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

Supplementary Information

New Type of Halogen Bond involving Multivalent Astatine: An *Ab Initio* Study

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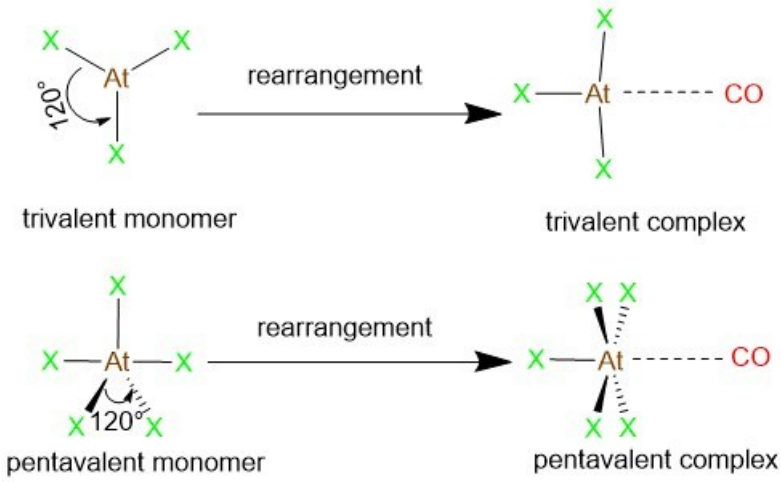

Fig. S1. The molecular rearrangement graph of trivalent and pentavalent monomers

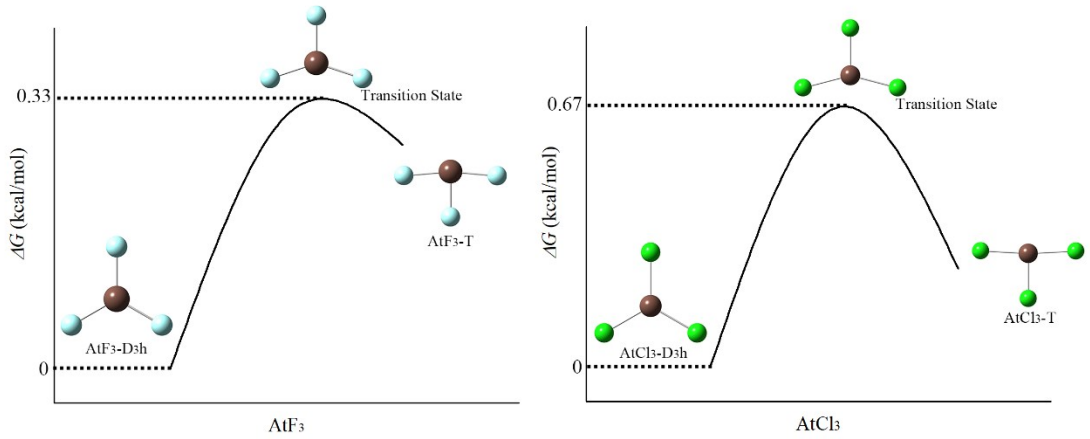

Fig. S2. The diagrams of a possible pathway for tautomeric interconversion of trivalent halide.

