Supporting Information

Intermolecular interactions in ionic crystals of nucleobase chlorides – combining topological analysis of electron densities with energies of electrostatic interactions

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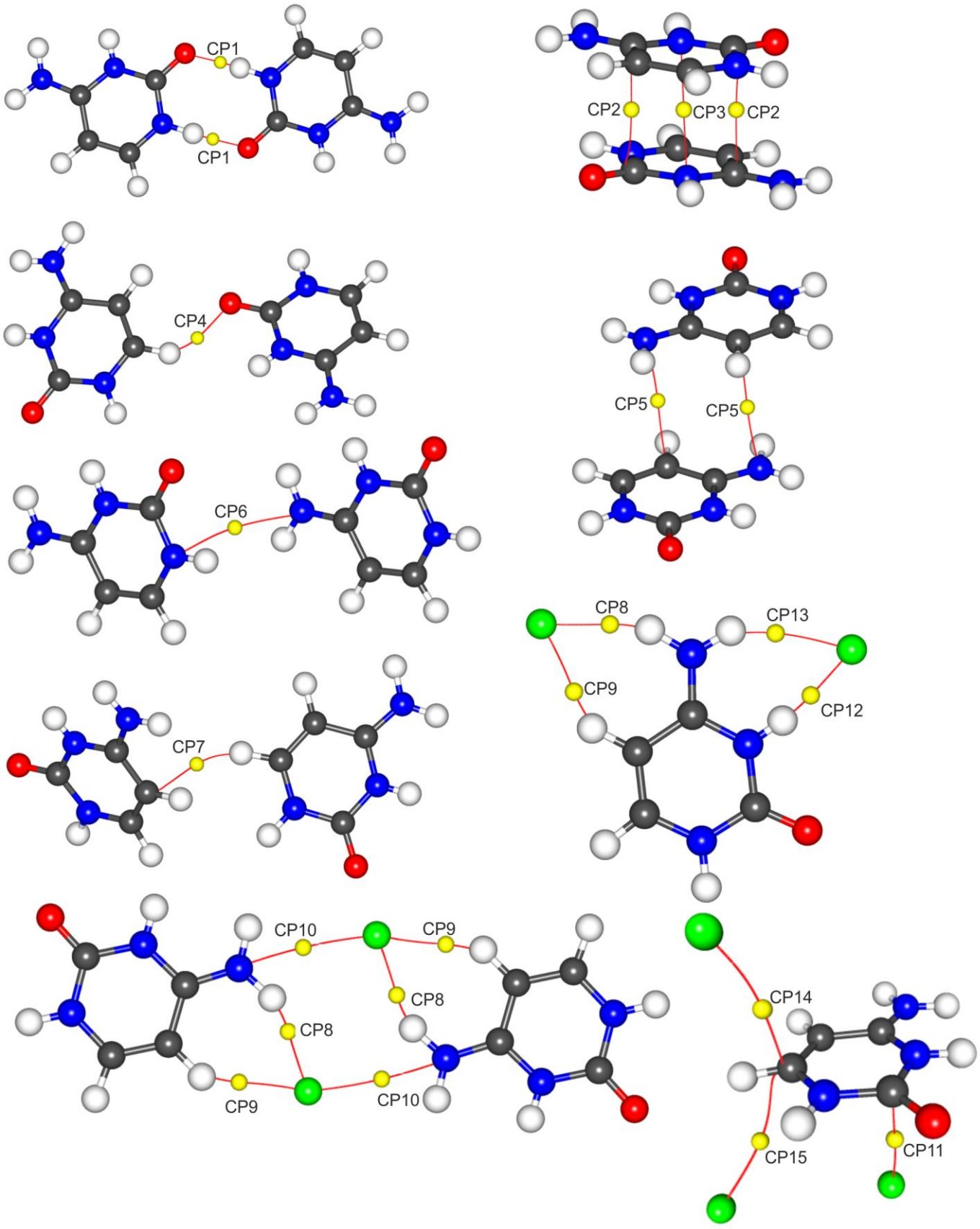

Figure S1

Interactions within dimers of the CC. Selected intermolecular bond critical points (CP) are presented as small yellow spheres and corresponding intermolecular bonding paths as red lines.

