Potential Energy Surface and Binding Energy in External Electric Field: Modulation of Anion–π Interactions for Graphene–Based Receptors

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Gauge dependency of dipole moment in charge systems

Gauge dependency of dipole moment in charged systems is a simple fact that could be understood based on the following justification.

For measuring the dipole moment one may employ the following equation:

$$\boldsymbol{\mu} = \sum_{A=i}^{A=N} Z(A)[\boldsymbol{R}(A) - \boldsymbol{R}_0] - \int \rho(r)(\boldsymbol{r} - \boldsymbol{R}_0)dr$$

In this equation *A* refers to atom *A* in an *N* atomic system, *Z(A)* represents the atomic numbers and R_0 denotes the spatial distance with respect to an arbitrary gauge origin like 0. A similar equation can be written for dipole moment with respect to another arbitrary gauge origin in a position like 1.

$$\boldsymbol{\mu}_1 = \sum_{A=i}^{A=N} Z(A)[\boldsymbol{R}(A) - \boldsymbol{R}_1] - \int \rho(r)(\boldsymbol{r} - \boldsymbol{R}_1)dr$$

If one subtracts the latter equation form the former, it results in:

$$\boldsymbol{\mu}_1 - \boldsymbol{\mu} = \sum_{A=i}^{A=N} Z(A)[\boldsymbol{R}_0 - \boldsymbol{R}_1] - \int \rho(r)(\boldsymbol{R}_0 - \boldsymbol{R}_1)dr = (\boldsymbol{R}_0 - \boldsymbol{R}_1)\{\sum_{A=i}^{A=N} Z(A) - \int \rho(r)dr\}$$

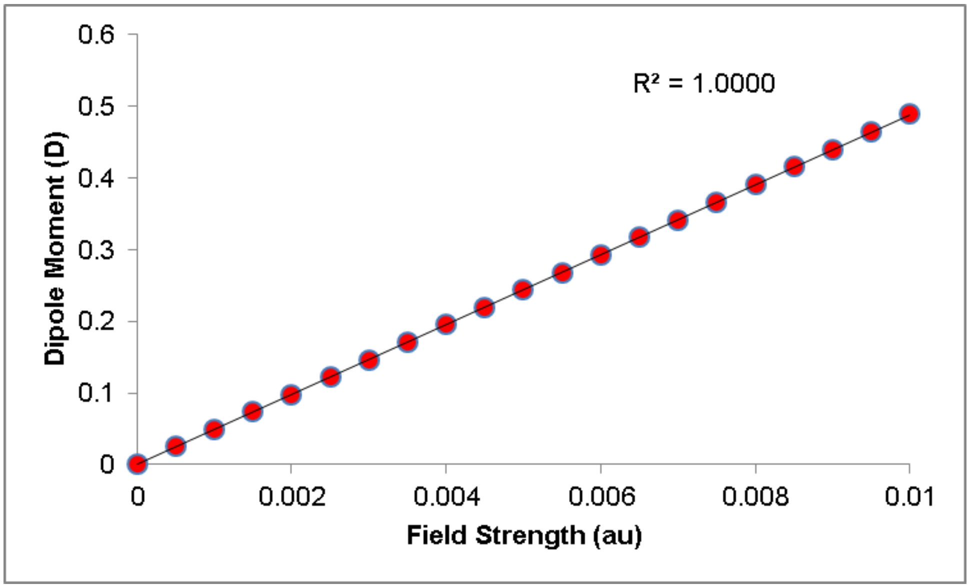
The right–hand–side expression represents the charge of the molecule, Q_{mol}, multiplied by the distance of two gauge origins.

$$(\boldsymbol{R}_0 - \boldsymbol{R}_1)\{\sum_{A=i}^{A=N} Z(A) - \int \rho(r)dr\} = (\boldsymbol{R}_0 - \boldsymbol{R}_1)\, Q_{mol}$$

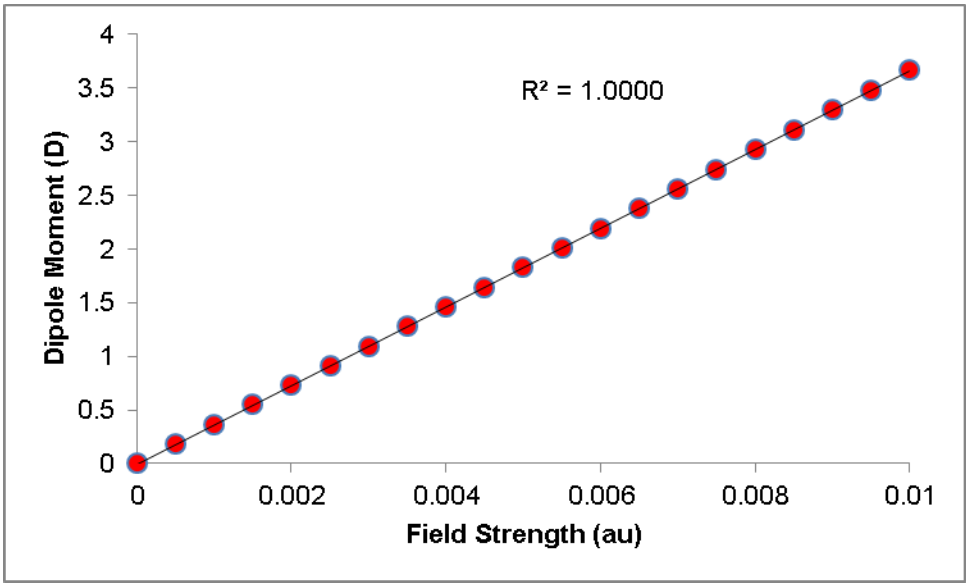
Evidently, the dipole moments will be the same if and only if the molecular charge is zero; unless, the dipole moment will be gauge–dependent. The gauge dependency of dipole moment in turn triggers the gauge dependency of the total energy in the EEF. Based on the equation (1) in the main text it is evident that changing the gauge origin will change total energy according to the following equation.

$$\Delta E = (\boldsymbol{R}_0 - \boldsymbol{R}_1)\, Q_{mol}.\boldsymbol{F}$$

Nevertheless, in spite of gauge dependency of the total energy, the binding energy as the energy difference between building blocks of each species can be determined. The only point for measuring the binding energy is that the energy of all ionic building blocks should be determined in the same position relative to the gauge origin in the main compound.

