Supporting Information

Halogen, Chalcogen and Pnictogen Interactions in $(XNO_2)_2$ (X=F, Cl, Br, I) Homodimers

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- **Table S1** Interaction energies, in kJ/mol, obtained at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ computational level, including BSSE at both levels and corrected interaction energies (+BSSE).
- **Table S2** Net atomic charges obtained with AIM at MP2/aug-cc-pVTZ computational level.
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Table S1. Interaction energies, in kJ/mol, obtained at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ computational level, including BSSE (in kj/mol) at both levels and corrected interaction energies (+BSSE).

		Ei		BSSE		Ei + BSSE	
Complex 1		MP2	CCSDT	MP2	CCSDT	MP2	CCSDT
F	D2D	-1.26	-3.26	0.9	0.9	-0.40	-2.37
Cl	C2	-7.26	-3.36	1.2	1.2	-6.02	-2.12
Br	C2h	-12.77	-5.83	4.7	4.5	-8.11	-1.35
I	C2h	-20.88	-11.15	8.5	8.1	-12.37	-3.07
Complex 2							
F	Ci	-21.84	-9.49	4.4	4.7	-17.47	-4.82
Cl	C1	-17.09	-10.64	4.2	4.2	-12.94	-6.46
Br	C1	-21.04	-15.32	8.7	8.5	-12.34	-6.78
I	Ci	-20.77	-15.89	8.9	6.0	-11.88	-8.08
Complex 3							
F	-	-	-	-	-	-	-
Cl	C1	-15.82	-11.31	4.1	4.2	-11.69	-7.15
Br	C1	-20.46	-14.73	7.9	7.8	-12.56	-6.93
I	C1	-21.59	-15.07	7.9	7.8	-13.64	-7.25
Complex 4							
F	-	-	-	-	-	-	-
Cl	Cs	-5.46	-7.01	1.5	1.5	-3.94	-5.51
Br	Cs	-9.05	-11.25	3.9	3.8	-5.17	-7.48
I	Cs	-16.15	-17.74	6.3	3.4	-9.81	-14.29
Complex 5							
F	Cs	-12.40	-10.45	3.1	3.3	-9.27	-7.15
Cl	Cs	-15.09	-10.73	3.3	3.3	-11.80	-7.42
Br	Cs	-17.29	-11.28	6.7	6.5	-10.61	-4.77
I	Cs	-23.41	-15.40	9.3	8.9	-14.12	-6.47
Complex 6							
F	C1	-8.16	-9.65	2.9	3.1	-5.21	-6.58
Cl	Cs	-12.38	-11.44	3.4	3.4	-8.94	-8.00
Br	Cs	-15.45	-13.77	5.7	5.7	-9.72	-8.08
I	Cs	-16.48	-14.33	5.7	5.6	-10.78	-8.63

Table S2. Net atomic charges obtained with AIM at MP2/aug-cc-pVTZ computational level.

	Unit 1				Unit 2			
Monomers	Q(X)	Q(N)	Q(O)	Q(O)	Q(X)	Q(N)	Q(O)	Q(O)
FNO_2	-0.38	1.00	-0.31	-0.31				
$ClNO_2$	-0.07	0.74	-0.33	-0.33				
$BrNO_2$	0.03	0.66	-0.34	-0.34				

