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

Supplementary Information: In-depth theoretical understanding of the chemical interaction of aromatic compounds with a gold nanoparticle

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Table S1 The Condensed Fukui Analysis of Au_{32}. The gold atoms are labeled as 5- and 6-coordinated.

Atom	f^-	f^+	f^0	Δf
Au(5)	0.028	0.047	0.037	0.020
Au(5)	0.028	0.047	0.038	0.019
Au(5)	0.028	0.047	0.037	0.019
Au(5)	0.028	0.047	0.037	0.019
Au(5)	0.027	0.047	0.037	0.020
Au(5)	0.027	0.047	0.037	0.020
Au(5)	0.028	0.047	0.038	0.019
Au(5)	0.028	0.047	0.037	0.019
Au(5)	0.028	0.047	0.038	0.019
Au(5)	0.028	0.047	0.037	0.020
Au(5)	0.027	0.047	0.037	0.020
Au(5)	0.028	0.047	0.037	0.020
Au(6)	0.034	0.022	0.028	-0.011
Au(6)	0.017	0.023	0.020	0.005
Au(6)	0.033	0.022	0.028	-0.011
Au(6)	0.033	0.022	0.027	-0.012
Au(6)	0.033	0.022	0.028	-0.011
Au(6)	0.017	0.023	0.020	0.005
Au(6)	0.033	0.022	0.028	-0.011
Au(6)	0.034	0.022	0.028	-0.011
Au(6)	0.033	0.022	0.027	-0.011
Au(6)	0.040	0.021	0.031	-0.019
Au(6)	0.033	0.022	0.027	-0.011
Au(6)	0.032	0.021	0.027	-0.011
Au(6)	0.040	0.021	0.031	-0.019
Au(6)	0.032	0.021	0.027	-0.011
Au(6)	0.032	0.021	0.027	-0.011
Au(6)	0.040	0.021	0.031	-0.019
Au(6)	0.032	0.021	0.027	-0.011
Au(6)	0.040	0.021	0.030	-0.019
Au(6)	0.040	0.021	0.030	-0.019
Au(6)	0.039	0.021	0.030	-0.018

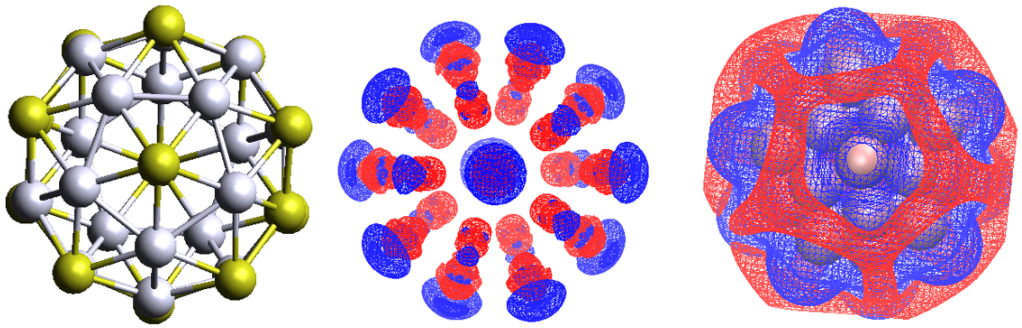

Fig. S1 The reactivity descriptors of Au_{32}:(left) geometry of Au_{32} with the yellow balls representing the five-coordinated gold atoms and the silver balls representing the six-coordinated gold atoms, (middle) dual descriptor $\Delta f(r)$ Fukui function and (right) molecular electrostatic potential, with blue lobes corresponding to electrophilic sites and red lobes corresponding to nucleophilic sites.

Table S2 Evaluation of the dependence of basis set superposition error (BSSE) in kcal/mol calculated with Counterpoise method on choice of basis set and the uncorrected interaction energies, in kcal/mol, of the complexes calculated with either the LC-RECP and SC-RECP.

Complexes	SC-def2-SVP E_{int}	BSSE	SC-def2-TZVP E_{int}	BSSE	LC-DZVP Uncorrected E_{int}	SC-DZVP Uncorrected E_{int}	SC-TZVP Uncorrected E_{int}
Flat							
Benzene	-9.1	-3.9	-9.3	-2.3	-14.7	-9.7	-9.9
Benzoic Acid	-10.3	-7.3	-8.0	-3.6	-17.8	-9.8	-10.4
Acetophenone	-11.4	-6.8	-9.1	-3.0	-18.4	-10.1	-10.23
Ethyl Benzoate	-10.6	-5.5	-9.9	-3.0	-18.3	-11.5	-11.7
Toluene	-10.8	-4.5	-10.5	-2.6	-17.7	-11.7	-11.9
Phenol	-12.2	-6.1	-10.6	-2.9	-16.6	-11.8	-12.3
Aniline	-15.2	-6.2	-13.6	-3.0	-19.7	-15.1	-15.5
Thiophenol	-16.2	-6.9	-14.9	-3.3	-20.9	-15.6	-15.4
Perpendicular							
Toluene	1.4	-1.8	1.4	-1.0	-9.5	1.0	0.9
Acetophenone	0.3	-2.2	0.3	-1.4	-10.8	-0.1	-0.7
Benzoic Acid	-13.9	-6.1	-10.7	-1.9	-15.0	-11.1	-11.8

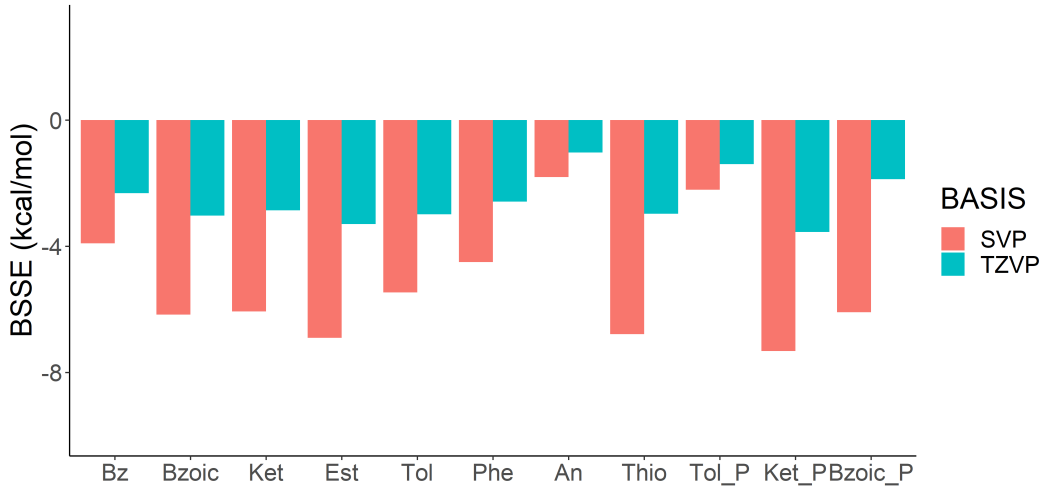

Fig. S2 BSSE estimates for SC-RECP associated with SVP or TZVP basis set.

Table S3 Energies of the complexes and fragments using SC-RECP and DZVP basis sets, along with the interaction energies and adsorption energies. "fr" stands for a frozen geometry of the fragments in the geometry of the complex. "opt" stands for an optimized geometry of the fragments.

Complexes	Total Energy (Ha)	E_{Au-fr} (Ha)	E_{Au-opt} (Ha)	E_{Org-fr} (Ha)	$E_{Org-opt}$ (Ha)	E_{Int} (kcal/mol)	E_{Ads} (kcal/mol)
Flat							
Benzene	-4582.8874	-4350.9346	-4350.9383	-231.9372	-231.9378	-9.8	-7.1
Benzoic Acid	-4771.3002	-4350.9333	-4350.9383	-420.3513	-420.3538	-9.8	-5.1
Acetophenone	-4735.3721	-4350.9333	-4350.9383	-384.4226	-384.4246	-10.2	-5.8
Ethyl Benzoate	-4849.7974	-4350.9343	-4350.9383	-498.8447	-498.8455	-11.6	-8.5
Toluene	-4622.1534	-4350.9348	-4350.9383	-271.2000	-271.2007	-11.8	-9.1
Phenol	-4658.0564	-4350.9348	-4350.9383	-307.1028	-307.1038	-11.9	-9.0
Aniline	-4638.2020	-4350.9345	-4350.9383	-287.2434	-287.2447	-15.2	-12.0
Thiophenol	-4980.7903	-4350.9329	-4350.9383	-629.8323	-629.8333	-15.8	-11.8
Perpendicular							
Toluene	-4622.1342	-4350.9355	-4350.9383	-271.2003	-271.2007	1.1	3.0
Acetophenone	-4735.3596	-4350.9355	-4350.9383	-384.4240	-384.4246	-0.1	2.0
Benzoic Acid	-4771.3047	-4350.9343	-4350.9383	-420.3526	-420.3538	-11.2	-7.9

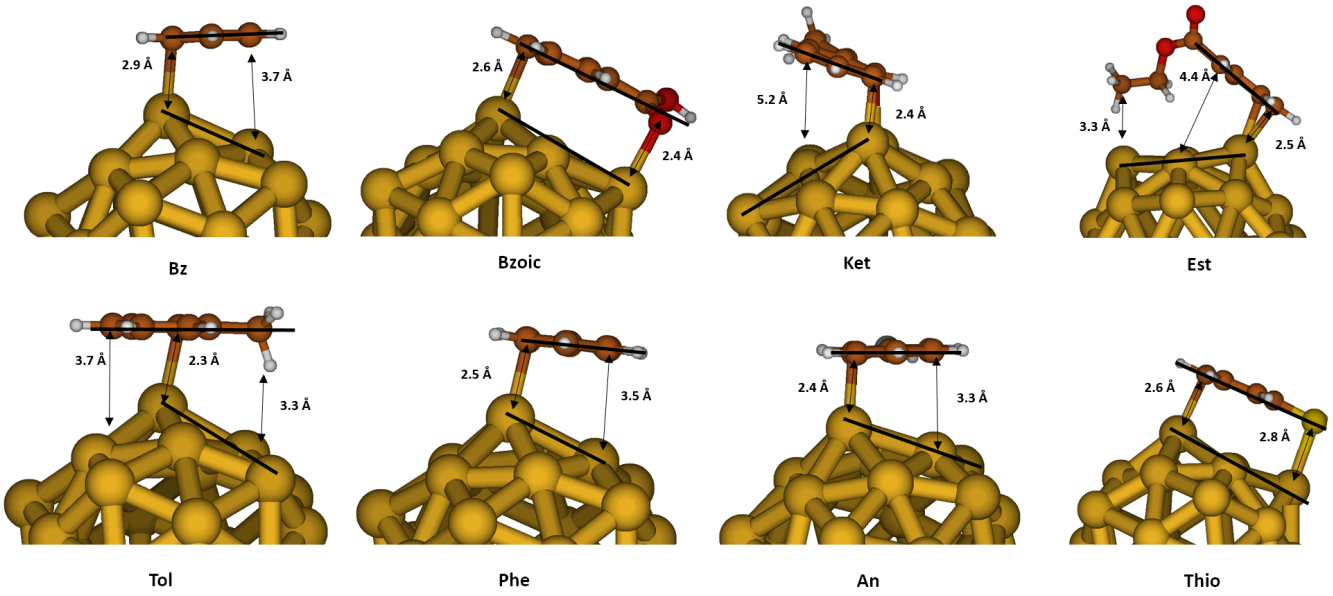

Fig. S3 A closer look at the geometry of the aromatic compounds on the surface of GNP: benzene, benzoic acid, acetophenone, ethyl benzoate, toluene, phenol, aniline, and thiophenol, with their respective distances of Au-C or Au-H, respectively. The black lines are guide for the eyes to highlight the planar region.