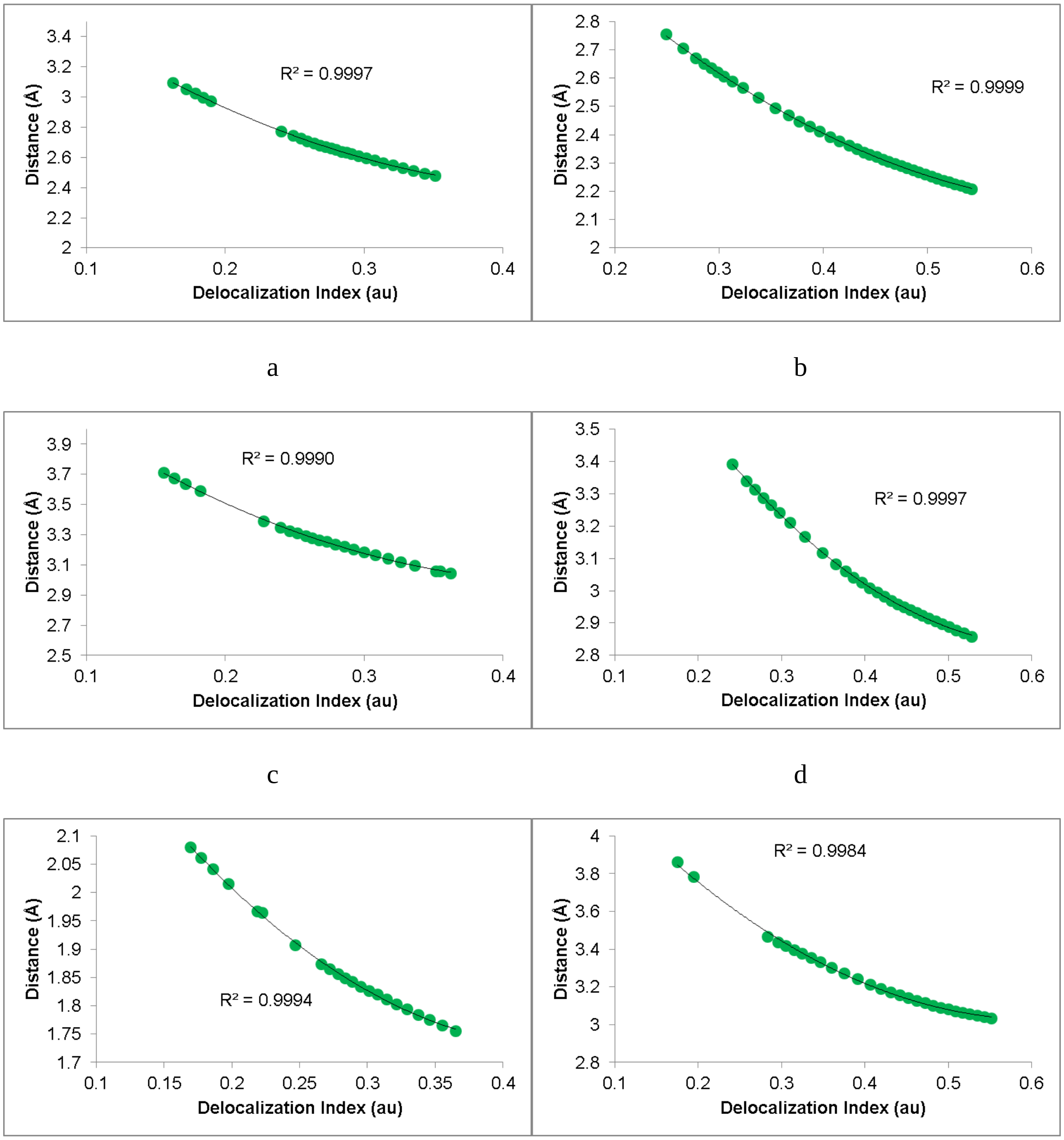


(a)



(b)

Figure S1. The plot of dipole moment in Debye versus electric field strength in atomic units for benzene (a) and coronene (b); the dipole moment increases linearly with increase of the field strength.



a

b

c

d

e

f

Figure S2. The plot of delocalization indices in atomic units versus distance in Angstroms for halide–π complexes; a, b, c, d, e, and f entries represent fluoride-benzene, fluoride-coronene, chloride-benzene, chloride-coronene, bromide-benzene, and bromide-coronene complexes, respectively. Distance and delocalization indices are correlated by a second order polynomial equation.

Table S1. Total electronic energy, dipole moment in z direction, μ_z, and first order polarizability in z direction, α_{zz}, of benzene and coronene in different field strengths from F = 0.0000 to F = 0.0100 atomic units in increments of 0.0005 au, along the main axis of symmetry. All data are presented in atomic units.