INO_2	0.20	0.54	-0.37	-0.37				
Complex 1								
F	-0.37	1.00	-0.32	-0.32				
Cl	-0.08	0.74	-0.33	-0.33				
Br	0.01	0.67	-0.34	-0.34				
I	0.17	0.56	-0.36	-0.36				
Complex 2								
F	-0.43	1.00	-0.29	-0.29				
Cl	-0.11	0.76	-0.32	-0.32				
Br	0.00	0.67	-0.34	-0.33				
I	0.19	0.54	-0.37	-0.36				
Complex 3								
F	-	-	-	-	-	-	-	-
Cl	-0.05	0.73	-0.35	-0.33	-0.10	0.75	-0.32	-0.32
Br	0.05	0.64	-0.36	-0.34	0.00	0.67	-0.33	-0.33
I	0.21	0.53	-0.38	-0.36	0.16	0.56	-0.35	-0.35
Complex 4								
F	-	-	-	-	-	-	-	-
Cl	-0.06	0.74	-0.33	-0.34	-0.06	0.74	-0.34	-0.34
Br	0.07	0.64	-0.34	-0.36	0.07	0.64	-0.36	-0.36
I	0.29	0.50	-0.37	-0.40	0.29	0.49	-0.39	-0.39
Complex 5								
F	-0.38	1.01	-0.32	-0.32	-0.39	1.00	-0.31	-0.30
Cl	-0.09	0.75	-0.33	-0.33	-0.08	0.75	-0.33	-0.33
Br	-0.01	0.68	-0.33	-0.33	0.03	0.65	-0.35	-0.35
I	0.14	0.58	-0.34	-0.34	0.21	0.51	-0.39	-0.38
Complex 6								
F	-0.38	1.00	-0.32	-0.32	-0.37	1.00	-0.31	-0.32
Cl	-0.07	0.74	-0.34	-0.34	-0.05	0.73	-0.33	-0.35
Br	0.03	0.66	-0.35	-0.35	0.05	0.65	-0.34	-0.36
I	0.19	0.55	-0.37	-0.37	0.21	0.53	-0.36	-0.38

Table S3. Net atomic charge differences respect to the isolated monomers obtained with AIM at MP2/aug-cc-pVTZ computational level, and total charge transfer (QT) between unit 1 and unit 2, in e, with NBO B3LYP/aug-cc-pVTZ computational level.

	Unit 1					Unit 2				
System	ΔQ(X)	ΔQ(N)	ΔQ(O)	ΔQ(O)	QT	ΔQ(X)	ΔQ(N)	ΔQ(O)	ΔQ(O)	QT
Complex 1										
F	0.01	0.00	-0.01	-0.01	0.00002					
Cl	-0.01	0.00	0.00	0.00	0.00003					
Br	-0.02	0.01	0.01	0.01	0.00003					
I	-0.03	0.02	0.01	0.01	0.00002					

Complex 2										
F	-0.04	0.00	0.02	0.02	0.00004					
Cl	-0.04	0.02	0.01	0.01	0.00003					
Br	-0.03	0.01	0.01	0.01	0.00003					
I	-0.01	0.00	0.00	0.01	0.00002					
Complex 3										
F	-	-	-	-		-	-	-		-
Cl	0.03	-0.01	-0.02	0.00	0.00230	-0.03	0.01	0.01	0.01	-0.00224
Br	0.04	-0.02	-0.02	0.00	0.00222	-0.03	0.01	0.01	0.01	-0.00217
I	0.04	-0.03	-0.02	0.00	0.00234	-0.04	0.02	0.01	0.01	-0.00230
Complex 4										
F	-	-	-	-	-	-	-	-	-	-
Cl	0.01	-0.01	0.00	-0.01	0.01029	0.01	-0.01	-0.01	-0.01	-0.01023
Br	0.04	-0.02	0.00	-0.02	0.01611	0.04	-0.02	-0.01	-0.01	-0.01606
I	0.09	-0.04	0.00	-0.04	0.03090	0.09	-0.05	-0.03	-0.03	-0.03085
Complex 5										
F	-0.01	0.01	0.00	0.00	-0.00029	-0.01	0.00	0.00	0.00	0.00034
Cl	-0.01	0.00	0.00	0.00	0.00190	-0.01	0.00	0.00	0.00	-0.00185
Br	-0.02	0.01	0.01	0.01	0.03069	0.00	-0.01	-0.01	-0.01	-0.03064
I	-0.03	0.03	0.02	0.02	0.07935	0.01	-0.02	-0.02	-0.02	-0.07930
Complex 6										
F	0.05	0.00	-0.03	-0.03	-0.00085	0.01	0.00	0.00	0.00	0.00091
Cl	0.04	-0.02	-0.02	-0.02	-0.00165	0.02	-0.01	0.00	0.00	0.00171
Br	0.03	-0.01	-0.01	-0.01	-0.00170	0.02	-0.01	0.00	0.00	0.00176
I	0.00	0.01	0.00	-0.01	-0.00259	0.01	-0.01	0.01	0.01	0.00265