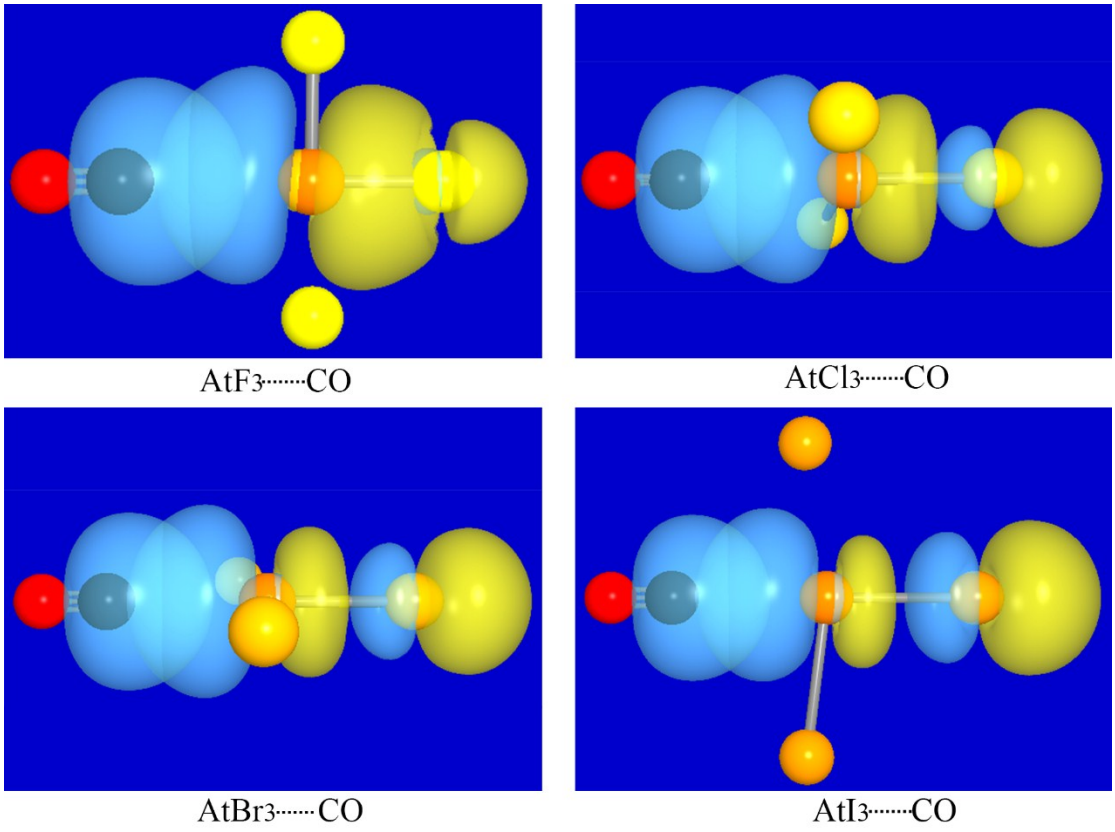

Fig. S3. The orbital-interaction diagrams of the At-C bond complexes formed by the trivalent halides.

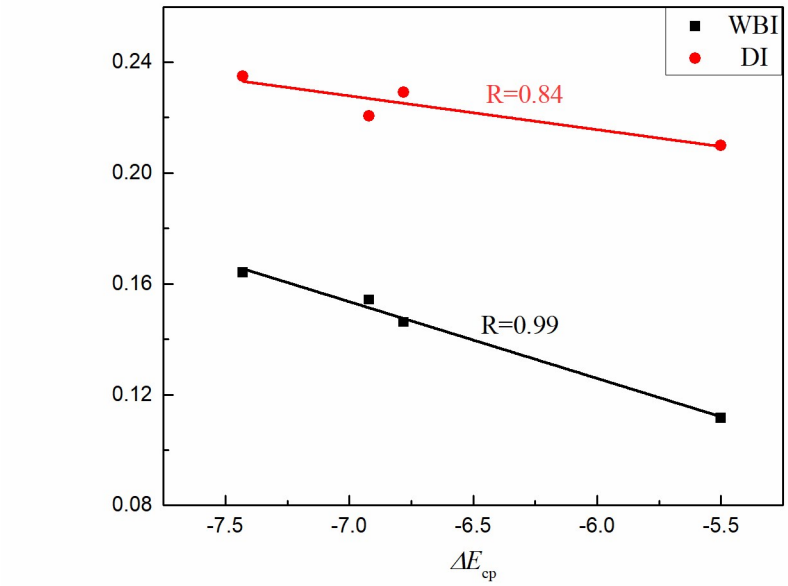

Fig. S4. The linear relationship between Wiberg index (WBI), delocalization index (*DI*) and interaction energies for At-C bond formed by trivalent halide in representative system.