	Benzene			**Coronene**		
Field Strength	**Energy**	**μ_z**	**α_{zz}**	**Energy**	**μ_z**	**α_{zz}**
0.0000	**–232.214508**	**0.0000**	**42.155**	**–921.801152**	**0.0000**	**122.601**
0.0005	**–232.214514**	**0.0098**	**42.204**	**–921.801171**	**0.1844**	**122.564**
0.0010	**–232.214533**	**0.0193**	**42.213**	**–921.801225**	**0.3662**	**122.575**
0.0015	**–232.214563**	**0.0289**	**42.221**	**–921.801314**	**0.5483**	**122.592**
0.0020	**–232.214606**	**0.0385**	**42.233**	**–921.801440**	**0.7305**	**122.616**
0.0025	**–232.214660**	**0.0481**	**42.257**	**–921.801601**	**0.9128**	**122.647**
0.0030	**–232.214727**	**0.0576**	**42.289**	**–921.801798**	**1.0951**	**122.684**
0.0035	**–232.214806**	**0.0672**	**42.326**	**–921.802031**	**1.2776**	**122.729**
0.0040	**–232.214898**	**0.0768**	**42.357**	**–921.802300**	**1.4602**	**122.780**
0.0045	**–232.215001**	**0.0864**	**42.378**	**–921.802610**	**1.6429**	**122.838**
0.0050	**–232.215117**	**0.0960**	**42.402**	**–921.802946**	**1.8258**	**122.903**
0.0055	**–232.215244**	**0.1056**	**42.427**	**–921.803323**	**2.0089**	**122.974**
0.0060	**–232.215384**	**0.1152**	**42.468**	**–921.803736**	**2.1922**	**123.053**
0.0065	**–232.215537**	**0.1248**	**42.511**	**–921.804185**	**2.3756**	**123.139**
0.0070	**–232.215701**	**0.1345**	**42.559**	**–921.804670**	**2.5593**	**123.231**
0.0075	**–232.215878**	**0.1441**	**42.609**	**–921.805191**	**2.7432**	**123.330**
0.0080	**–232.216067**	**0.1538**	**42.663**	**–921.805749**	**2.9273**	**123.436**
0.0085	**–232.216268**	**0.1635**	**42.720**	**–921.806342**	**3.1116**	**123.549**
0.0090	**–232.216482**	**0.1731**	**42.780**	**–921.806972**	**3.2962**	**123.669**
0.0095	**–232.216708**	**0.1828**	**42.844**	**–921.807639**	**3.4810**	**123.796**
0.0100	**–232.216946**	**0.1926**	**42.844**	**–921.808341**	**3.6660**	**123.929**

Table S2. Total energy of halide ions in different field strengths from F = 0.0000 to F = 0.0100 atomic units in increments of 0.0005 au, along the main axis of symmetry. All data are presented in atomic units.

Field Strength	**Fluoride**	**Chloride**	**Bromide**
0.0000	**–99.842468**	**–460.268035**	**–2574.256654**
0.0005	**–99.842468**	**–460.268038**	**–2574.256650**
0.0010	**–99.842470**	**–460.268047**	**–2574.256654**
0.0015	**–99.842473**	**–460.268062**	**–2574.256667**
0.0020	**–99.842477**	**–460.268083**	**–2574.256689**
0.0025	**–99.842483**	**–460.268110**	**–2574.256720**
0.0030	**–99.842489**	**–460.268143**	**–2574.256760**
0.0035	**–99.842497**	**–460.268182**	**–2574.256809**
0.0040	**–99.842506**	**–460.268227**	**–2574.256866**
0.0045	**–99.842517**	**–460.268278**	**–2574.256932**
0.0050	**–99.842528**	**–460.268335**	**–2574.257007**
0.0055	**–99.842541**	**–460.268398**	**–2574.257091**
0.0060	**–99.842555**	**–460.268467**	**–2574.257184**
0.0065	**–99.842570**	**–460.268542**	**–2574.257286**
0.0070	**–99.842587**	**–460.268623**	**–2574.257397**
0.0075	**–99.842604**	**–460.268711**	**–2574.257516**
0.0080	**–99.842623**	**–460.268804**	**–2574.257645**
0.0085	**–99.842643**	**–460.268903**	**–2574.257782**
0.0090	**–99.842664**	**–460.269009**	**–2574.257929**
0.0095	**–99.842687**	**–460.269120**	**–2574.258084**
0.0100	**–99.842711**	**–460.269238**	**–2574.258249**

Table S3. Binding energies in kcal.mol^{-1} with gauge in the center of positive charge (center of mass), $E_{binding(CM)}$, binding energies based on Equation (5) $E_{binding\ (Hal)}$, fluoride–benzene distance in Å, $r_{x–Ar}$, first order polarizability in au in z direction, α_{zz}, number of imaginary frequencies, NImag, the smallest frequency of fluoride–benzene complex, delocalization index between halide ion and π–system, DI, and charge transfer from halide to the π–system, CT, in different field strengths from F = –0.0100 to F = +0.0025 atomic units in increments of 0.0005 au, along the main axis of symmetry.