Table S4. MP2 Optimized Geometries (Cartesian Coordinates in Å) of the Stationary Points in Gas Phase.

complex_1a_F				complex_1_Cl			
N	0.00000	0.00000	2.91104	N	0.07002	3.44191	-0.00001
F	0.00000	0.00000	1.40259	Cl	0.35433	1.56519	0.00001
O	0.00000	1.09971	3.33854	O	1.08440	4.07040	0.00095
O	0.00000	-1.09971	3.33854	O	-1.08440	3.74378	-0.00098
F	0.00000	0.00000	-1.40259	Cl	-0.35433	-1.56519	0.00001
N	0.00000	0.00000	-2.91104	N	-0.07002	-3.44191	-0.00001
O	-1.09971	0.00000	-3.33854	O	1.08440	-3.74378	-0.00098
O	1.09971	0.00000	-3.33854	O	-1.08440	-4.07040	0.00095

complex_1_Br				complex_1_I			
N	-3.56884	0.15054	0.00000	N	0.85768	-3.68044	0.00000
Br	-1.57492	-0.29206	0.00000	O	0.05980	-4.58218	0.00000
O	-4.27283	-0.81720	0.00000	O	2.06116	-3.69321	0.00000
O	-3.80293	1.32402	0.00000	N	-0.85768	3.68044	0.00000

Br	1.57492	0.29206	0.00000	O	-2.06116	3.69321	0.00000
N	3.56884	-0.15054	0.00000	O	-0.05980	4.58218	0.00000
O	3.80293	-1.32402	0.00000	I	0.05980	1.65527	0.00000
O	4.27283	0.81720	0.00000	I	-0.05980	-1.65527	0.00000

complex_2_F				complex_2_Cl			
N	-0.93608	-2.62772	1.10029	N	1.75450	0.10260	0.30937
O	-1.92378	-3.19820	1.37432	Cl	0.70415	-0.69394	1.69937
O	0.06562	-2.27465	1.59605	O	2.50135	-0.66779	-0.20433
N	-2.55259	-0.05244	-0.14566	O	1.51212	1.25867	0.15569
O	-1.80929	0.65629	-0.71052	N	-1.75448	0.10274	-0.30929
O	-3.52667	-0.67586	-0.34215	Cl	-0.70413	-0.69289	-1.69980
F	-2.11364	-0.20616	1.35691	O	-2.50135	-0.66799	0.20389
F	-0.95830	-2.21995	-0.41881	O	-1.51216	1.25873	-0.15491

complex_2_Br				complex_2_I			
N	1.75048	0.12068	0.47110	N	1.30624	1.34996	0.68625
Br	0.55896	-0.79293	1.84597	O	0.99431	1.15622	1.83466
O	2.57743	-0.60183	-0.00022	O	1.27612	2.35671	0.02551
O	1.48027	1.27326	0.29815	I	2.04113	-0.42158	-0.37155
N	-1.75049	0.12095	-0.47099	N	-1.30614	-1.34987	0.68646
Br	-0.55889	-0.79132	-1.84668	O	-1.27754	-2.35703	0.02626
O	-2.57738	-0.60205	-0.00032	O	-0.99259	-1.15569	1.83436
O	-1.48038	1.27339	-0.29700	I	-2.04119	0.42153	-0.37138

complex_3_Br				complex_3_Cl			
N	-1.17827	-2.69290	0.86210	N	-1.20162	-2.69650	0.84179
O	-1.86055	-2.68563	-0.12744	O	-1.88467	-2.68196	-0.14246
O	-1.45927	-2.58463	2.02253	O	-1.45985	-2.61827	2.00601
N	-2.95767	-0.02348	0.10445	N	-3.00251	-0.01758	0.11876
O	-3.32032	-0.02976	-1.03414	O	-3.33348	0.03984	-1.02373
O	-3.48703	-0.33402	1.13138	O	-3.54599	-0.35389	1.12517
Br	-1.04038	0.63405	0.34985	Cl	0.62341	-2.86963	0.48089
Br	0.78080	-2.91910	0.50169	Cl	-1.19743	0.53955	0.40401