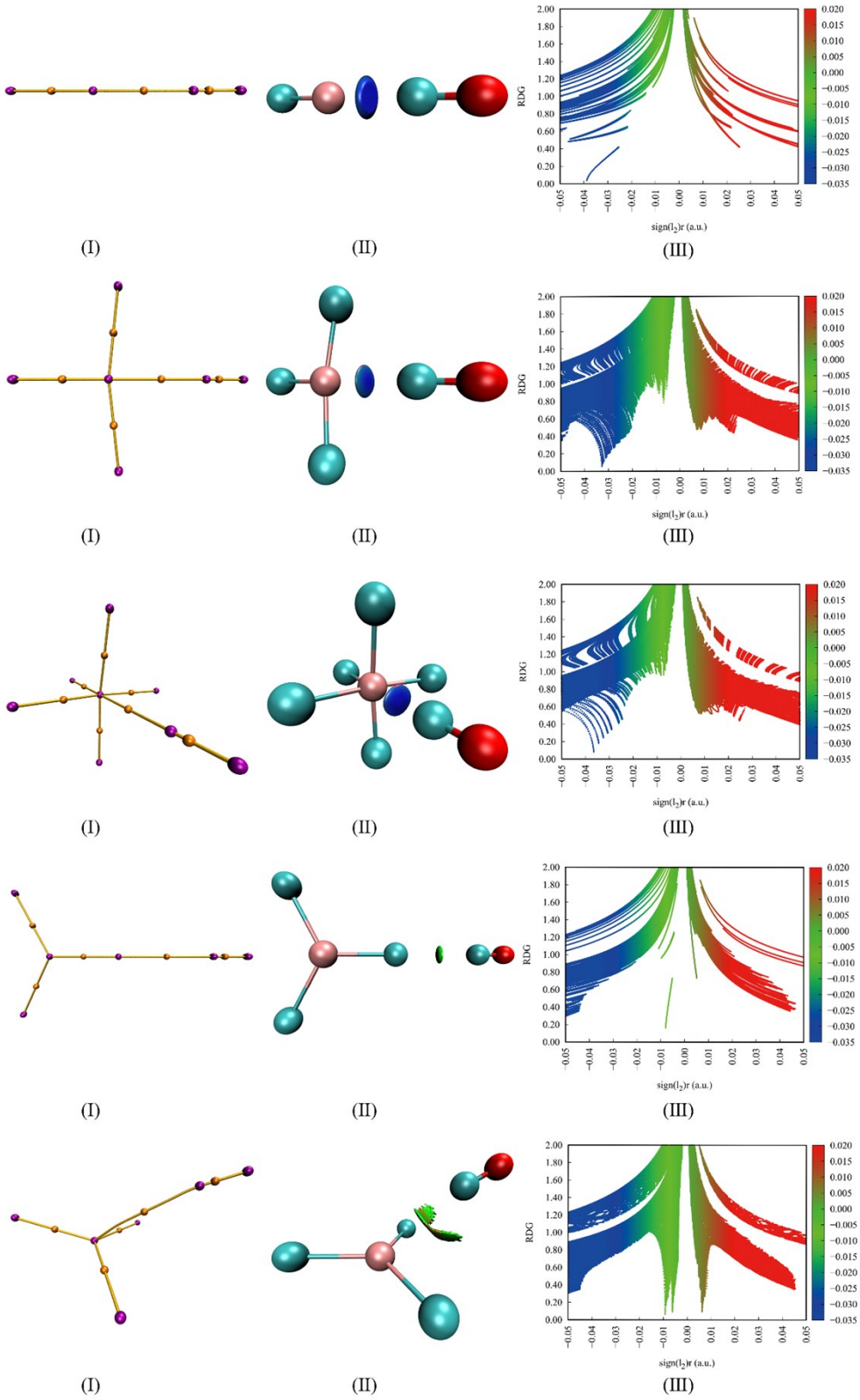

Fig. S5. The AIM diagram of the complexes and the RDG color-filled isosurface map with the scatter graphs.