Field Strength	$E_{binding\ (CM)}$	$E_{binding\ (Hal)}$	$r_{x–Ar}$	α_{zz}	NImag	Smallest Freq	DI	CT
0.0025	–2.8	1.2	3.095	54.340	2	–61.79	0.1626	-0.0151
0.0020	–2.1	0.8	3.050	54.508	2	–38.45	0.1720	-0.0157
0.0015	–1.4	0.4	3.021	54.783	1	–10.76	0.1786	-0.0163
0.0010	–0.7	0.1	2.997	55.062	0	11.76	0.1844	-0.0169
0.0005	–0.1	–0.3	2.974	55.224	2	–17.27	0.1898	-0.0175
0.0000	0.6	–0.6	2.770	56.159	2	–76.64	0.2406	-0.0194
–0.0005	1.2	–0.9	2.742	56.393	2	–53.84	0.2488	-0.0203
–0.0010	1.8	–1.2	2.724	56.718	2	–39.62	0.2544	-0.0211
–0.0015	2.4	–1.5	2.708	57.151	2	–29.67	0.2593	-0.0220
–0.0020	3.0	–1.8	2.693	57.622	1	–23.41	0.2641	-0.0228
–0.0025	3.6	–2.1	2.681	58.105	0	16.72	0.2684	-0.0237
–0.0030	4.2	–2.5	2.670	58.588	0	34.94	0.2724	-0.0245
–0.0035	4.7	–2.8	2.658	59.083	0	45.80	0.2765	-0.0254
–0.0040	5.3	–3.1	2.649	59.576	0	51.53	0.2799	-0.0263
–0.0045	5.9	–3.4	2.638	60.117	0	54.40	0.2841	-0.0273
–0.0050	6.5	–3.7	2.630	60.674	0	48.67	0.2875	-0.0283
–0.0055	7.1	–4.0	2.621	61.268	0	33.52	0.2912	-0.0293
–0.0060	7.6	–4.3	2.608	61.935	1	–32.64	0.2962	-0.0304
–0.0065	8.2	–4.5	2.594	62.649	2	–60.55	0.3019	-0.0316
–0.0070	8.7	–4.8	2.579	63.413	2	–75.59	0.3077	-0.0328
–0.0075	9.2	–5.0	2.564	64.239	2	–84.40	0.3139	-0.0341
–0.0080	9.7	–5.3	2.547	65.112	2	–90.37	0.3209	-0.0355
–0.0085	10.1	–5.5	2.530	66.081	2	–96.54	0.3281	-0.0370
–0.0090	10.6	–5.7	2.512	67.084	2	–101.95	0.3357	-0.0386
–0.0095	11.0	–5.9	2.493	68.150	2	–105.47	0.3438	-0.0403
–0.0100	11.5	–6.1	2.477	69.296	2	–103.83	0.3513	-0.0420

Table S4. Binding energies in kcal.mol^{-1} with gauge in the center of positive charge (center of mass), $E_{binding(CM),}$ binding energies based on Equation (5) $E_{binding\ (Hal)}$, chloride–benzene distance in Å, $r_{x\text{–}Ar}$, first order polarizability in au in z direction, α_{zz}, number of imaginary frequencies, NImag, the smallest frequency of chloride–benzene complex, delocalization index between halide ion and π–system, DI, and charge transfer from halide to the π–system, CT, in different field strengths from F = –0.0100 to F = +0.0010 atomic units in increments of 0.0005 au, along the main axis of symmetry.

Field Strength	**$E_{binding\ (CM)}$**	**$E_{binding\ (Hal)}$**	**$r_{x\text{–}Ar}$**	**α_{zz}**	**NImag**	**Smallest Freq**	**DI**	**CT**
0.0010	**–2.1**	**0.9**	**3.710**	**81.094**	**0**	**33.97**	**0.1557**	**-0.0230**
0.0005	**–1.2**	**0.6**	**3.674**	**81.674**	**0**	**43.47**	**0.1632**	**-0.0243**
0.0000	**–0.4**	**0.4**	**3.637**	**81.909**	**0**	**29.04**	**0.1713**	**-0.0258**
–0.0005	**0.4**	**0.3**	**3.587**	**82.408**	**2**	**–16.26**	**0.1823**	**-0.0275**
–0.0010	**1.1**	**0.2**	**3.389**	**82.266**	**2**	**–46.86**	**0.2279**	**-0.0321**
–0.0015	**1.8**	**–0.1**	**3.345**	**82.713**	**0**	**16.47**	**0.2400**	**-0.0338**
–0.0020	**2.6**	**–0.3**	**3.325**	**83.162**	**0**	**43.80**	**0.2465**	**-0.0352**
–0.0025	**3.3**	**–0.5**	**3.309**	**83.616**	**0**	**60.25**	**0.2518**	**-0.0365**
–0.0030	**4.1**	**–0.7**	**3.290**	**84.104**	**0**	**62.32**	**0.2581**	**-0.0379**
–0.0035	**4.9**	**–0.9**	**3.278**	**84.654**	**0**	**56.97**	**0.2627**	**-0.0393**
–0.0040	**5.6**	**–1.1**	**3.265**	**85.164**	**0**	**51.97**	**0.2679**	**-0.0407**
–0.0045	**6.3**	**–1.3**	**3.251**	**85.743**	**0**	**47.16**	**0.2732**	**-0.0421**
–0.0050	**7.1**	**–1.5**	**3.235**	**86.252**	**0**	**43.18**	**0.2794**	**-0.0437**
–0.0055	**7.8**	**–1.7**	**3.219**	**86.987**	**0**	**39.25**	**0.2857**	**-0.0453**
–0.0060	**8.5**	**–1.8**	**3.202**	**87.793**	**0**	**28.91**	**0.2925**	**-0.0470**
–0.0065	**9.1**	**–2.0**	**3.184**	**88.668**	**1**	**–4.76**	**0.2999**	**-0.0487**
–0.0070	**9.8**	**–2.1**	**3.164**	**89.533**	**2**	**–30.08**	**0.3083**	**-0.0506**
–0.0075	**10.4**	**–2.2**	**3.142**	**90.177**	**2**	**–42.21**	**0.3172**	**-0.0526**
–0.0080	**10.9**	**–2.3**	**3.119**	**90.985**	**2**	**–51.29**	**0.3267**	**-0.0547**
–0.0085	**11.5**	**–2.4**	**3.096**	**92.401**	**2**	**–53.83**	**0.3366**	**-0.0569**
–0.0090	**11.9**	**–2.3**	**3.059**	**94.309**	**2**	**–25.92**	**0.3518**	**-0.0597**
–0.0095	**12.7**	**–2.6**	**3.057**	**95.727**	**2**	**–25.09**	**0.3548**	**-0.0614**
–0.0100	**13.3**	**–2.8**	**3.044**	**97.260**	**0**	**17.47**	**0.3623**	**-0.0636**

