C23	-0.314	-0.329	-0.329	0.011	0.003	0.007
C24	0.326	0.281	0.256	0.044	0.024	0.019
C25	-0.246	-0.238	-0.209	-0.008	-0.029	0.020
C27	-0.168	-0.192	-0.222	0.023	0.029	-0.005
C28	-0.118	-0.179	-0.227	0.060	0.048	0.011

Table S4. Quantum chemical parameters for protonated **APCB** in the gas phase, THF, and water solvents.

Parameter	Gas-phase	THF	Water
E_{HOMO} (eV)	-8.766	-6.772	-6.542
E_{LUMO} (eV)	-6.186	-3.288	-2.841
ΔE (eV)	2.579	3.484	3.700
η (eV)	1.289	1.742	1.850
χ (eV)	7.476	5.030	4.692
σ $(eV)^{-1}$	0.775	0.574	0.540
$\mu(D)$	15.335	20.317	21.702
ΔN	-0.184	0.560	0.623
ΔG_{Solv} (kJ/mol)	-	170.054	-36.74
$\langle\alpha\rangle$ (au)	233.044	293.159	300.264
Molecular Volume ($Å^3$)	791.230	792.450	793.320

Table S5. Parameters obtained from Monte Carlo simulation.

# molecules	Total Energy (kcal/mol)	Adsorption Energy (kcal/mol)	Deformation Energy (kcal/mol)	Rigid adsorption Energy (kcal/mol)
1	-119.379	-67.170	-0.830	-66.170
2	-239.024	-134.569	-1.324	-133.244
3	-358.487	-201.805	-2.510	-199.295
4	-478.932	-270.023	-2.991	-267.031
5	-599.078	-377.941	-2.651	-335.290
6	-716.635	-403.271	-3.380	-399.891

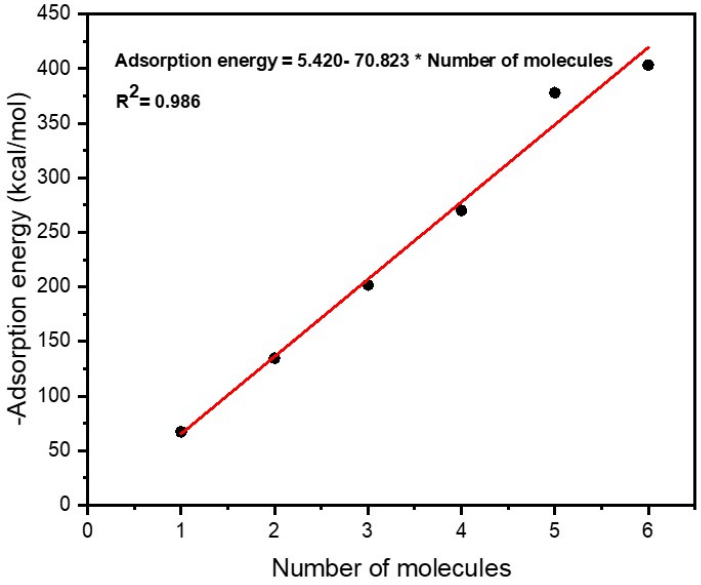

Fig. S10 Relation between the adsorption energy and number of molecules obtained from MC simulations.