Table S1. The Gibbs free energy of isolated AtX_n (X=F, Cl, Br, I; n= 3, 5) monomers.

Complex	ΔG (kcal/mol)	Complex	ΔG (kcal/mol)
AtF_3-D_3h	-16.03	AtF_5-Tb	-16.75
$AtCl_3$-D_3h	-19.44	$AtCl_5$- Tb	-21.04
$AtBr_3$-D_3h	-22.08	$AtBr_5$- Tb	-25.46
AtI_3-D_3h	-23.97	AtI_5- Tb	-28.68
AtF_3-T	-15.50	AtF_5-Sp	-14.45
$AtCl_3$-T	-19.27	$AtCl_5$-Sp	-21.19

Table S2. Natural bond orbital (NBO) analysis for all complexes at wB97XD/aug-cc-pVTZ level. Second-order perturbation energy ($E^{(2)}$, kcal/mol), charge transfer value (Δq), Wiberg bond indexes (WBI) and delocalization index (*DI*) on the intermolecular bond critical points.

Complex	Donor orbital	Acceptor orbital	$E^{(2)}$	Δq	WBI	*DI*
At···C						
AtF	LP C	σ*(At-F)	94.64	0.0604	0.6233	0.6387
AtCl	LP C	σ*(At-Cl)	43.83	0.0772	0.2932	0.3877
AtBr	LP C	σ*(At-Br)	32.55	0.0696	0.2142	0.3228
AtI	LP C	σ*(At-I)	20.18	0.0533	0.1287	0.2451
AtF_3-D_3h/T	LP C	σ*(At-F)	22.26	0.0605	0.1543	0.2205
$AtCl_3$-D_3h/T	LP C	σ*(At-Cl)	33.21	0.0957	0.1640	0.2350
$AtBr_3$-D_3h	LP C	σ*(At-Br)	30.76	0.0898	0.1462	0.2290
AtI_3-D_3h	LP C	σ*(At-I)	24.50	0.0698	0.1116	0.2098
AtF_5-Tb	LP C	σ*(At-F)	2.18	0.0204	0.0449	0.1008
$AtCl_5$-Tb	LP C	σ*(At-Cl)	40.21	0.1194	0.1644	0.2022
$AtBr_5$-Tb	LP C	σ*(At-Br)	41.55	0.1106	0.1557	0.2138
AtI_5-Tb	LP C	σ*(At-I)	35.76	0.0813	0.1273	0.2133
At···O						
AtF	LP O	σ*(At-F)	6.47	0.0105	0.0352	0.1407
AtCl	LP O	σ*(At-Cl)	4.22	0.0082	0.0212	0.1121
AtBr	LP O	σ*(At-Br)	3.75	0.0071	0.0181	0.1061
AtI	LP O	σ*(At-I)	3.08	0.0053	0.0144	0.0981
AtF_3-D_3h/T	LP O	σ*(At-F)	2.47	0.0040	0.0191	0.0946
$AtCl_3$-D_3h/T	LP O	σ*(At-Cl)	5.66	0.0128	0.0224	0.0977
$AtBr_3$-D_3h	LP O	σ*(At-Br)	5.63	0.0119	0.0208	0.0955
AtI_3-D_3h	LP O	σ*(At-I)	4.06	0.0056	0.0145	0.0817
AtF_5-Tb	LP At	σ*(C-O)	0.53	0.0005	0.0108	0.0617
	LP O	σ*(At-F)	0.55	0.0006		
$AtCl_5$-Tb	LP O	σ*(At-Cl)	8.61	0.0194	0.0278	0.0932
$AtBr_5$-Tb	LP O	σ*(At-Br)	9.15	0.0155	0.0252	0.0902
AtI_5-Tb	LP O	σ*(At-I)	5.49	0.0035	0.0157	0.0762
X···C						
AtCl	LP C	σ*(At-Cl)	1.27	0.0056	0.0106	0.0728
AtBr	LP C	σ*(At-Br)	3.37	0.0145	0.0238	0.1063
AtI	LP C	σ*(At-I)	7.94	0.0280	0.0535	0.1571
$AtCl_3$-D_3h	LP Cl	σ*(C-O)	0.11	0.0001	0.0072	0.0520
	LP C	σ*(At-Cl)	0.10	0.0002		
$AtBr_3$-D_3h	LP C	σ*(At-Br)	0.65	0.0070	0.0115	0.0778
AtI_3-D_3h	LP C	σ*(At-I)	2.19	0.0141	0.0223	0.1037
$AtCl_3$-T	LP C	σ*(At-Cl)	1.90	0.0110	0.0158	0.0876
$AtCl_5$-Tb	LP C	σ*(At-Cl)	0.36	0.0044	0.0071	0.0634
$AtBr_5$-Tb	LP C	σ*(At-Br)	1.40	0.0107	0.0147	0.0873
AtI_5-Tb	LP C	σ*(At-I)	3.83	0.0211	0.0306	0.1174