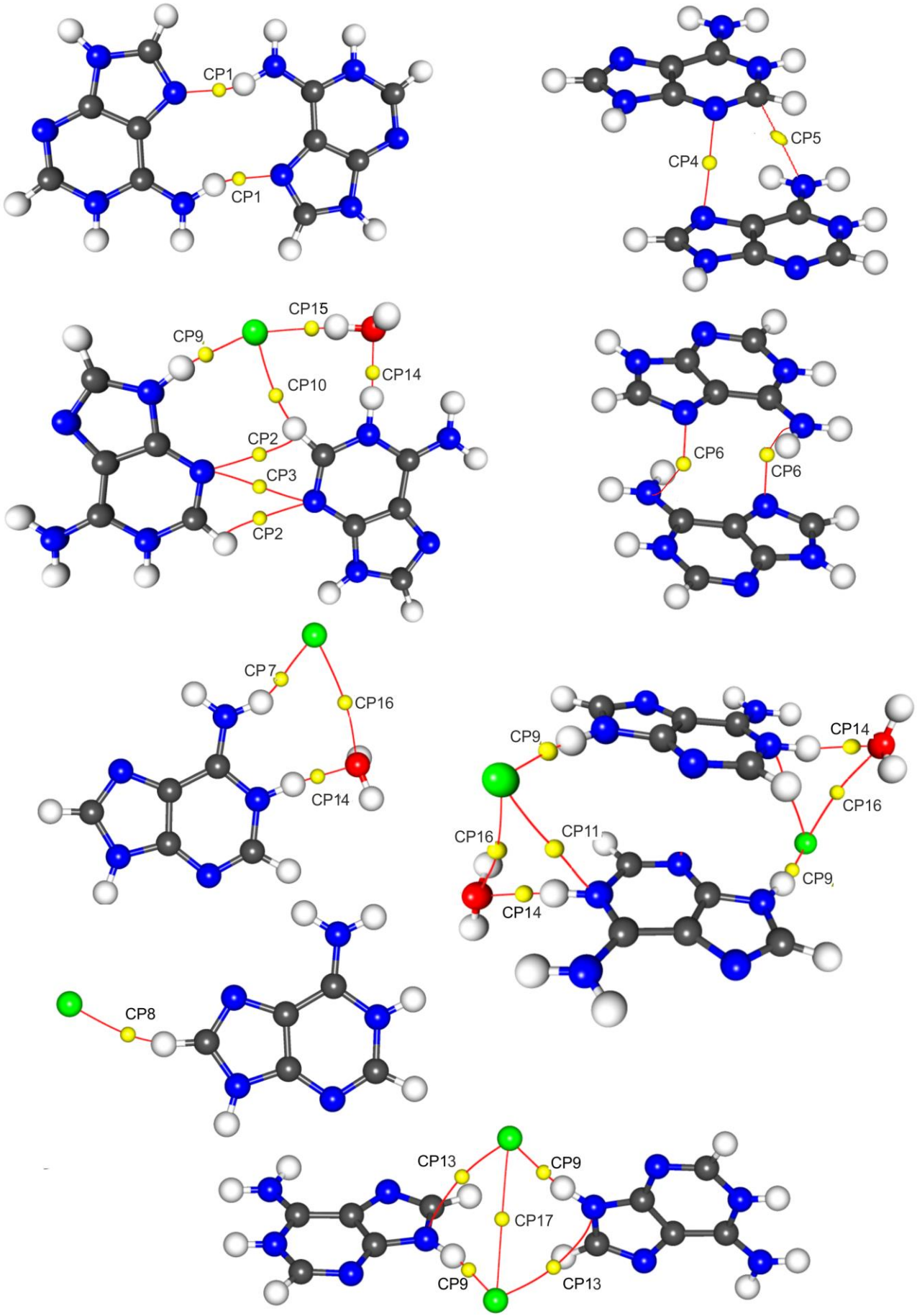

Figure S2

Interactions within dimers of the ACH. Selected intermolecular bond critical points (CP) are presented as small yellow spheres and corresponding intermolecular bonding paths as red lines.