Table S5. Binding energies in kcal.mol^{-1} with gauge in the center of positive charge (center of mass), $E_{binding(CM)}$, binding energies based on Equation (5) $E_{binding\ (Hal)}$, bromide–benzene distance in Å, $r_{x\text{–}Ar}$, first order polarizability in au in z direction, α_{zz}, number of imaginary frequencies, NImag, the smallest frequency of bromide–benzene complex, delocalization index between halide ion and π–system, DI, and charge transfer from halide to the π–system, CT, in different field strengths from F = –0.0100 to F = +0.0005 atomic units in increments of 0.0005 au, along the main axis of symmetry.

Field Strength	$E_{binding\ (CM)}$	$E_{binding\ (Hal)}$	$r_{x\text{–}Ar}$	α_{zz}	NImag	Smallest Freq	DI	CT
0.0005	–1.9	0.9	3.818	95.426	0	42.82	0.1697	-0.0276
0.0000	–0.7	0.7	3.785	96.132	0	50.98	0.1775	-0.0291
–0.0005	0.6	0.5	3.750	96.454	0	39.05	0.1860	-0.0308
–0.0010	1.7	0.3	3.701	96.988	0	27.29	0.1976	-0.0327
–0.0015	2.7	0.2	3.615	96.994	2	–44.63	0.2187	-0.0354
–0.0020	3.6	0.2	3.506	97.396	2	–39.16	0.2470	-0.0385
–0.0025	5.1	–0.2	3.610	97.471	2	–52.35	0.2227	-0.0375
–0.0030	5.7	–0.1	3.445	98.535	0	43.30	0.2661	-0.0421
–0.0035	6.8	–0.3	3.428	99.172	0	56.32	0.2725	-0.0437
–0.0040	7.8	–0.4	3.412	99.812	0	64.54	0.2786	-0.0453
–0.0045	8.9	–0.6	3.401	100.276	0	63.32	0.2836	-0.0469
–0.0050	10.0	–0.8	3.389	101.099	0	59.27	0.2891	-0.0485
–0.0055	11.0	–0.9	3.375	101.710	0	53.58	0.2952	-0.0503
–0.0060	12.0	–1.1	3.362	102.671	0	49.74	0.3013	-0.0521
–0.0065	13.1	–1.3	3.349	103.501	0	47.14	0.3074	-0.0539
–0.0070	14.1	–1.4	3.334	104.545	0	44.92	0.3145	-0.0559
–0.0075	15.0	–1.6	3.319	105.802	0	42.85	0.3216	-0.058
–0.0080	16.0	–1.7	3.303	107.182	0	33.31	0.3295	-0.0602
–0.0085	17.0	–1.8	3.287	108.592	0	20.13	0.3375	-0.0625
–0.0090	17.9	–1.9	3.270	109.938	1	–13.46	0.3462	-0.0649
–0.0095	18.8	–2.0	3.252	111.314	2	–25.80	0.3555	-0.0675
–0.0100	19.6	–2.1	3.234	112.976	2	–32.69	0.3650	-0.0702

Table S6. Binding energies in kcal.mol^{-1} with gauge in the center of positive charge (center of mass), $E_{\text{binding(CM)}}$, binding energies based on Equation (5) $E_{\text{binding (Hal)}}$, fluoride–coronene distance in Å, $r_{\text{x–Ar}}$, first order polarizability in au in z direction, α_{zz}, number of imaginary frequencies, NImag, the smallest frequency of fluoride–coronene complex, delocalization index between halide ion and π–system, DI, and charge transfer from halide to the π–system, CT, in different field strengths from F = –0.0100 to F = +0.0085 atomic units in increments of 0.0005 au, along the main axis of symmetry.