$AtCl_5$-Sp	LP C	σ*(At-Cl)	3.27	0.0160	0.0200	0.1000
X···O						
AtCl	LP O	σ*(At-Cl)	0.35	0.0004	0.0041	0.0499
AtBr	LP O	σ*(At-Br)	0.79	0.0013	0.0061	0.0619
AtI	LP O	σ*(At-I)	1.56	0.0025	0.0092	0.0800
$AtCl_3$-D_3h	LP Cl	σ*(C-O)	0.13	0.0003	0.0030	0.0452
$AtBr_3$-D_3h	LP Br	σ*(C-O)	0.15	0.0001	0.0043	0.0514
	LP O	σ*(At-Br)	0.17	0.0003		
AtI_3-D_3h	LP O	σ*(At-I)	0.42	0.0002	0.0054	0.0610
$AtCl_3$-T	LP O	σ*(At-Cl)	0.39	0.0007	0.0045	0.0523
$AtCl_5$-Tb	LP Cl	σ*(C-O)	0.14	0.0001	0.0031	0.0449
	LP O	σ*(At-Cl)	0.14	0.0002		
$AtBr_5$-Tb	LP O	σ*(At-Br)	0.35	0.0002	0.0047	0.0546
AtI_5-Tb	LP O	σ*(At-I)	0.68	0.0009	0.0063	0.0649
$AtCl_5$-Sp	LP O	σ*(At-Cl)	0.50	0.0011	0.0044	0.0544
π (At)···C						
$AtBr_3$-D_3h	LP C	σ*(At-Br)	1.65	0.0025	0.0091	0.0675
AtI_3-D_3h	LP C	σ*(At-I)	1.10	0.0082	0.0074	0.0669
AtF_3-T	LP At	σ*(C-O)	0.42	0.0005	0.0120	0.0580
	LP C	σ*(At-F)	0.43	0.0010		
$AtCl_3$-T	LP C	σ*(At-Cl)	0.36	0.0049	0.0067	0.0630
π (At)···O						
$AtCl_3$-D_3h	LP At	σ*(C-O)	0.24	0.0003	0.0045	0.0438
	LP O	σ*(At-Cl)	0.27	0.0004		
$AtBr_3$-D_3h	LP At	σ*(C-O)	0.23	0.0003	0.0043	0.0461
	LP O	σ*(At-Br)	0.25	0.0004		
AtI_3-D_3h	LP At	σ*(C-O)	0.21	0.0002	0.0044	0.0480
	LP O	σ*(At-I)	0.26	0.0004		
AtF_3-T	LP At	σ*(C-O)	0.51	0.0022	0.0040	0.0398
$AtCl_3$-T	LP At	σ*(C-O)	0.39	0.0022	0.0036	0.0459

Table S3. Topological properties of the bond critical points obtained at MP2/aug-cc-pVTZ level. ρ_c is the electron density, $\Delta^2\rho_c$ is the laplacian of the electron density, H_c is the electron energy density, G_c is the electron kinetic energy density, and V_c is the electron potential energy density.