complex_3_I			
N	1.02204	1.29385	-0.21348
O	0.49663	1.71956	0.78871
O	0.87112	1.62334	-1.36392
N	-2.27854	1.13664	0.19910
O	-2.57822	1.42483	1.32706
O	-2.19588	1.81046	-0.79472
I	-1.77284	-0.99453	-0.10447
I	2.45296	-0.31942	0.11284

complex_4_Br				complex_4_Cl			
N	3.73328	-1.56039	0.16163	N	3.31803	0.06781	0.00000
O	4.22513	-1.45901	1.25273	O	3.78277	0.17586	1.09591
O	4.22601	-1.75211	-0.91686	O	3.78277	0.17586	-1.09591
N	-1.57471	-0.01070	-0.04205	N	-2.07485	0.11785	0.00000
O	-0.91214	0.98119	-0.17358	O	-1.67045	1.24222	0.00000
O	-1.26205	-1.16212	0.10806	O	-1.52735	-0.94542	0.00000
Br	1.74261	-1.37707	0.13606	Cl	-3.94551	-0.00900	0.00000
Br	-3.54555	0.29659	-0.07765	Cl	1.48999	-0.35596	0.00000

complex_4_I			
N	0.17008	-4.23502	0.00000
O	0.24500	-4.75425	1.09277
O	0.24500	-4.75425	-1.09277
N	0.24496	1.48577	0.00000
O	1.39953	1.12606	0.00000
O	-0.76307	0.80763	0.00000
I	-0.08710	3.60836	0.00000
I	-0.13750	-2.10181	0.00000

complex_5_F				complex_5_Cl			
N	-1.91549	0.05703	0.00000	N	-2.21304	0.18481	0.00000
O	-1.44825	1.13846	0.00000	O	-1.62698	1.22573	0.00000
O	-2.97771	-0.44663	0.00000	O	-3.36811	-0.11010	0.00000
N	1.64901	0.30569	0.00000	N	1.49268	0.76629	0.00000
O	1.46202	0.68738	1.09923	O	1.22806	1.15587	1.09615
O	1.46202	0.68738	-1.09923	O	1.22806	1.15587	-1.09615
F	2.32495	-1.04811	0.00000	Cl	2.56064	-0.79972	0.00000
F	-0.80668	-1.00660	0.00000	Cl	-1.05095	-1.31351	0.00000

complex_5_Br				complex_5_I			
N	-0.61826	2.63840	-0.08092	N	-3.41769	0.18534	0.00000
O	-1.72758	2.42167	0.32090	O	-3.66214	1.37028	0.00000
O	-0.05053	3.65715	-0.35824	O	-4.17785	-0.75535	0.00000
N	-0.33079	-2.21050	0.20501	N	1.79886	1.53505	0.00000
O	-1.13618	-2.29240	-0.67261	O	1.72247	2.01440	1.09607
O	-0.41709	-2.12857	1.39305	O	1.72247	2.01440	-1.09607
Br	1.60860	-2.21007	-0.47013	I	2.15325	-0.67884	0.00000
Br	0.49929	0.97324	-0.33707	I	-1.29236	-0.32963	0.00000

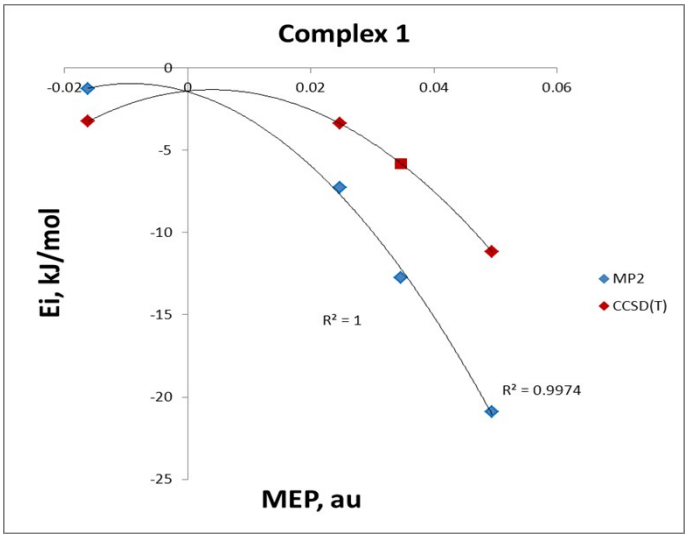
complex_6_F				complex_6_Cl			
N	-0.64112	-2.08029	0.00024	N	-1.73768	-0.62183	0.00000
O	-1.06840	-2.09086	-1.09868	O	-1.49628	-1.03121	1.09562
O	-1.06498	-2.09125	1.10048	O	-1.49628	-1.03121	-1.09562
N	-2.05185	0.95992	0.00269	N	1.57727	-0.07186	0.00000