Field Strength	$E_{\text{binding (CM)}}$	$E_{\text{binding (Hal)}}$	$r_{\text{x–Ar}}$	α_{zz}	NImag	Smallest Freq	DI	CT
0.0085	–29.9	–0.5	2.754	138.367	1	–15.28	0.2491	0.0308
0.0080	–28.6	–1.5	2.705	137.886	0	20.83	0.2656	0.0332
0.0075	–27.3	–2.3	2.670	137.977	0	41.63	0.2780	0.0353
0.0070	–26.1	–3.0	2.650	138.062	0	55.08	0.2860	0.0369
0.0065	–24.9	–3.7	2.635	138.049	0	56.84	0.2925	0.0383
0.0060	–23.7	–4.3	2.621	138.126	0	53.52	0.2985	0.0398
0.0055	–22.5	–4.9	2.607	138.204	0	45.36	0.3050	0.0413
0.0050	–21.4	–5.5	2.589	138.354	0	30.42	0.3127	0.0429
0.0045	–20.2	–6.1	2.565	138.425	1	–18.00	0.3232	0.0450
0.0040	–19.1	–6.8	2.531	138.676	2	–36.03	0.3379	0.0478
0.0035	–18.1	–7.4	2.494	138.573	2	–43.30	0.3542	0.0510
0.0030	–17	–8.0	2.468	138.946	2	–39.48	0.3668	0.0536
0.0025	–16	–8.6	2.447	139.126	2	–32.42	0.3772	0.0560
0.0020	–15	–9.2	2.429	139.300	2	–29.51	0.3870	0.0583
0.0015	–14	–9.7	2.410	140.732	2	–24.93	0.3967	0.0607
0.0010	–13.1	–10.2	2.393	139.673	2	–22.61	0.4065	0.0631
0.0005	–12.1	–10.7	2.376	139.865	2	–16.56	0.4157	0.0654
0.0000	–11.2	–11.2	2.361	140.073	0	15.31	0.4248	0.0677
–0.0005	–10.3	–11.7	2.349	140.258	0	25.62	0.4322	0.0698
–0.0010	–9.4	–12.1	2.338	140.460	0	34.20	0.4393	0.0718
–0.0015	–8.5	–12.6	2.330	140.658	0	39.67	0.4448	0.0735
–0.0020	–7.6	–13.1	2.321	140.873	0	44.19	0.4510	0.0754
–0.0025	–6.8	–13.5	2.313	141.113	0	45.49	0.4571	0.0773
–0.0030	–5.9	–14.0	2.304	141.322	0	45.33	0.4631	0.0792
–0.0035	–5.1	–14.4	2.297	141.611	0	44.16	0.4689	0.0811
–0.0040	–4.3	–14.9	2.289	141.821	0	42.29	0.4747	0.0830
–0.0045	–3.5	–15.3	2.282	142.151	0	40.03	0.4805	0.0848
–0.0050	–2.7	–15.7	2.274	142.349	0	37.76	0.4863	0.0867
–0.0055	–1.9	–16.2	2.267	142.625	0	35.68	0.4921	0.0886
–0.0060	–1.2	–16.6	2.260	142.910	0	34.01	0.4979	0.0905
–0.0065	–0.4	–17.0	2.252	143.203	0	32.81	0.5038	0.9092
–0.0070	0.4	–17.4	2.245	143.511	0	31.98	0.5096	0.0943
–0.0075	1.1	–17.8	2.238	143.801	0	31.37	0.5153	0.0962
–0.0080	1.8	–18.2	2.232	144.148	0	30.76	0.5210	0.0980
–0.0085	2.5	–18.6	2.225	144.473	0	29.90	0.5266	0.0999
–0.0090	3.2	–19.0	2.219	144.831	0	28.62	0.5321	0.1018
–0.0095	3.9	–19.3	2.213	145.171	0	27.23	0.5374	0.1036
–0.0100	4.6	–19.7	2.208	145.532	0	24.22	0.5427	0.1054

Table S7. Binding energies in kcal.mol^{-1} with gauge in the center of positive charge (center of mass), $E_{binding(CM)}$, binding energies based on Equation (5) $E_{binding\ (Hal)}$, chloride–coronene distance in Å, $r_{x–Ar}$, first order polarizability in au in z direction, α_{zz}, number of imaginary frequencies, NImag, the smallest frequency of chloride–coronene complex, delocalization index between halide ion and π–system, DI, and charge transfer from halide to the π–system, CT, in different field strengths from F = –0.0100 to F = +0.0040 atomic units in increments of 0.0005 au, along the main axis of symmetry.

Field Strength	$E_{binding\ (CM)}$	$E_{binding\ (Hal)}$	$r_{x–Ar}$	α_{zz}	NImag	Smallest Freq	DI	CT
0.0040	16.4	0.0	3.391	163.847	2	–16.48	0.2413	0.0431
0.0035	14.8	–0.7	3.339	163.836	0	17.04	0.2582	0.0462
0.0030	13.1	–1.2	3.312	163.776	0	20.83	0.2685	0.0486
0.0025	11.6	–1.7	3.287	163.658	0	20.87	0.2784	0.0508
0.0020	10.0	–2.2	3.265	164.202	0	17.54	0.2875	0.0530
0.0015	8.5	–2.7	3.24	164.312	0	5.68	0.2980	0.0555
0.0010	7.0	–3.1	3.21	163.438	2	–13.76	0.3107	0.0582
0.0005	5.5	–3.6	3.168	164.258	2	–21.13	0.3281	0.0615
0.0000	4.0	–4.1	3.117	164.062	2	–23.89	0.3492	0.0654
–0.0005	2.7	–4.5	3.082	164.622	1	–14.55	0.3652	0.0686
–0.0010	1.3	–4.9	3.059	164.788	0	5.55	0.3766	0.0712
–0.0015	0.0	–5.3	3.041	164.676	0	8.2	0.3865	0.0737
–0.0020	–1.4	–5.7	3.025	164.952	0	3.39	0.3961	0.0761
–0.0025	–2.7	–6.1	3.009	165.213	0	5.52	0.4056	0.0786
–0.0030	–3.9	–6.4	2.994	165.865	0	15.01	0.4148	0.0811
–0.0035	–5.2	–6.8	2.981	166.167	0	23.12	0.4235	0.0835
–0.0040	–6.4	–7.2	2.969	167.513	0	28.83	0.4317	0.0859
–0.0045	–7.6	–7.6	2.959	167.175	0	32.37	0.4395	0.0883
–0.0050	–8.8	–7.9	2.949	168.216	0	34.19	0.4470	0.0907
–0.0055	–10.0	–8.3	2.94	167.774	0	34.65	0.4544	0.0931
–0.0060	–11.2	–8.7	2.931	168.221	0	34.03	0.4618	0.0955
–0.0065	–12.4	–9.0	2.923	168.516	0	32.53	0.4693	0.0979
–0.0070	–13.5	–9.4	2.914	169.186	0	30.34	0.4769	0.1004
–0.0075	–14.6	–9.7	2.905	169.712	0	27.6	0.4847	0.1030
–0.0080	–15.7	–10.1	2.896	170.329	0	24.55	0.4927	0.1056
–0.0085	–16.8	–10.4	2.887	170.844	0	21.44	0.5011	0.1083
–0.0090	–17.9	–10.7	2.877	171.541	0	18.49	0.5097	0.1111
–0.0095	–19.0	–11	2.867	172.211	0	16.04	0.5186	0.1140
–0.0100	–20.0	–11.3	2.857	172.751	0	14.16	0.5278	0.1169

Table S8. Binding energies in kcal.mol^{-1} with gauge in the center of positive charge (center of mass), $E_{binding(CM)}$, binding energies based on Equation (5) $E_{binding\ (Hal)}$, bromide–coronene distance in Å, $r_{x–Ar}$, first order polarizability in au in z direction, α_{zz}, number of imaginary frequencies, NImag, the smallest frequency of bromide–coronene complex , delocalization index between halide ion and π–system, DI, and charge transfer from halide to the π–system, CT, in different field strengths from F = –0.0100 to F = +0.0035 atomic units in increments of 0.0005 au, along the main axis of symmetry.