Complex	ρ_c	$\Delta^2\rho_c$	G_c	V_c	$-G_c/V_c$	H_c
At···C						
AtF	0.0640	0.1585	0.0563	-0.0730	0.7712	-0.0167
AtCl	0.0389	0.1024	0.0306	-0.0357	0.8571	-0.0050
AtBr	0.0323	0.0876	0.0247	-0.0274	0.9015	-0.0028
AtI	0.0242	0.0689	0.0178	-0.0184	0.9674	-0.0006
AtF_3-D_3h/T	0.0285	0.0712	0.0196	-0.0214	0.9159	-0.0018
$AtCl_3$-D_3h/T	0.0328	0.0764	0.0223	-0.0256	0.8711	-0.0032
$AtBr_3$-D_3h	0.0318	0.0749	0.0216	-0.0246	0.8780	-0.0029
AtI_3-D_3h	0.0282	0.0692	0.0191	-0.0209	0.9139	-0.0018
AtF_5	0.0174	0.0447	0.0107	-0.0102	1.0490	0.0005
$AtCl_5$	0.0371	0.0717	0.0229	-0.0279	0.8208	-0.0050
$AtBr_5$	0.0382	0.0748	0.0241	-0.0295	0.8169	-0.0054
AtI_5	0.0353	0.0737	0.0227	-0.0269	0.8439	-0.0042
At···O						
AtF	0.0155	0.0720	0.0156	-0.0131	1.1908	0.0024
AtCl	0.0126	0.0553	0.0117	-0.0095	1.2316	0.0022
AtBr	0.0120	0.0516	0.0108	-0.0087	1.2414	0.0021
AtI	0.0111	0.0465	0.0097	-0.0077	1.2597	0.0019
AtF_3-D_3h/T	0.0140	0.0573	0.0122	-0.0100	1.2200	0.0022
$AtCl_3$-D_3h/T	0.0156	0.0631	0.0136	-0.0115	1.1826	0.0021
$AtBr_3$-D_3h	0.0152	0.0616	0.0133	-0.0111	1.1982	0.0021
AtI_3-D_3h	0.0125	0.0505	0.0106	-0.0086	1.2326	0.0020
AtF_5	0.0128	0.0487	0.0102	-0.0082	1.2439	0.0020
$AtCl_5$	0.0193	0.0723	0.0162	-0.0143	1.1329	0.0019
$AtBr_5$	0.0184	0.0709	0.0157	-0.0137	1.1460	0.0020
AtI_5	0.0137	0.0538	0.0114	-0.0094	1.2128	0.0020
X···C						
AtCl	0.0077	0.0303	0.0059	-0.0042	1.4048	0.0017
AtBr	0.0112	0.0389	0.0083	-0.0068	1.2206	0.0015
AtI	0.0155	0.0467	0.0107	-0.0097	1.1031	0.0010
$AtCl_3$-D_3h	0.0062	0.0220	0.0043	-0.0030	1.4333	0.0012
$AtBr_3$-D_3h	0.0080	0.0271	0.0054	-0.0041	1.3171	0.0013
AtI_3-D_3h	0.0100	0.0297	0.0063	-0.0052	1.2115	0.0011
$AtCl_3$-T	0.0101	0.0380	0.0077	-0.0059	1.3051	0.0018
$AtCl_5$	0.0069	0.0254	0.0048	-0.0033	1.4545	0.0015
$AtBr_5$	0.0094	0.0311	0.0064	-0.0050	1.2800	0.0014
AtI_5	0.0117	0.0339	0.0074	-0.0063	1.1746	0.0011