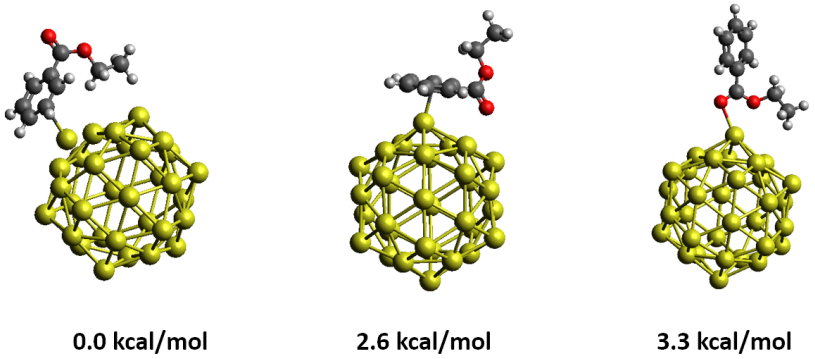

Fig. S4 Optimized configurations of ethyl benzoate and their relative electronic energy.

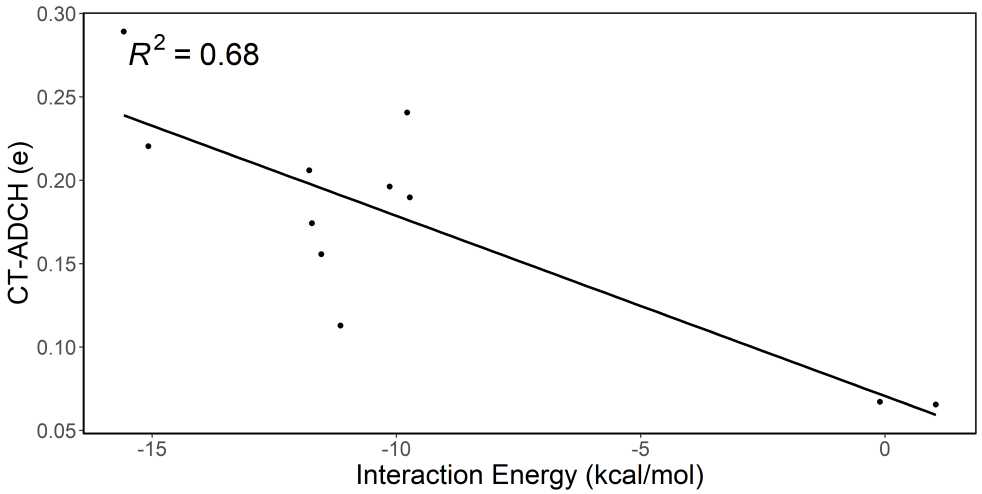

Fig. S5 Correlation of interaction energy and charge transfer as calculated using the ADCH scheme.

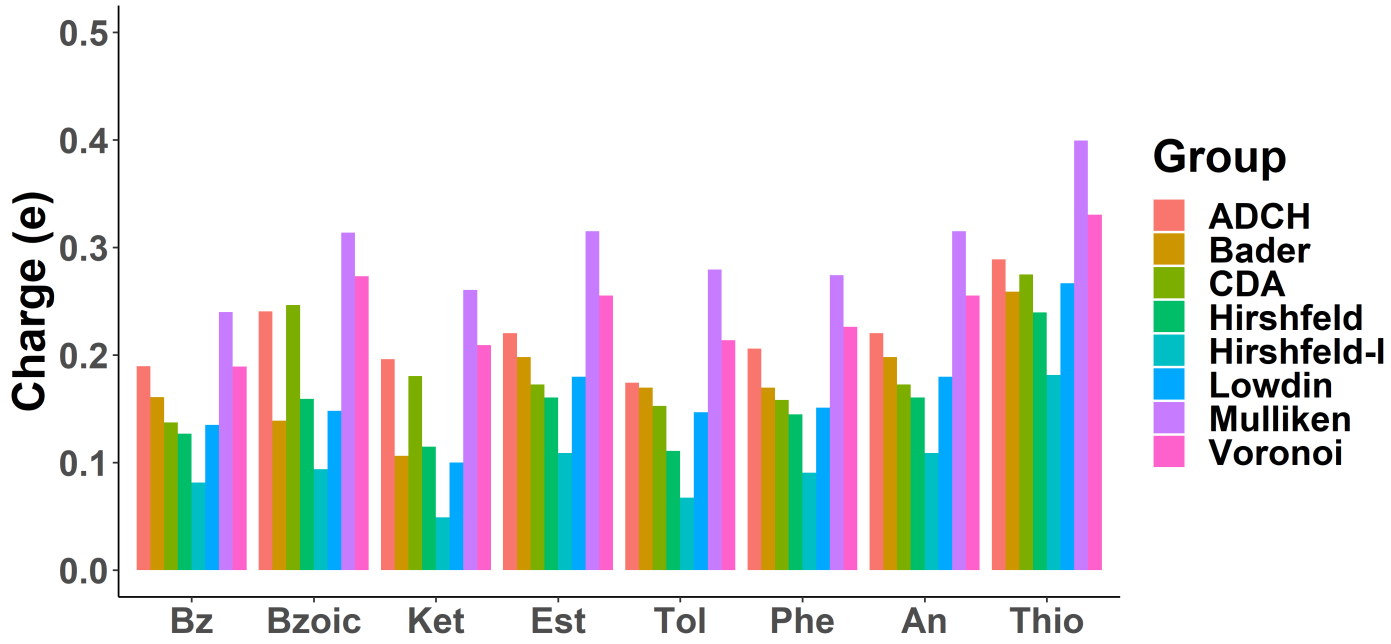

Fig. S6 Charge transfer values between GNP and aromatic fragments, calculated with different populations schemes for flat configurations.

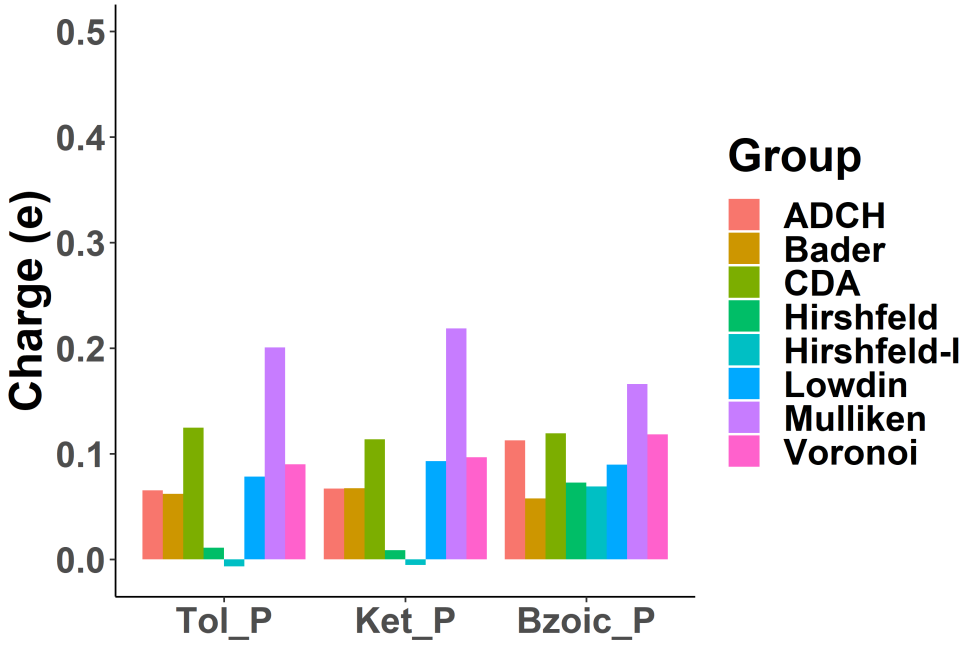

Fig. S7 Charge transfer values between GNP and aromatic fragments, calculated with different populations schemes for perpendicular configurations.

Table S4 Charge Decomposition Analysis framework applied to each of the complex to obtain donation (d), back-donation (b), d−b, polarization, re-arranged electrons, extended CDA (ECDA).

Complex	donation	back-donation	d−b	r (polarization)	re-arranged electron	ECDA
Flat						
Benzene	0.053	-0.085	0.137	-0.475	0.612	0.240
Benzoic Acid	0.104	-0.143	0.247	-0.693	0.939	0.314
Acetophenone	0.057	-0.124	0.180	-0.601	0.781	0.261
Ethyl Benzoate	0.055	-0.102	0.157	-0.591	0.748	0.283
Toluene	0.052	-0.101	0.153	-0.537	0.690	0.280
Phenol	0.064	-0.095	0.158	-0.506	0.664	0.274
Aniline	0.073	-0.099	0.172	-0.554	0.726	0.316
Thiophenol	0.136	-0.139	0.275	-0.783	1.058	0.399
Perpendicular						
Toluene	-0.008	-0.133	0.125	-0.286	0.411	0.201
Acetophenone	-0.022	-0.136	0.114	-0.320	0.434	0.218
Benzoic Acid	0.068	-0.051	0.119	-0.286	0.405	0.166

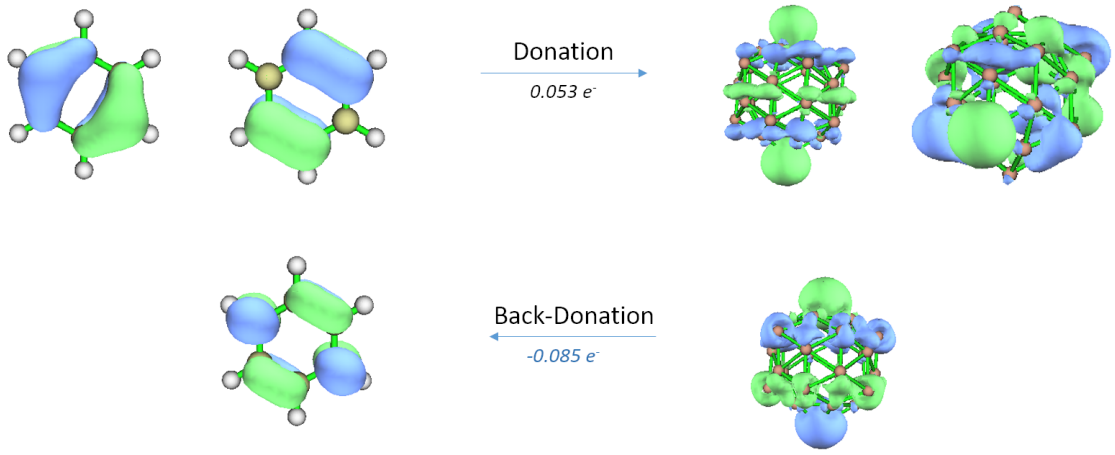

Fig. S8 The interacting molecular orbitals of benzene and GNP as obtained within Charge Decomposition Analysis (CDA) framework.