Field Strength	$E_{binding\ (CM)}$	$E_{binding\ (Hal)}$	$r_{x–Ar}$	α_{zz}	NImag	Smallest Freq	DI	CT
0.0035	**14.6**	**1.6**	**3.860**	**176.162**	**0**	**5.20**	**0.1753**	**0.0368**
0.0030	**12.7**	**0.9**	**3.785**	**177.250**	**1**	**–8.28**	**0.1945**	**0.0407**
0.0025	**10.9**	**–0.6**	**3.467**	**179.378**	**0**	**7.41**	**0.2836**	**0.0545**
0.0020	**9.2**	**–1.0**	**3.438**	**179.578**	**0**	**17.99**	**0.2956**	**0.0573**
0.0015	**7.6**	**–1.5**	**3.416**	**179.914**	**0**	**20.09**	**0.3055**	**0.0598**
0.0010	**6.0**	**–1.9**	**3.395**	**180.028**	**0**	**18.70**	**0.3152**	**0.0623**
0.0005	**4.4**	**–2.4**	**3.375**	**180.031**	**0**	**15.19**	**0.3250**	**0.0649**
0.0000	**2.8**	**–2.8**	**3.353**	**180.132**	**0**	**10.31**	**0.3357**	**0.0676**
–0.0005	**1.2**	**–3.2**	**3.331**	**180.043**	**0**	**3.79**	**0.3469**	**0.0704**
–0.0010	**–0.3**	**–3.6**	**3.303**	**180.642**	**1**	**–8.09**	**0.3605**	**0.0735**
–0.0015	**–1.8**	**–3.9**	**3.274**	**180.182**	**1**	**–11.90**	**0.3753**	**0.0768**
–0.0020	**–3.3**	**–4.3**	**3.242**	**180.289**	**1**	**–13.53**	**0.3911**	**0.0804**
–0.0025	**–4.7**	**–4.6**	**3.214**	**177.240**	**1**	**–10.50**	**0.4064**	**0.0838**
–0.0030	**–6.1**	**–4.9**	**3.191**	**179.593**	**0**	**5.17**	**0.4194**	**0.0870**
–0.0035	**–7.5**	**–5.3**	**3.172**	**180.820**	**0**	**11.76**	**0.4309**	**0.0901**
–0.0040	**–8.8**	**–5.6**	**3.156**	**181.426**	**0**	**13.84**	**0.4416**	**0.0930**
–0.0045	**–10.2**	**–6.0**	**3.141**	**181.463**	**0**	**14.89**	**0.4520**	**0.0960**
–0.0050	**–11.5**	**–6.3**	**3.127**	**181.767**	**0**	**16.42**	**0.4621**	**0.0990**
–0.0055	**–12.8**	**–6.6**	**3.114**	**182.334**	**0**	**19.07**	**0.472**	**0.1019**
–0.0060	**–14.1**	**–7.0**	**3.102**	**182.489**	**0**	**22.41**	**0.4817**	**0.1049**
–0.0065	**–15.3**	**–7.3**	**3.091**	**184.067**	**0**	**24.75**	**0.4910**	**0.1079**
–0.0070	**–16.6**	**–7.6**	**3.081**	**184.545**	**0**	**26.73**	**0.5000**	**0.1109**
–0.0075	**–17.8**	**–7.9**	**3.071**	**184.748**	**0**	**28.46**	**0.5088**	**0.1139**
–0.0080	**–19.0**	**–8.3**	**3.063**	**185.988**	**0**	**29.85**	**0.5174**	**0.1169**
–0.0085	**–20.2**	**–8.6**	**3.055**	**186.807**	**0**	**30.88**	**0.5259**	**0.1199**
–0.0090	**–21.4**	**–8.9**	**3.047**	**186.961**	**0**	**31.29**	**0.5345**	**0.1230**
–0.0095	**–22.6**	**–9.3**	**3.039**	**188.128**	**0**	**31.91**	**0.5431**	**0.1262**
–0.0100	**–23.8**	**–9.6**	**3.032**	**190.523**	**0**	**31.82**	**0.5517**	**0.1294**

A Brief Discussion on the validity of the Concept of Binding Energy in the Presence of an External Electric Field

As mentioned in the article, Equation (2) cannot be used to assess the binding energy in the presence of an external electric field, i.e. the energy that is required for dissociating the molecule. This not only is true for the charged systems but also it is valid for the neutral systems. For more clarity a simple example is presented here to clarify it more.

In absence of the electric field, the binding energy of a molecular system like *AB* can be calculated simply from Equation S1.

$$\text{Eq (S1)} \qquad E_{\text{Binding } AB} = E_{AB} - [E_{A} - E_{B}]$$

Accordingly, for a molecule like H_2, the binding energy in the absence of an electric field is simply equal to $[E_{\text{Hydrogen Molecule}} - 2(E_{\text{Hydrogen atom}})]$. Obviously, this energy corresponds to the energy difference between the energy of the structure of H_2 in local minimum and the flat of energy on the PES plot, Figure S3.