AtCl5-Sp	0.0121	0.0438	0.0092	-0.0073	1.2603	0.0018
X···O						
AtCl	0.0065	0.0311	0.0059	-0.0041	1.4390	0.0018
AtBr	0.0078	0.0344	0.0068	-0.0050	1.3600	0.0018
AtI	0.0092	0.0374	0.0076	-0.0059	1.2881	0.0017
$AtCl_3$-D_3h	0.0056	0.0236	0.0045	-0.0031	1.4516	0.0014
$AtBr_3$-D_3h	0.0064	0.0261	0.0051	-0.0037	1.3784	0.0014
AtI_3-D_3h	0.0069	0.0251	0.0051	-0.0039	1.3077	0.0012
$AtCl_3$-T	0.0072	0.0345	0.0066	-0.0046	1.4348	0.0020
$AtCl_5$	0.0060	0.0266	0.0051	-0.0035	1.4571	0.0016
$AtBr_5$	0.0070	0.0287	0.0057	-0.0042	1.3571	0.0015
AtI_5	0.0075	0.0277	0.0056	-0.0043	1.3023	0.0013
AtCl5-Sp	0.0078	0.0372	0.0072	-0.0051	1.4118	0.0021
π (At)···C						
$AtBr_3$-D_3h	0.0093	0.0272	0.0057	-0.0046	1.2391	0.0011
AtI_3-D_3h	0.0086	0.0251	0.0052	-0.0042	1.2381	0.0010
AtF_3-T	0.0090	0.0273	0.0057	-0.0046	1.2391	0.0011
$AtCl_3$-T	0.0089	0.0260	0.0055	-0.0044	1.2500	0.0011
π (At)···O						
$AtCl_3$-D_3h	0.0074	0.0269	0.0055	-0.0042	1.3095	0.0013
$AtBr_3$-D_3h	0.0073	0.0262	0.0053	-0.0041	1.2927	0.0012
AtI_3-D_3h	0.0069	0.0245	0.0049	-0.0038	1.2895	0.0012
AtF_3-T	0.0071	0.0268	0.0054	-0.0040	1.3500	0.0013
$AtCl_3$-T	0.0073	0.0258	0.0052	-0.0040	1.3000	0.0012

Table S4. Energy decomposition of the I-substituted sample complexes on MP2/aug-cc-pVTZ level. All the values are in kcal/mol.

Complex	ΔE_{ele}	ΔE_{ex}	ΔE_{rep}	$\Delta E_{ex}+\Delta E_{rep}$	ΔE_{pol}	ΔE_{disp}	ΔE_{int}
At···C							
AtI	-14.29	-35.05	65.05	30.00	-9.82	-10.24	-4.36
AtI_3-D_3h	-18.96	-47.71	89.79	42.08	-13.11	-14.66	-4.64
AtI_5-Tb	-29.69	-77.59	148.58	70.99	-20.16	-26.94	-5.80
At···O							
AtI	-4.35	-8.97	16.06	7.09	-1.80	-1.82	-0.88
AtI_3-D_3h	-6.06	-13.61	24.58	10.97	-2.67	-3.60	-1.36
AtI_5	-7.68	-20.26	36.85	16.59	-3.53	-9.18	-3.80
X···C							
AtI	-4.86	-11.94	20.87	8.93	-2.29	-3.90	-2.12
AtI_3-D_3h	-2.51	-7.38	12.54	5.16	-1.02	-2.47	-0.84
AtI_5	-3.27	-9.46	16.29	6.83	-1.55	-2.23	-0.22
X···O							
AtI	-1.96	-3.85	6.75	2.90	-0.62	-1.41	-1.09
AtI_3-D_3h	-1.15	-3.24	5.63	2.39	-0.36	-1.43	-0.56
AtI_5	-1.44	-3.97	6.96	2.99	-0.51	-1.57	-0.54
π (At)···C							
AtI_3-D_3h	-3.75	-12.24	20.59	8.35	-1.55	-4.78	-1.74
π (At)···O							
AtI_3-D_3h	-2.41	-6.65	11.45	4.80	-0.68	-2.85	-1.15