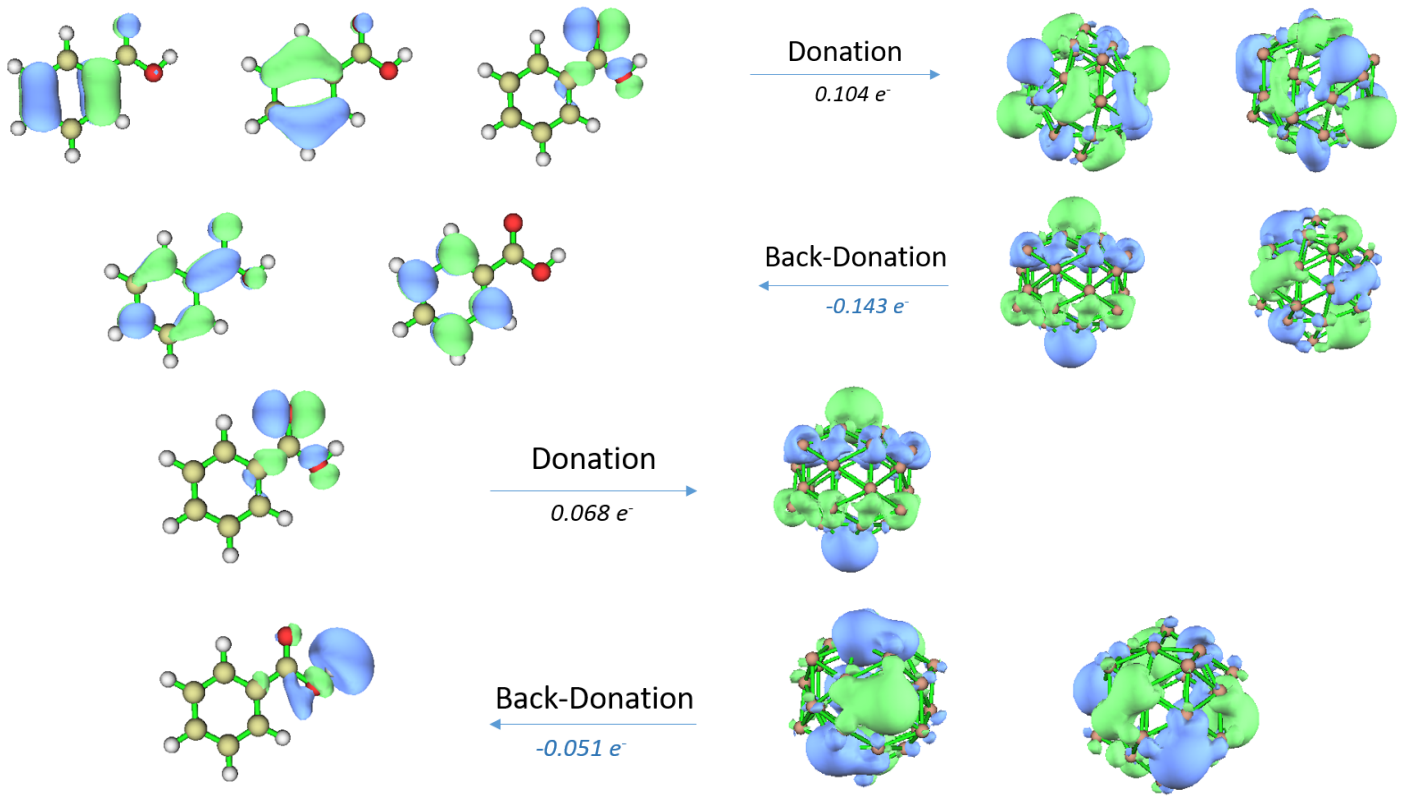

Fig. S9 The interacting molecular orbitals of benzoic acid and GNP adopting either flat (top) or perpendicular (bottom) configuration, as obtained within CDA framework.

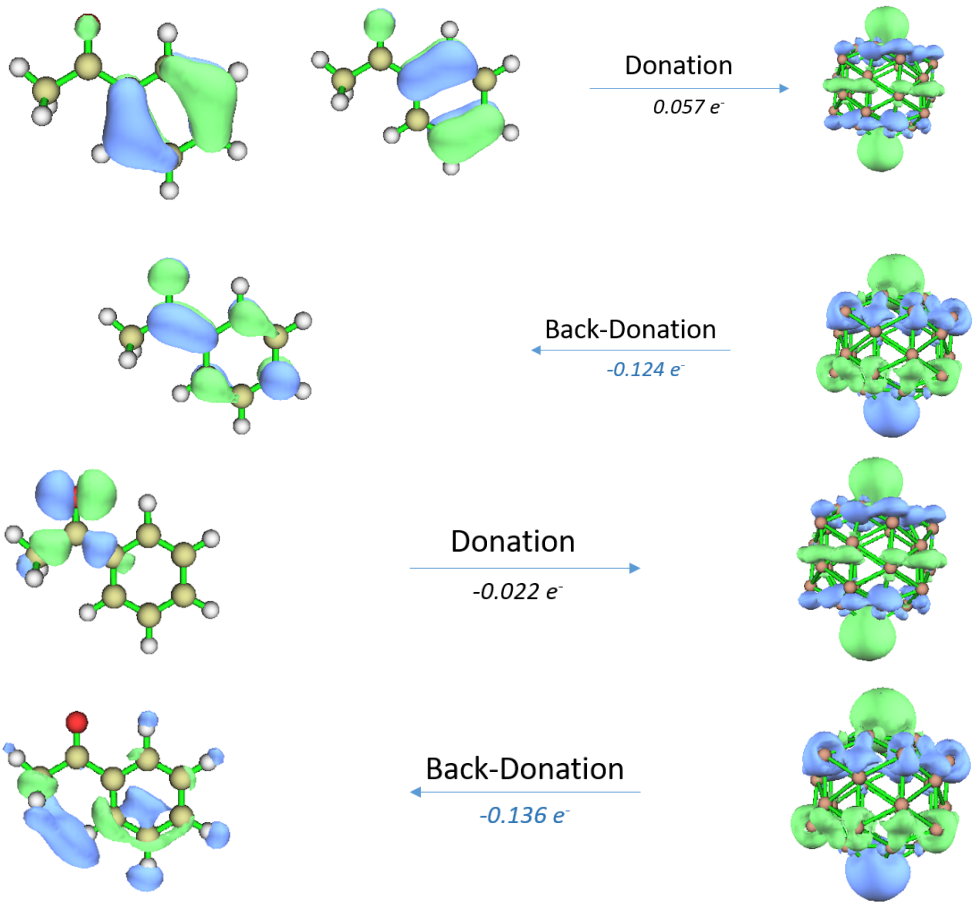

Fig. S10 The interacting molecular orbitals of acetophenone and GNP adopting either flat (top) or perpendicular (bottom) configuration, as obtained within CDA framework.

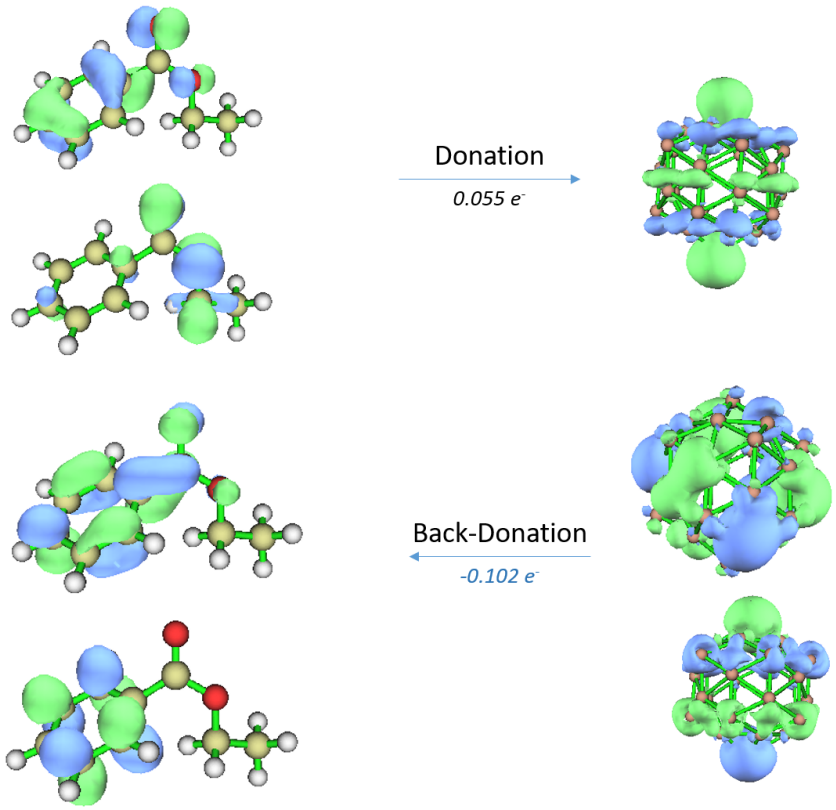

Fig. S11 The interacting molecular orbitals of ethyl benzoate and GNP, as obtained within CDA framework.