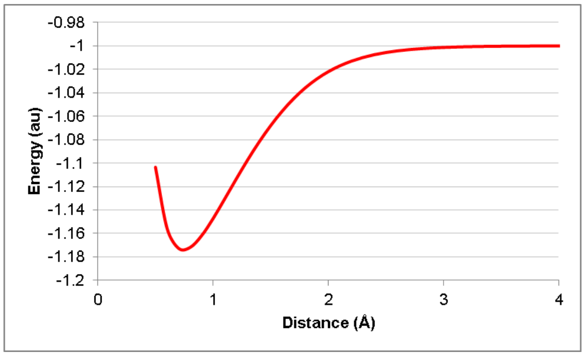


Figure S3. The plot of total electronic energy of hydrogen molecule versus the distance between hydrogen atoms at CCSD(T)/aug-cc-pVTZ level of computation.

However, as indicated in Figure S4 and Table S9 the binding energies computed from Equation S1 are not equal to the binding energy obtained from the PES scan.

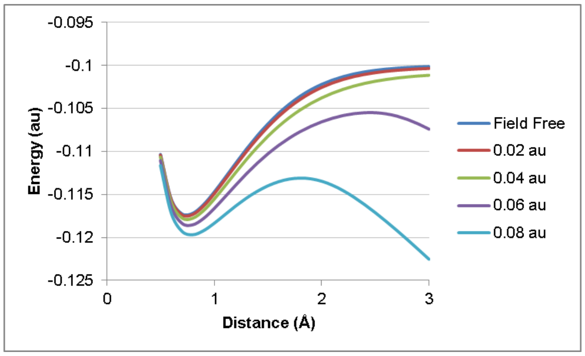
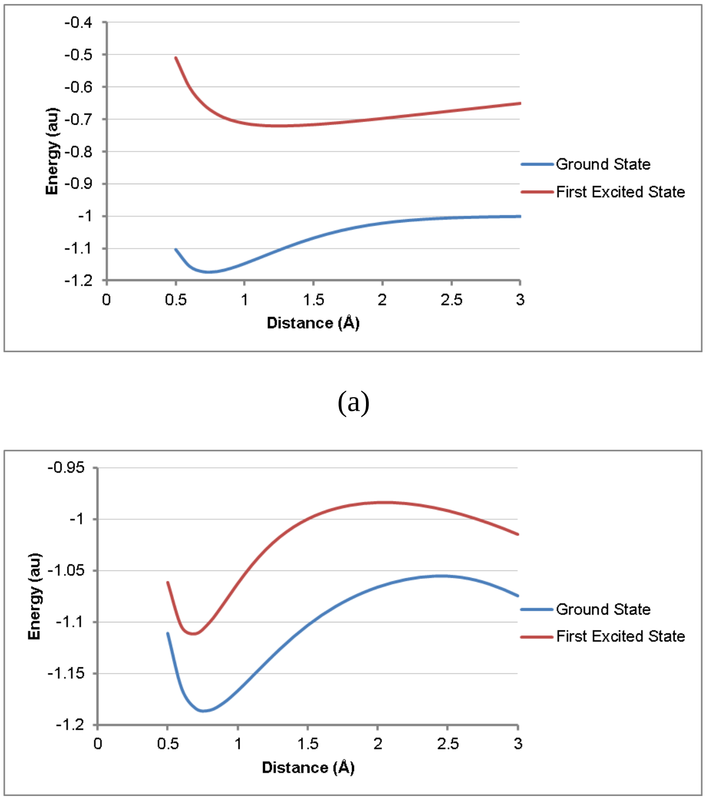


Figure S4. The plot of the potential energy of the hydrogen molecule versus distance between the hydrogen atoms at different field strengths, computed at CCSD(T)/aug-cc-pVTZ computational level; the electric field is parallel to the H-H bond.

Table S9. The binding energy for the hydrogen molecule at different field strengths based on Equation S1, and the energy of two isolated hydrogen atoms at the same field strength; these energies can be compared to those obtained from the PES of the H_2 shown in Figure S4.

Field Strength (au)	**Binding Energy**	**$E_H \times 2$**
0.0000	**-0.17397**	**-1.0000**
0.0200	**-0.17345**	**-1.0017**
0.0400	**-0.17182**	**-1.0073**
0.0600	**-0.16896**	**-1.0171**
0.0800	**-0.16487**	**-1.0321**

The difference between the binding energies, computed form Equation S1 and those obtained from the PES scan (Figure S4) originates from the difference between the first singlet excited-state of H_2 and the excited-states of hydrogen atom. The first singlet excited-state of the hydrogen atom corresponds to an ionic system, i.e. H^+H^-. The energy of this ionic system decreases considerably in the presence of an electric field, see Figure S5. This affects the ground-state energy of the molecule so dramatically that the curvature of the PES changes.



(a)

(b)

Figure S5. Potential energy surface scan of ground- and the first-singlet-excited-states of hydrogen molecule in (a) field-free condition, and (b) in the presence of an electric field with strength of 0.06 au, parallel to the H_2 bond. Figure S5(b) clearly shows how the energy of the excited-state decreases in the presence of an electric field.

Equation 2 in the manuscript compares the energy of two isolated hydrogen molecule with that of the hydrogen molecule in the presence of an external electric field. This comparison is not meaningful because hydrogen molecule benefits from a considerable energy decrease because of configuration interaction between the ground-state and the ionic excited-state whereas isolated hydrogen atoms cannot experience similar energy decrease. Accordingly, we highly recommend measuring the ***binding energy*** of neutral molecules in the presence of strong electric fields ***only by scanning the PES***.