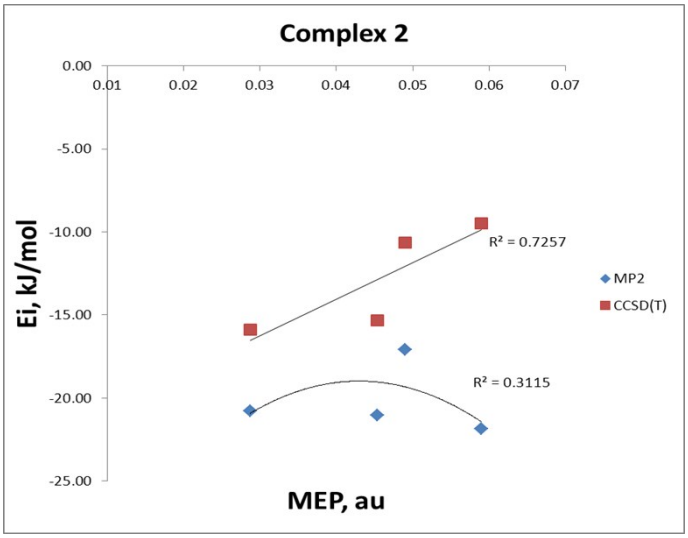
O	-3.00961	0.27013	0.00108	O	1.45644	-1.26201	0.00000
O	-0.87949	0.81428	0.00390	O	0.78022	0.82127	0.00000
F	-2.42053	2.41548	0.00341	Cl	3.35392	0.51087	0.00000
F	0.86969	-2.03116	-0.00210	Cl	-2.68269	1.00616	0.00000
	complex_6_Br				complex_6_I		
N	-1.76216	-0.88866	0.00000	N	2.29059	0.00967	0.00000
O	-1.51805	-1.30978	1.09467	O	2.29059	0.51665	1.09331
O	-1.51805	-1.30978	-1.09467	O	2.29059	0.51665	-1.09331
N	1.52799	-0.28307	0.00000	N	-0.90221	1.11530	0.00000
O	1.40194	-1.47648	0.00000	O	-0.16727	2.07252	0.00000
O	0.71649	0.60180	0.00000	O	-0.63503	-0.06255	0.00000
Br	3.43106	0.35280	0.00000	I	-3.03558	1.57189	0.00000
Br	-2.76103	0.86354	0.00000	I	2.28181	-2.17983	0.00000

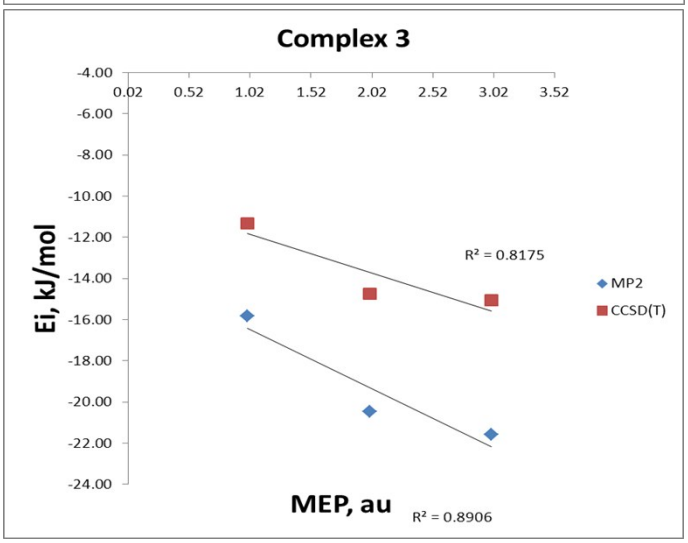
Table S5. Percentage of each attractive component to the total attractive energy obtained with SAPT-DFT/ aug-cc-pVTZ/aug-cc-pVTZ-PP computational level.