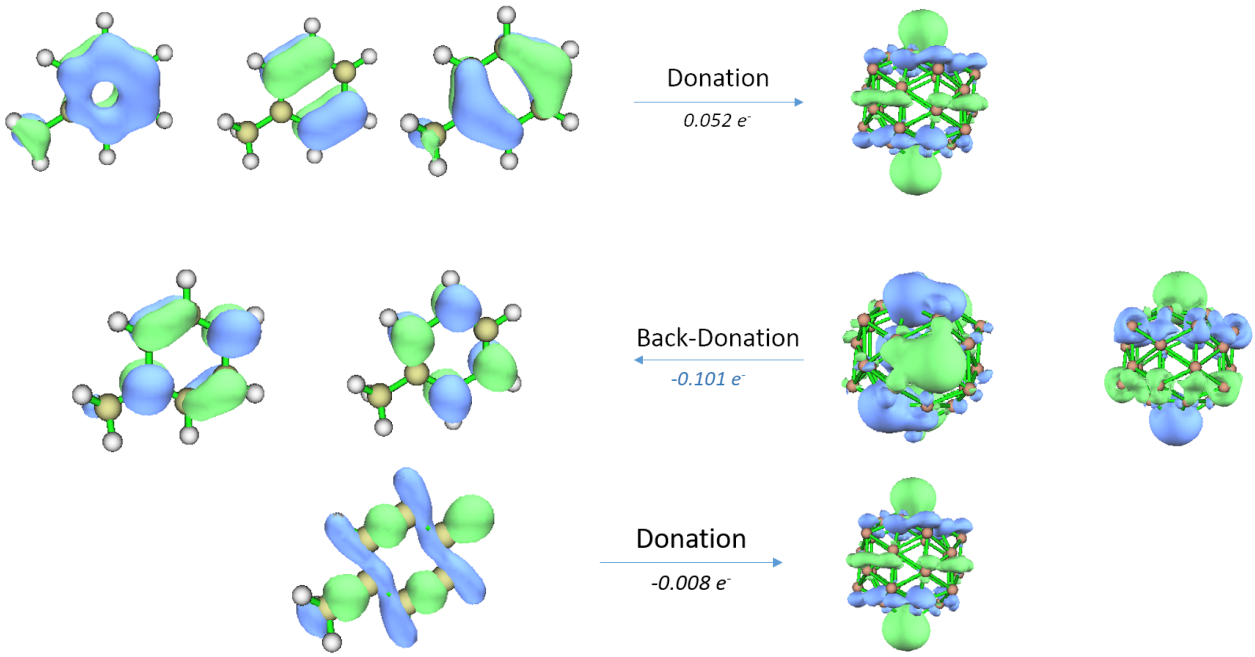

Fig. S12 The interacting molecular orbitals of toluene and GNP adopting either flat (top) or perpendicular (bottom) configuration, as obtained within CDA framework.

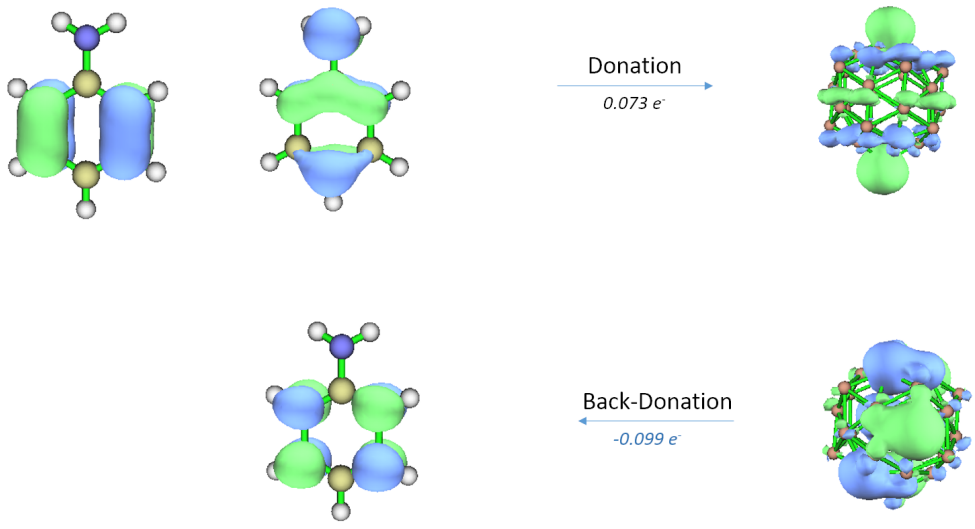

Fig. S13 The interacting molecular orbitals of aniline and GNP, as obtained within CDA framework.

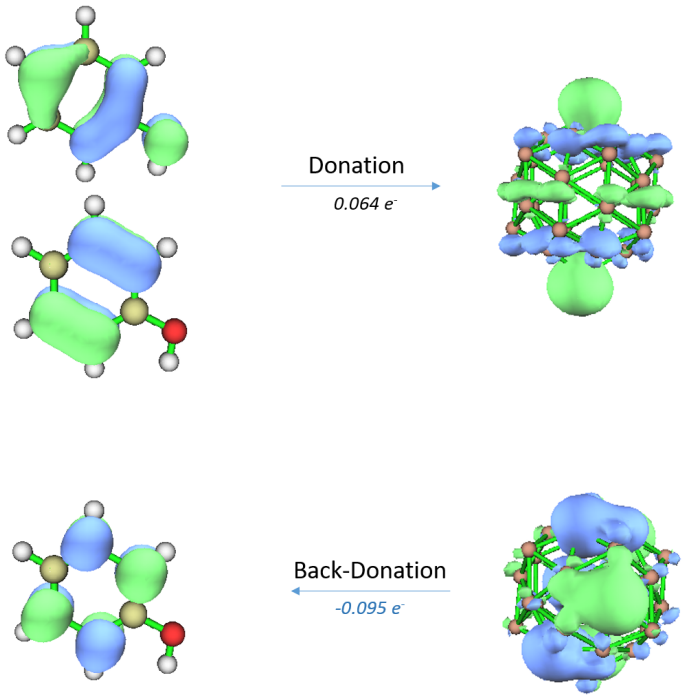

Fig. S14 The interacting molecular orbitals of phenol and GNP, as obtained within CDA framework.

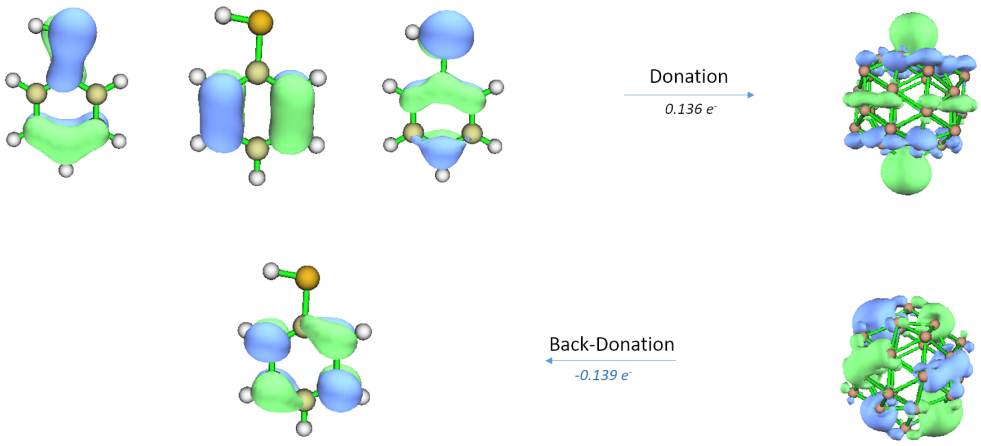

Fig. S15 The interacting molecular orbitals of thiophenol, as obtained within CDA framework

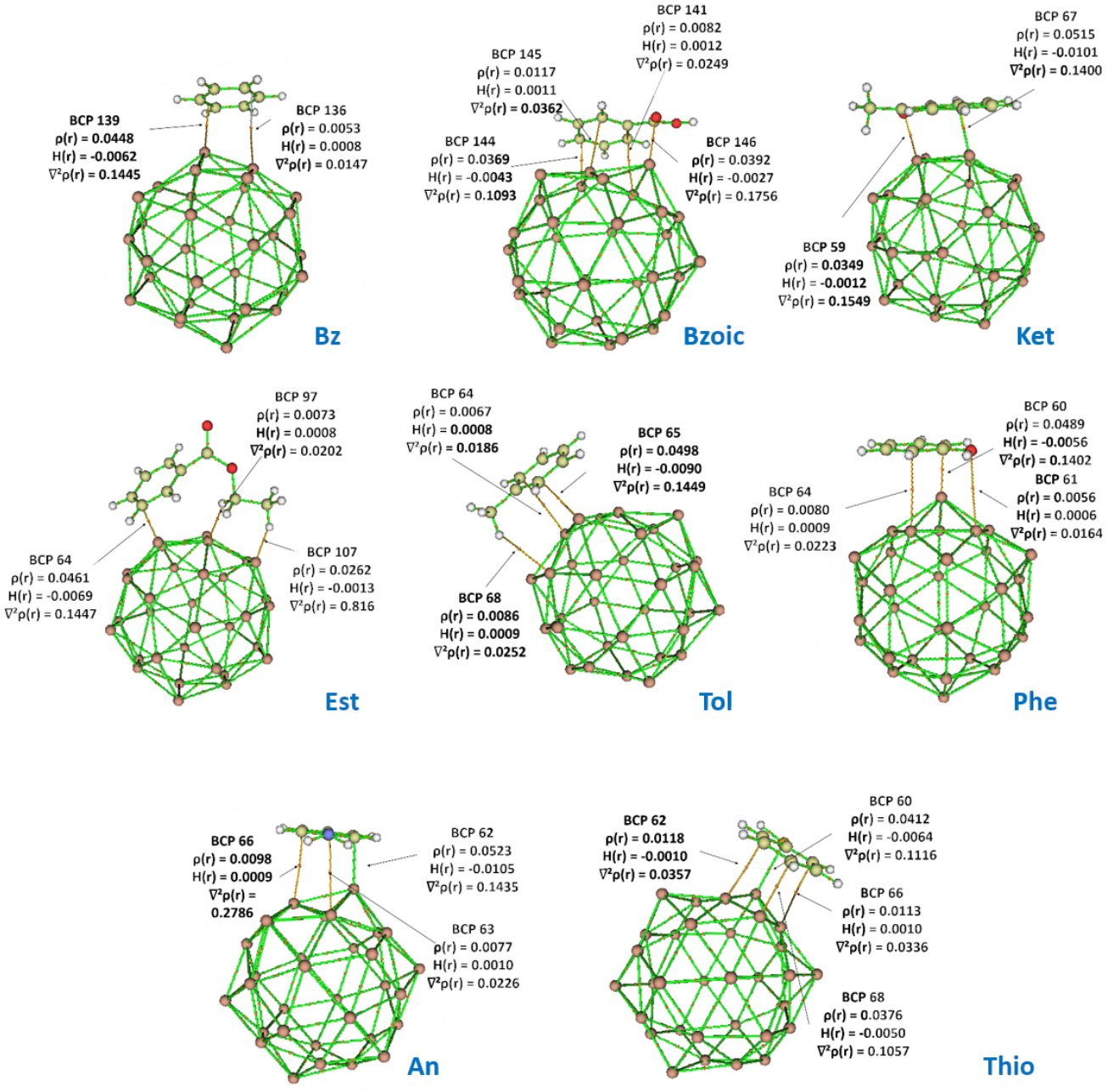

Fig. S16 BCPs calculated within the QTAIM, along with the values of local properties, for flat configurations

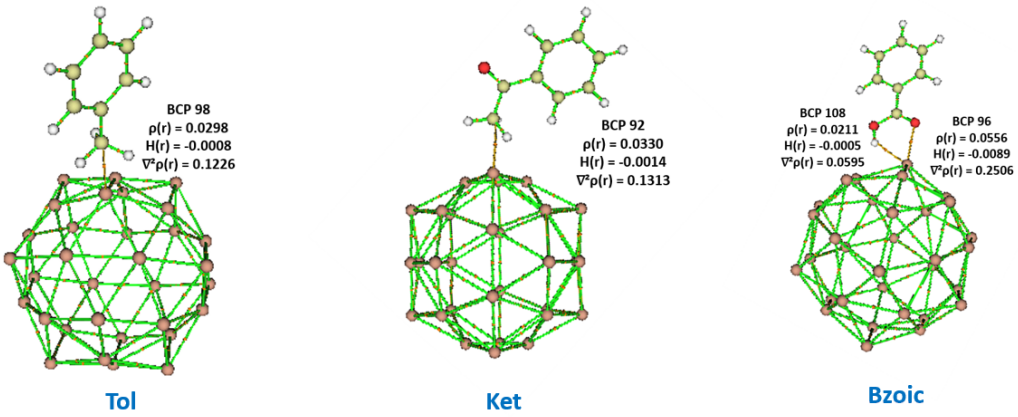

Fig. S17 BCPs calculated within the QTAIM, along with the values of local properties, for perpendicular configurations

Table S5 Electron density, Laplacian of electron density and energy density values at respective BCPs.

Compounds	BCP	Electron density (a.u.)	Laplacian (a.u.)	H(rho)	Characterization
Flat					
Benzene	BCP-136	0.0053	0.0147	0.0008	Dispersive
	BCP-139	0.0448	0.1445	-0.0062	Dative
Benzoic Acid	BCP-141	0.0082	0.0249	0.0012	Dispersive
	BCP-144	0.0369	0.1093	-0.0043	Dative
	BCP-145	0.0117	0.0362	0.0011	Dispersive
	BCP-146	0.0392	0.1756	-0.0027	Dative
Acetophenone	BCP-59	0.0349	0.1549	-0.0012	Dative
	BCP-67	0.0515	0.1400	-0.0101	Dative
Ethylbenzoate	BCP-64	0.0461	0.1447	-0.0069	Dative
	BCP-97	0.0073	0.0202	0.0008	Dispersive
	BCP-107	0.0262	0.816	-0.0013	Dative
Toluene	BCP-64	0.0067	0.0186	0.0008	Dispersive
	BCP-65	0.0498	0.1449	-0.0090	Dative
	BCP-68	0.0086	0.0252	0.0009	Dispersive
Phenol	BCP-60	0.0489	0.1402	-0.0056	Dative
	BCP-61	0.0056	0.0164	0.0006	Dispersive
	BCP-64	0.0080	0.0223	0.0009	Dispersive
Aniline	BCP-62	0.0523	0.1435	-0.0105	Dative
	BCP-63	0.0077	0.0226	0.0010	Dispersive
	BCP-66	0.0098	0.2786	0.0009	Dispersive
Thiophenol	BCP-60	0.0412	0.1116	-0.0064	Dative
	BCP-62	0.0118	0.0357	-0.0010	Dative
	BCP-66	0.0113	0.0336	0.0010	Dispersive
	BCP-68	0.0376	0.1057	-0.0050	Dative
Perpendicular					
Toluene	BCP-98	0.0298	0.1226	-0.0008	Dative
Acetophenone	BCP-92	0.0330	0.1313	-0.0014	Dative
Benzoic Acid	BCP-96	0.0556	0.2506	-0.0089	Dative
	BCP-108	0.0211	0.0595	-0.0005	Dative

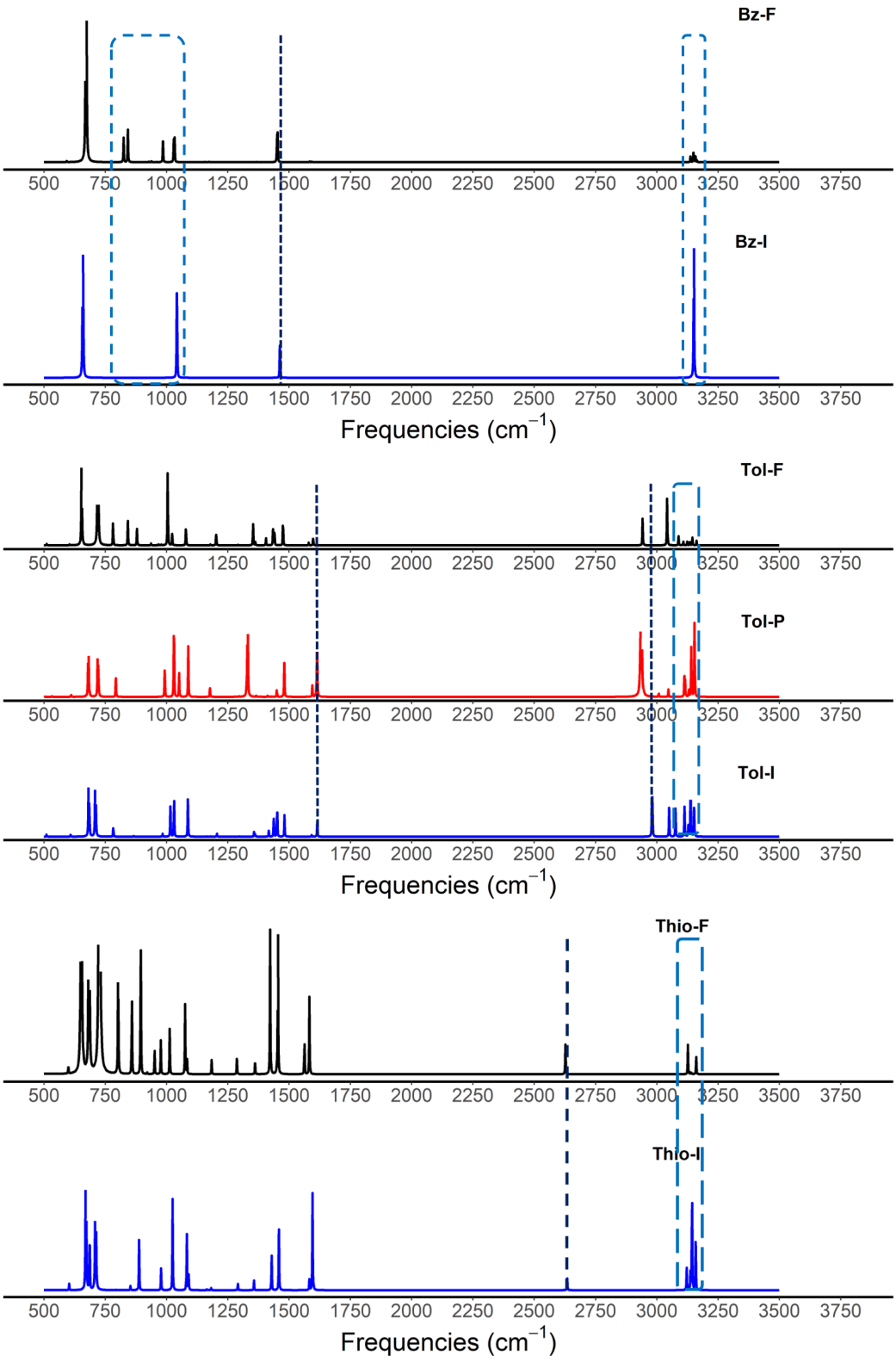

Fig. S18 IR spectra of organic compounds in both isolated (I in blue) and adsorbed state (F/P): benzene, toluene, and thiophenol, respectively. "F" (in black) and "P" (in red) stand for flat and perpendicular configurations, respectively.