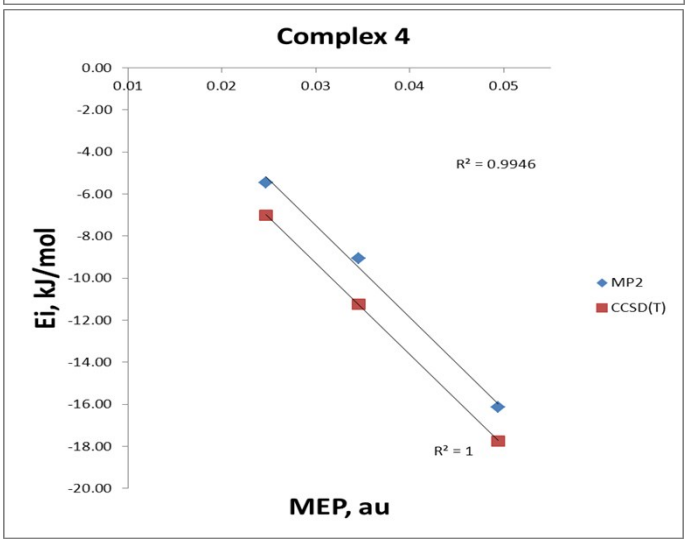
	$E^{(1)}_{el}$	$E^{(2)}_{i}$	$E^{(2)}_{D}$
Complex 1			
F	-3.4	2.4	97.7
Cl	27.5	6.9	65.7
Br	36.6	12.9	50.5
I	25.6	49.5	24.8
Complex 2			
F	50.8	7.0	42.1
Cl	32.9	4.2	62.9
Br	34.6	3.5	62.0
I	29.2	10.8	60.0
Complex 3			
F	-	-	-
Cl	28.1	4.9	67.1
Br	31.3	4.1	64.6
I	27.6	10.1	62.3
Complex 4			
F	-	-	-
Cl	35.3	3.1	61.6
Br	44.4	5.6	49.9
I	43.7	22.1	34.2
Complex 5			
F	39.4	4.3	56.4
Cl	33.7	2.8	63.5

Br	42.6	7.6	49.8
I	30.7	40.8	28.5
Complex 6			
F	23.2	5.3	71.4
Cl	32.8	3.1	64.1
Br	36.5	2.4	61.1
I	36.4	3.7	59.9