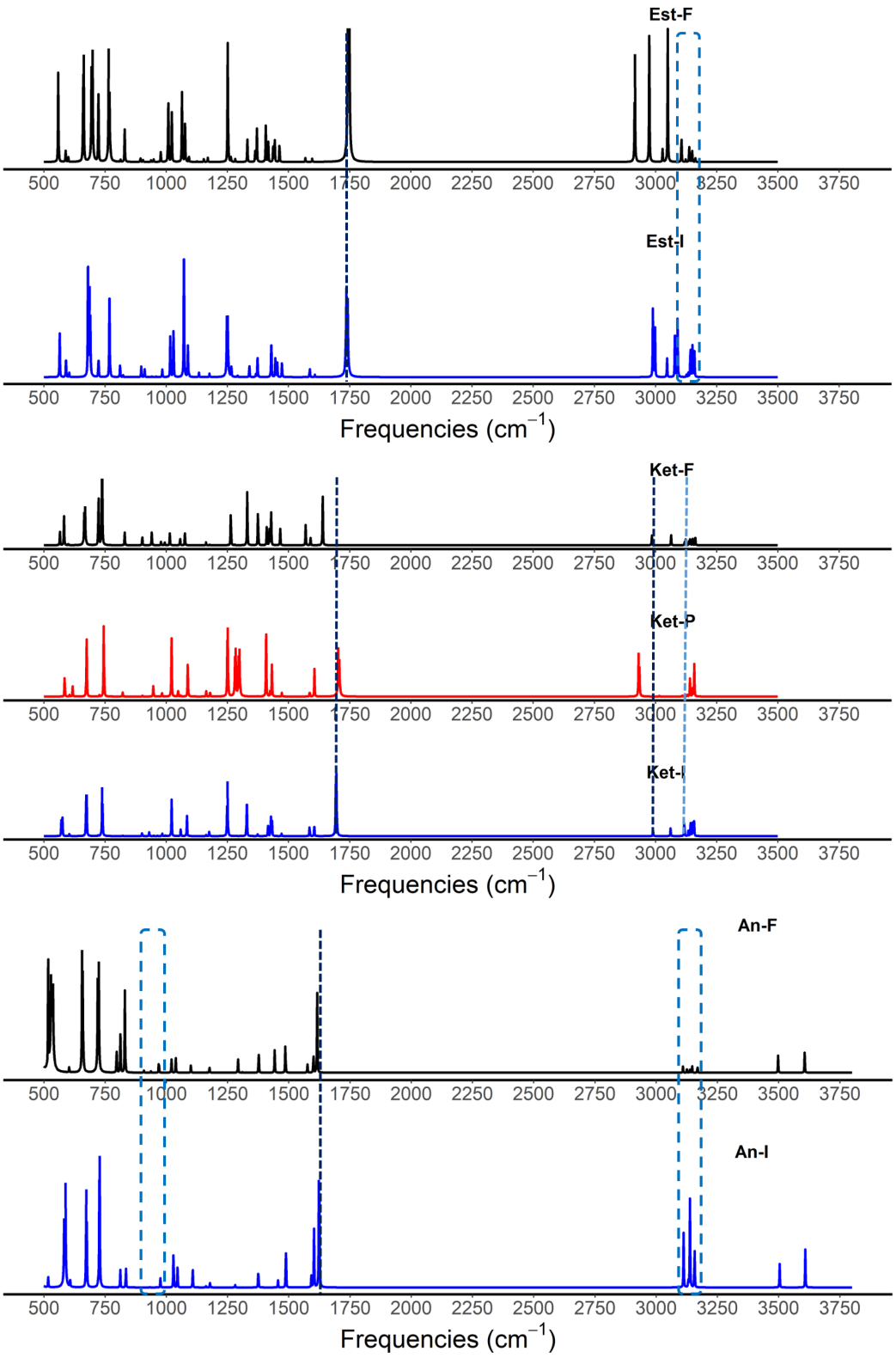

Fig. S19 IR spectra of aromatic compounds in both isolated (I in blue) and adsorbed (F/P) states: ethylbenzoate, acetophenone, and aniline, respectively. "F" (in black) and "P" (in red stand for flat and perpendicular configurations, respectively.

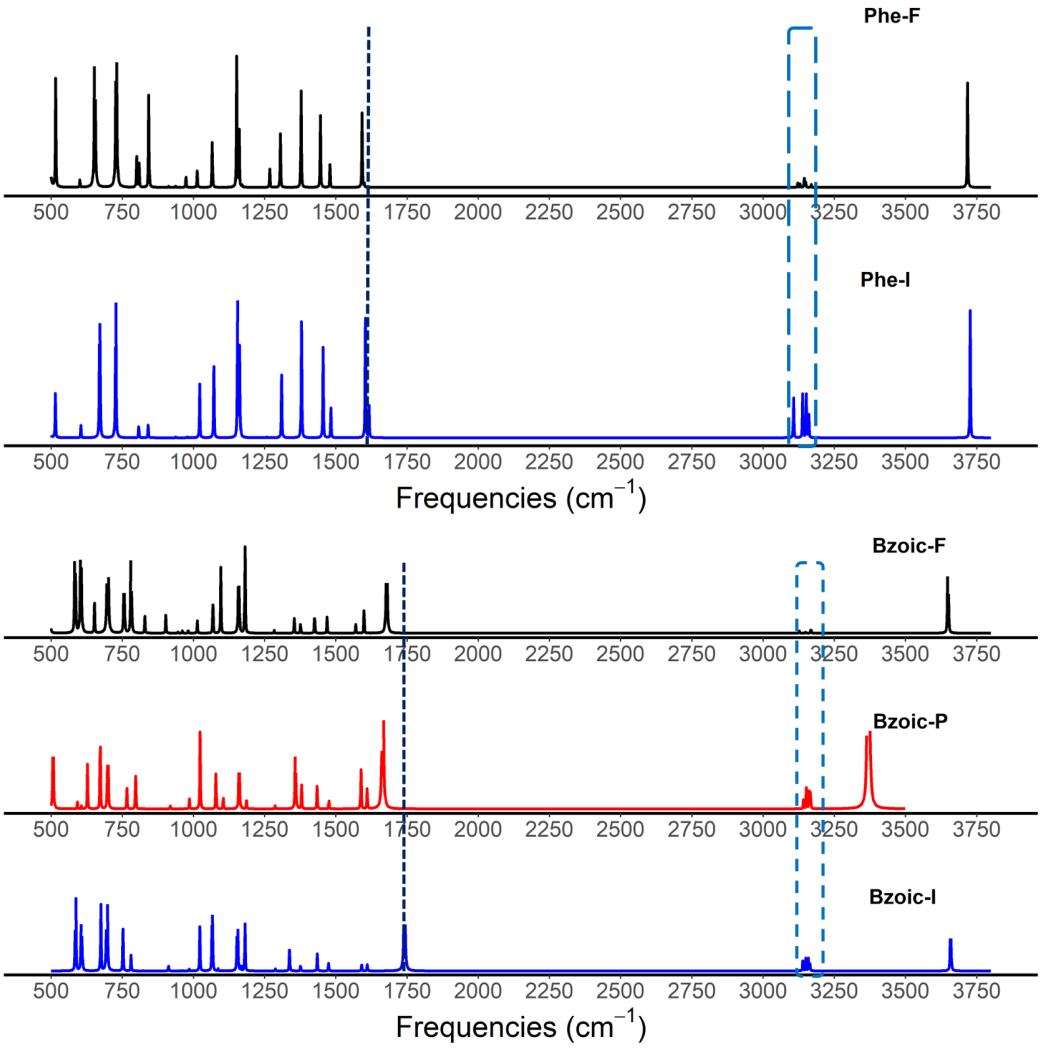

Fig. S20 IR spectra of aromatic compounds in both isolated (I in blue) and adsorbed (F/P) states: phenol and benzoic acid, respectively. "F" (in black) and "P" (in red) stand for flat and perpendicular configurations, respectively.

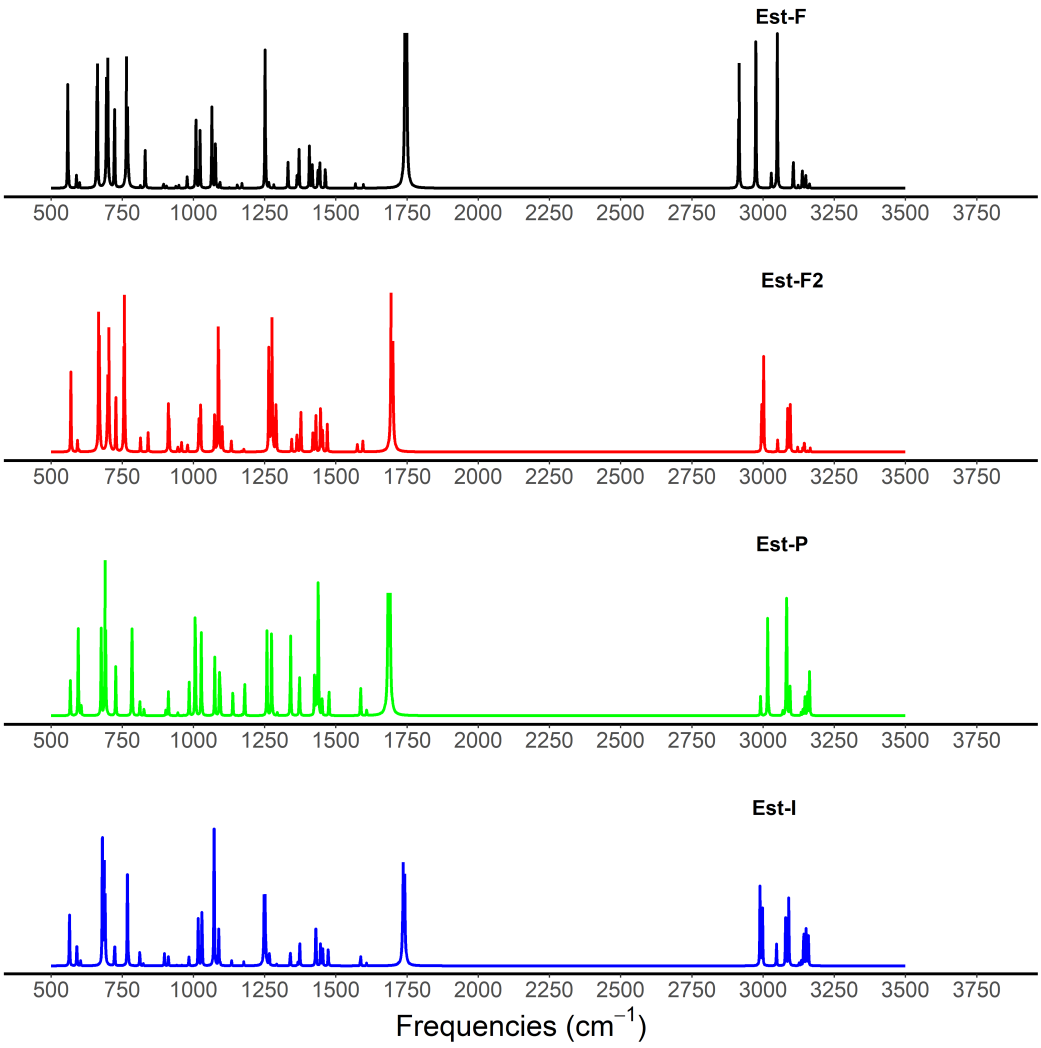

Fig. S21 IR spectra of the different conformations of ethyl benzoate: isolated (I in blue) and adsorbed (F/P) states. "F" and "F2" (in black and red) and "P" (in green) stand for flat and perpendicular configurations, respectively.

Table S6 Integration of NCI basins for the interaction between Au_{32} and aromatic compound.

Compounds	Dative	Dispersive	Repulsive	Volume
Flat				
Benzene	4.05	32.11	12.05	67.30
Benzoic Acid	10.29	33.71	15.17	102.70
Acetophenone	9.79	25.30	9.02	71.67
Ethyl Benzoate	6.95	44.64	8.91	79.62
Toluene	5.38	40.22	9.06	77.78
Phenol	5.44	36.74	9.95	74.98
Aniline	6.10	38.33	11.18	84.16
Thiophenol	20.32	25.49	16.13	113.38
Perpendicular				
Toluene	4.65	0.14	2.73	17.67
Acetophenone	3.94	5.79	3.39	23.37
Benzoic Acid	3.85	5.31	3.62	24.78

Table S7 BLW-EDA decomposition of the interaction energy (kcal/mol) between Au_{32} and aromatic compounds.

Compounds	Frozen Term	Polarization Energy	Charge Transfer Energy	Interaction Energy
Flat				
Benzene	18.44	-7.72	-23.03	-12.31
Benzoic Acid	21.38	-9.35	-25.29	-13.25
Acetophenone	27.24	-10.71	-29.16	-12.63
Ethyl Benzoate	22.77	-8.25	-28.52	-14.00
Toluene	19.03	-8.52	-25.36	-14.85
Phenol	17.74	-8.05	-23.85	-14.16
Aniline	18.91	-9.50	-26.77	-17.36
Thiophenol	22.58	-9.01	-33.23	-19.66
Perpendicular				
Toluene	11.91	-2.82	-7.54	1.54
Acetophenone	13.00	-3.35	-9.84	-0.20
Benzoic Acid	16.53	-10.08	-16.29	-9.84

Table S8 SAPT decomposition of the interaction energy (kcal/mol) between Au_{32} and aromatic compounds.

Compounds	Electrostatic Energy	Exchange Energy	Dispersion Energy	Induction Energy	SAPT
Flat					
Benzene	-35.80	60.80	-35.21	-18.69	-28.90
Benzoic Acid	-50.90	85.74	-49.78	-20.58	-35.52
Acetophenone	-45.32	81.18	-42.16	-24.72	-31.01
Ethyl Benzoate	-38.28	71.37	-42.08	-21.35	-30.33
Toluene	-39.69	67.45	-40.36	-20.39	-32.99
Phenol	-38.60	65.03	-38.30	-19.30	-31.16
Aniline	-44.08	71.96	-42.11	-21.57	-35.79
Thiophenol	-57.16	92.04	-53.39	-23.34	-41.85
Perpendicular					
Toluene	-11.76	26.74	-13.33	-5.52	-3.87
Acetophenone	-12.92	30.14	-15.62	-6.62	-5.02
Benzoic Acid	-29.59	47.36	-17.69	-16.02	-15.94

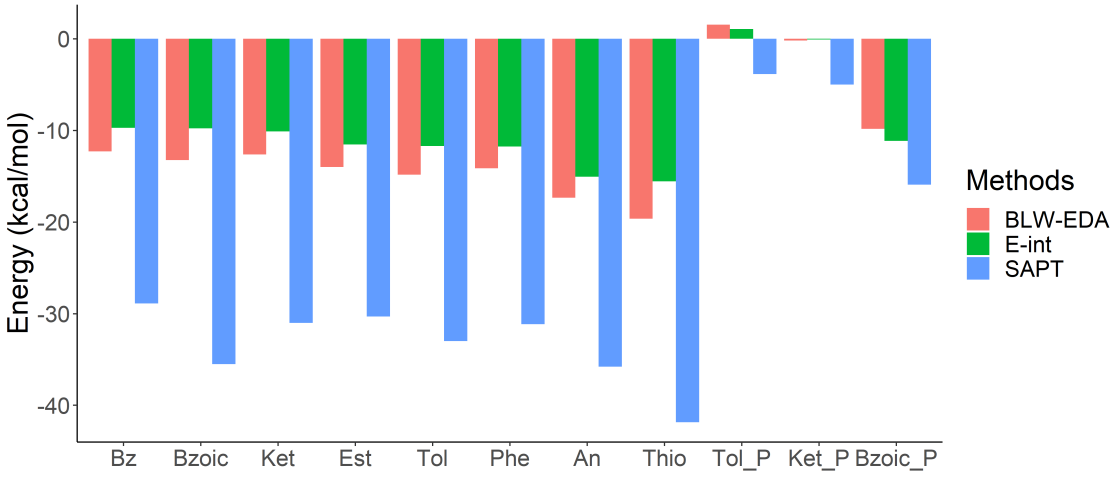

Fig. S22 Comparison between total BLW-EDA, interaction energy, and total SAPT.

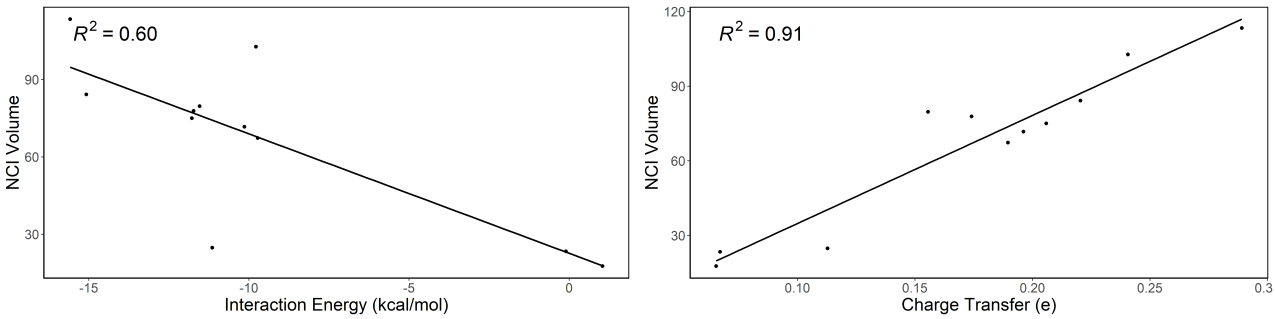

Fig. S23 Correlation between the volume of NCI basins with interaction energy (left) and ADCH charge transfer (right)

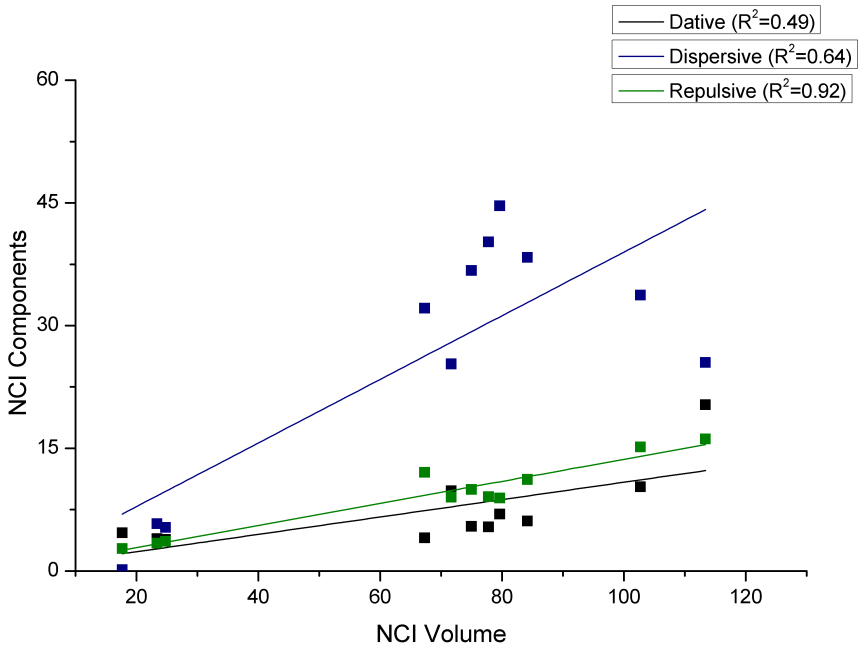

Fig. S24 Correlation of the three NCI basin components with the NCI basin volumes.

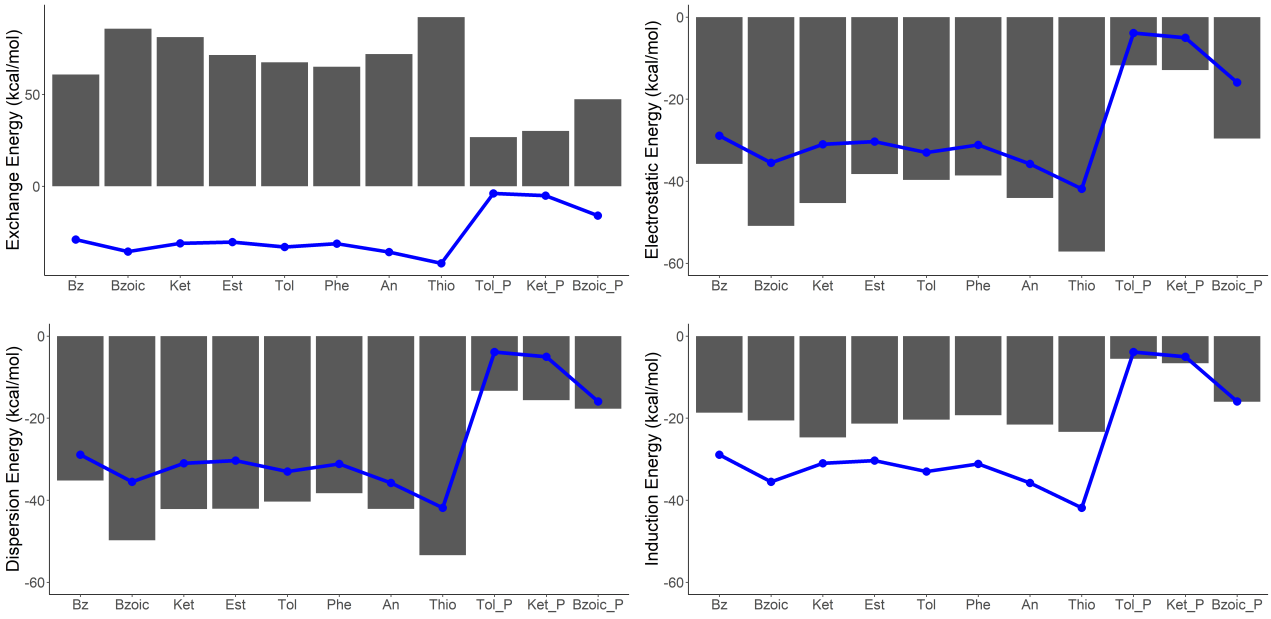

Fig. S25 SAPT decomposition of the interaction energy between Au_{32} and aromatic compounds. The blue line represents the total SAPT energy. Correlation between electrostatic component and the total SAPT energy. "P" stands for perpendicular configuration.