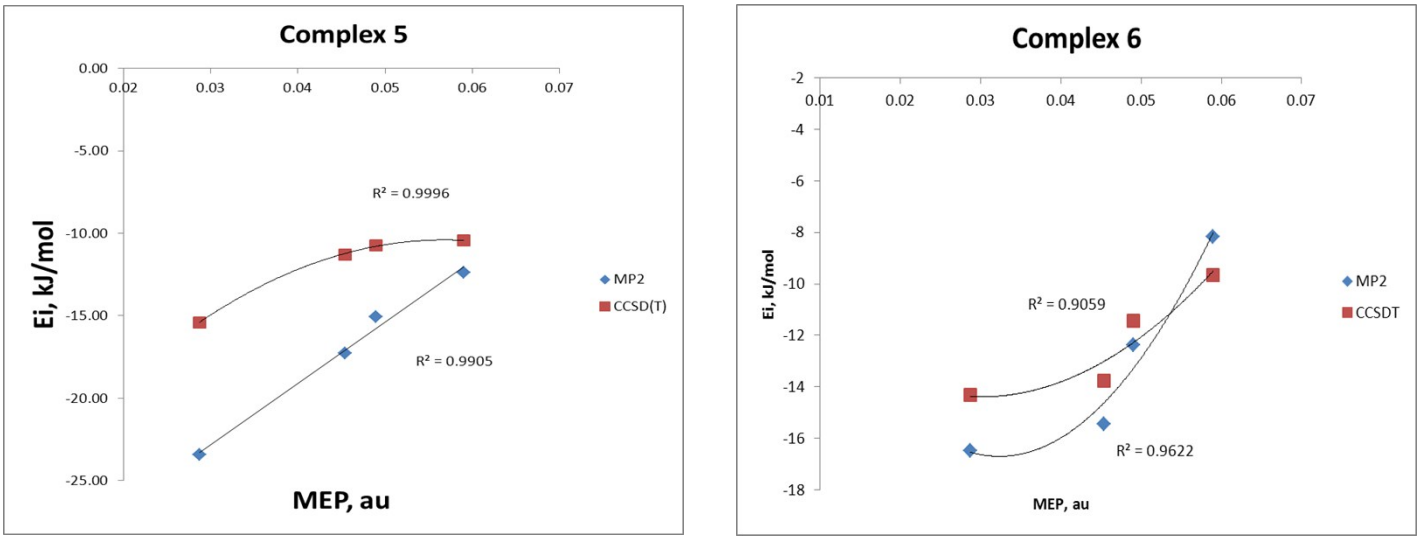


Figure S1. Correlation between interaction energies and MEP values at MP2 and CCSD(T)/aug-cc-pVTZ computational level.

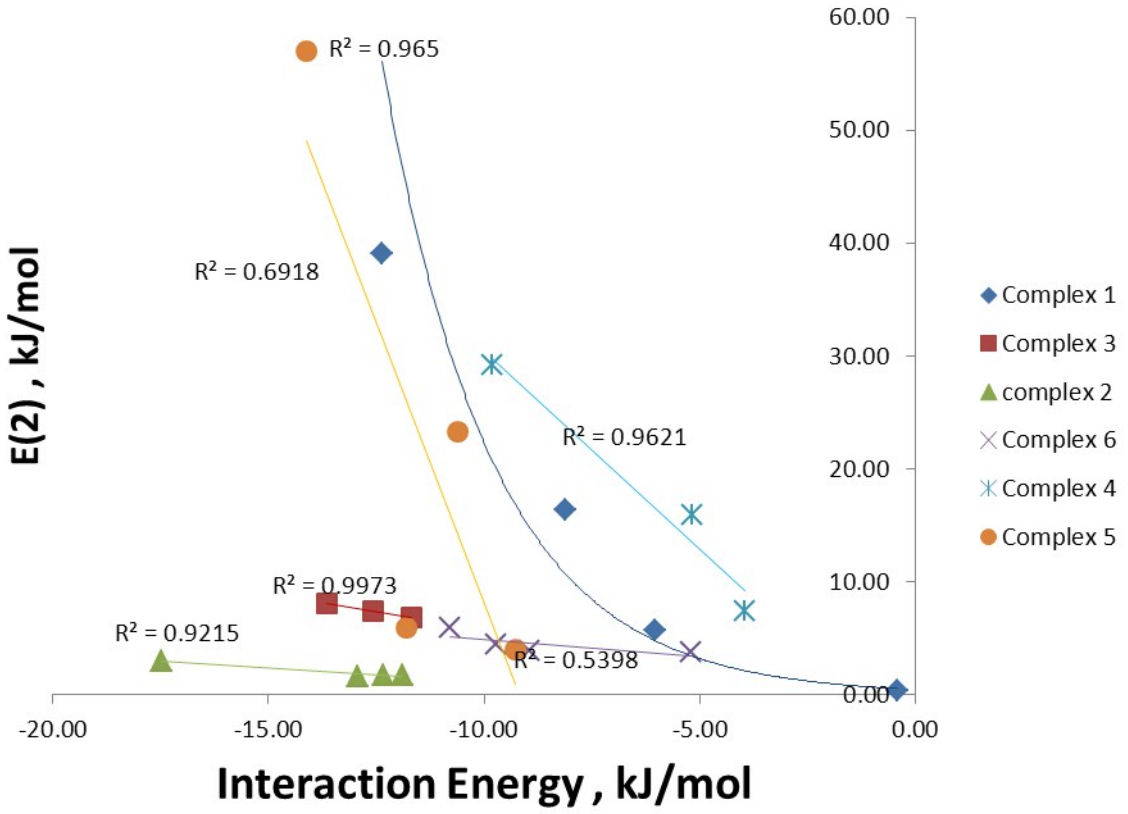


Figure S2. Correlation between interaction energies and NBO E(2) orbital interaction energies.