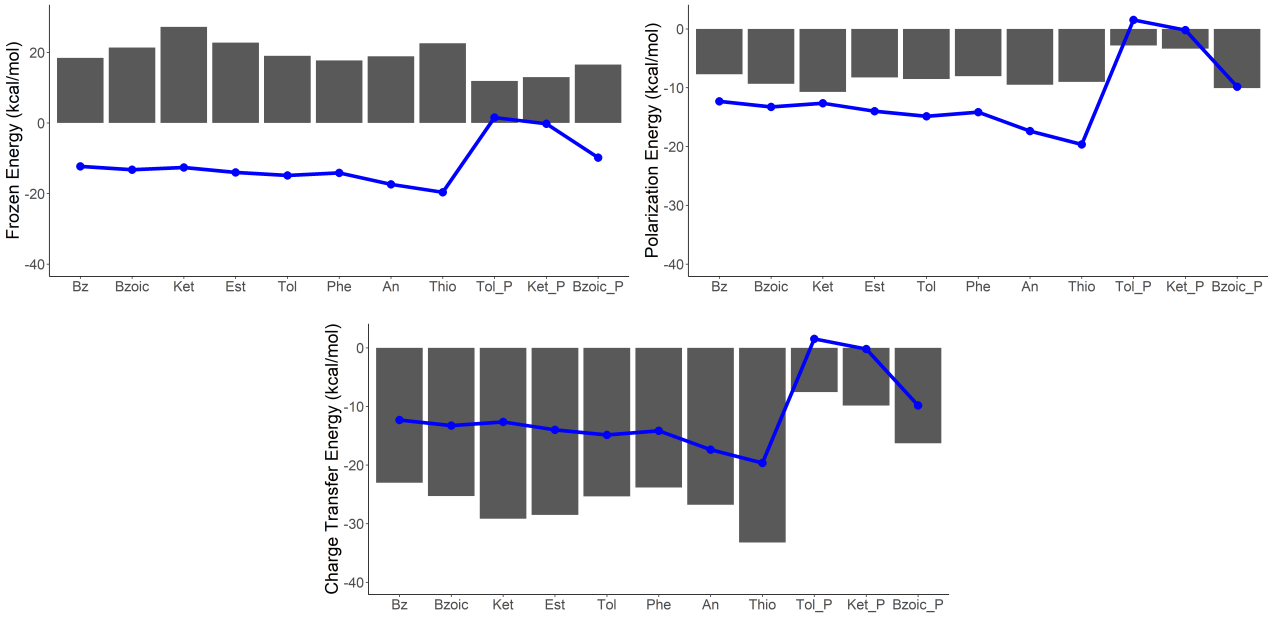

Fig. S26 BLW-EDA decomposition of the interaction energy between Au_{32} and aromatic compounds. The blue line represents the total BLW-EDA energy. "P" stands for perpendicular configuration.

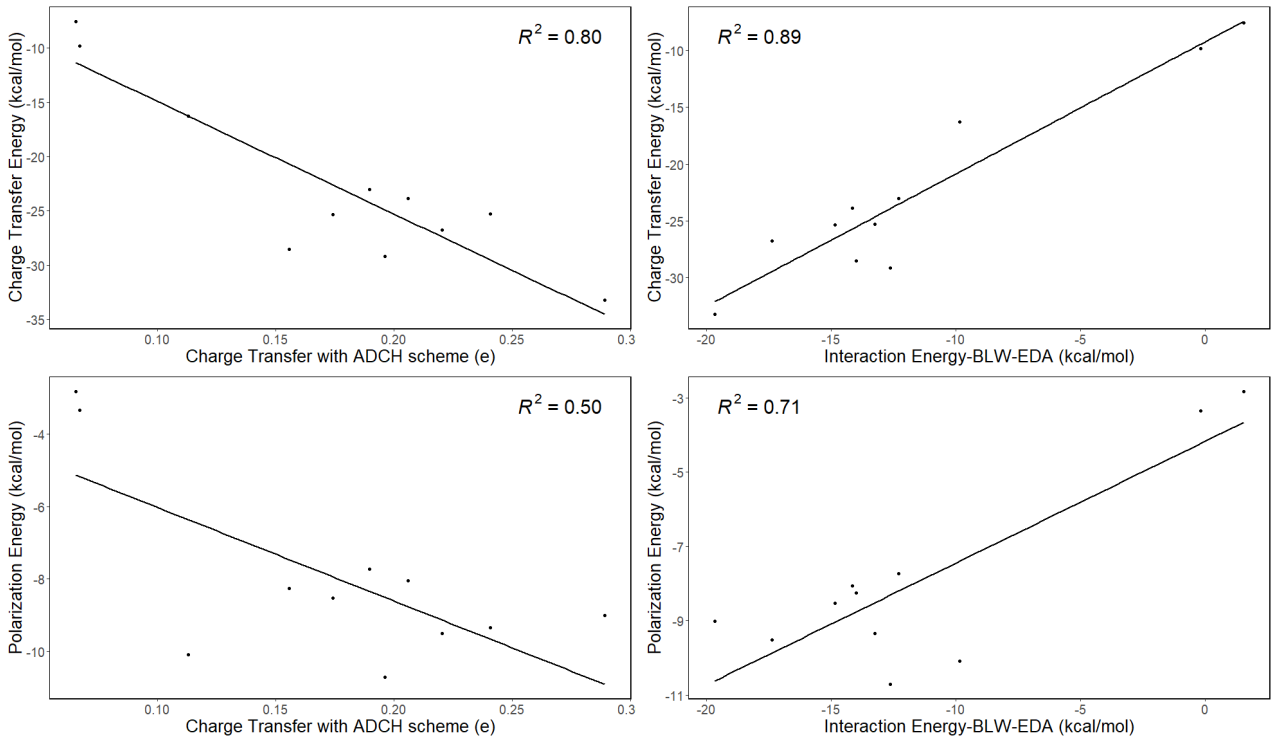

Fig. S27 Correlation between BLW-EDA charge transfer (top) and polarization (bottom) energy components with interaction energy and ADCH charge transfer, respectively.

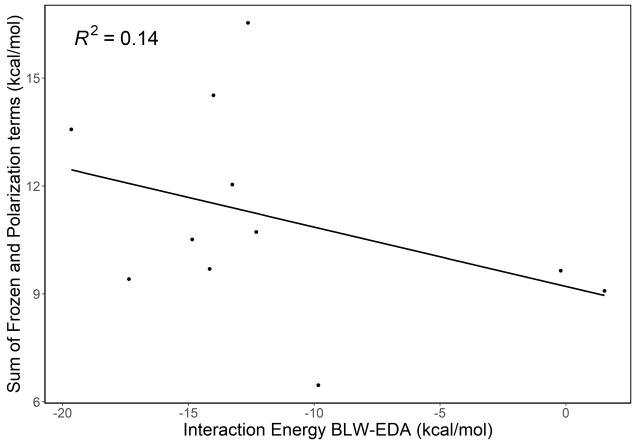

Fig. S28 Correlation between the sum of frozen and polarization terms and interaction energy (slope of -0.165).

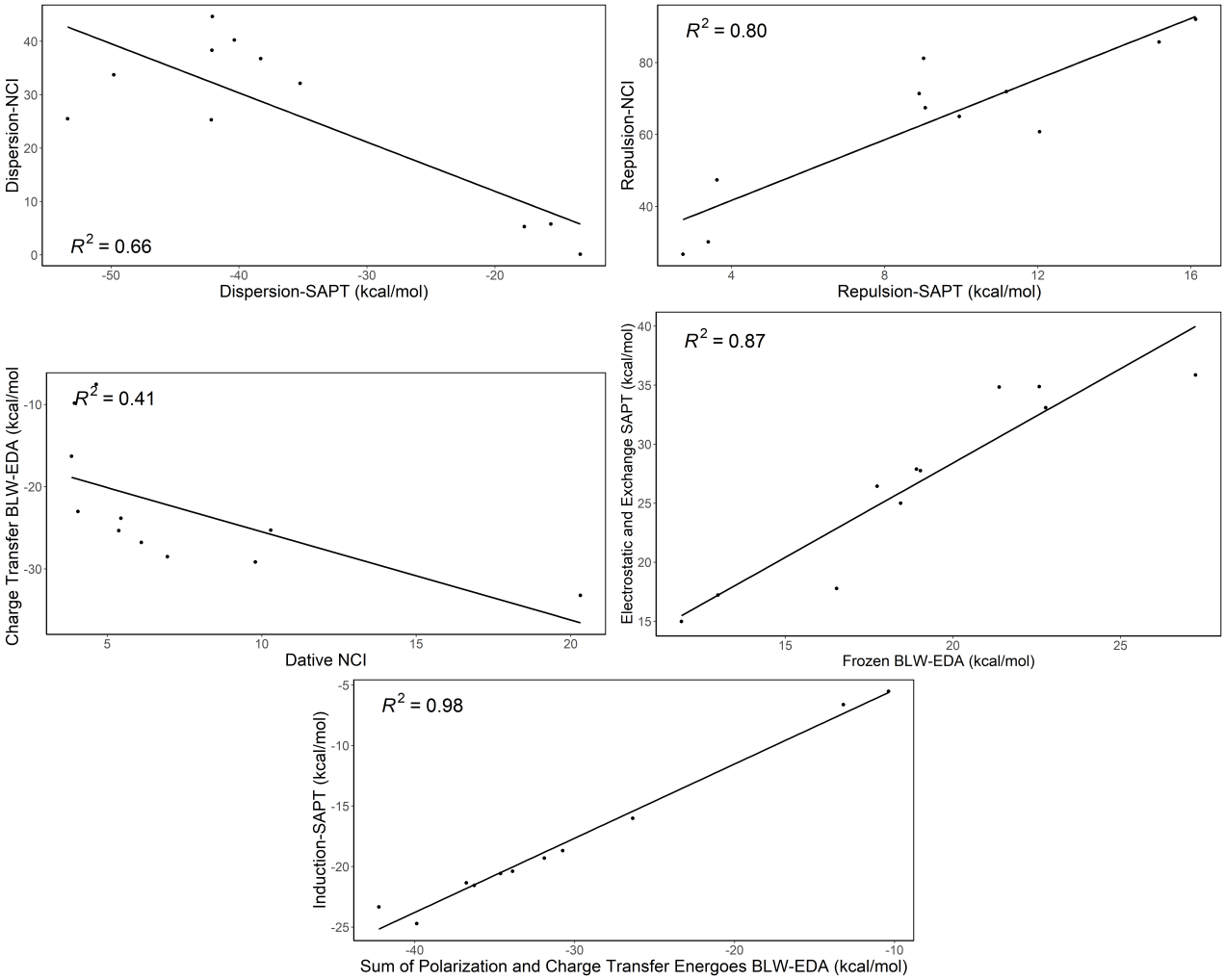

Fig. S29 Correlation across the different approaches: (top) correlation between the terms from NCI and SAPT, for dispersion with slope of -0.92 (left) and repulsion, with slope of 4.22 (right); (middle-left) correlation between charge transfer obtained with BLW-EDA and the dative term from NCI with slope of -1.07, (middle-right) correlation between the sum of electrostatic and exchange terms in SAPT and the frozen term in BLW-EDA with slope of 1.6; (bottom) correlation between the SAPT induction energy term and the sum of BLW-EDA polarization and charge transfer with slope of 0.613.