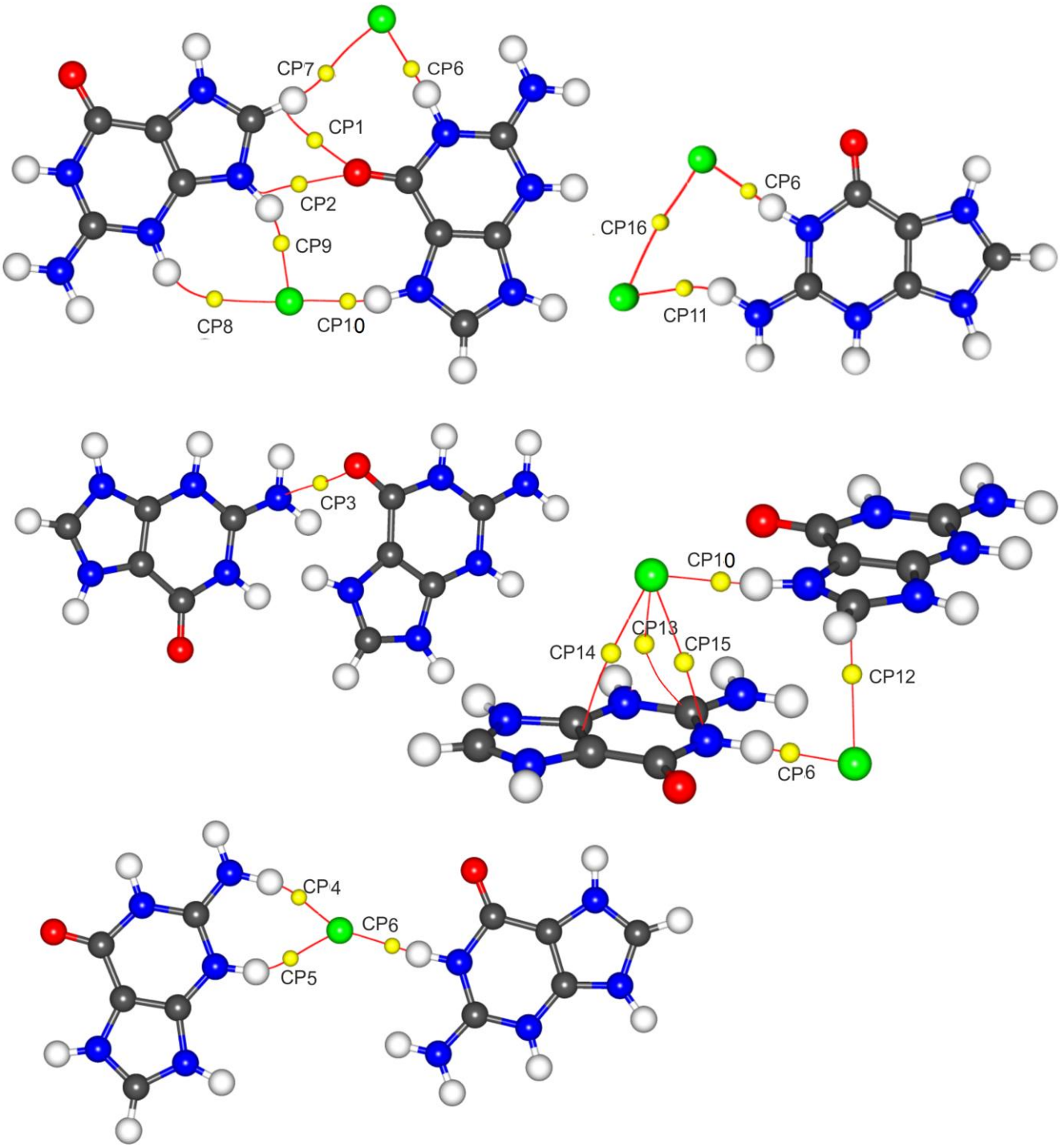

Figure S3

Interactions within dimers of the GDC. Selected intermolecular bond critical points (CP) are presented as small yellow spheres and corresponding intermolecular bonding paths as red lines.

Table S1 Selected QTAIM parameters of intermolecular interactions at BCPs detected in the electron densities of the CC, ACH and GDC crystals by experiment, UBDB model and periodic quantum calculations for with structure optimization (Theoretical (opt)). R_{ab} - distance (Å) between interacting atoms; $d1_{BPL}$ and $d2_{BPL}$ - bonding path lengths (Å) from the first or the second atom to the BCP, respectively; $\rho(r)$ - electron density (eÅ^{-3}) at BCP; $\nabla^2\rho(r)$ - Laplacian of electron density (eÅ^{-5}) at BCP; ε - ellipticity at BCP, E_{EML} - interaction energy (kcal mol^{-1}) estimated from Espinosa-Molins-Lecomte approach and Abramov approximation of the virial density $V(r)_{BCP}$; *ex.* E_{EML} - interaction energy (kcal mol^{-1}) estimated from Espinosa-Molins-Lecomte approach and exact values of $V(r)_{BCP}$. For the symmetry operations required to build particular dimers see Table S2 in SI.

			Experimental							UBDB							Theoretical (opt)							
			R_{ab}	$d1_{BPL}$	$d2_{BPL}$	$\rho(r)$	$\nabla^2\rho(r)$	ε	E_{EML}	R_{ab}	$d1_{BPL}$	$d2_{BPL}$	$\rho(r)_{BCP}$	$\nabla^2\rho(r)$	ε	E_{EML}	R_{ab}	$d1_{BPL}$	$d2_{BPL}$	$\rho(r)$	$\nabla^2\rho(r)$	ε	E_{EML}	*ex.* E_{EML}
Cytosinium chloride (CC)																								
AA1	H1	O2	1.766	0.634	1.134	0.329	1.14	0.06	-12.96	1.766	0.603	1.165	0.234	2.59	0.01	-9.45	1.734	0.632	1.149	0.277	3.33	0.03	-12.39	-10.03
AA2	C4	C2	3.312	1.670	1.769	0.047	0.42	0.66	-0.91	3.312	1.648	1.715	0.042	0.36	1.68	-0.77								
AA2	N3	N3	3.312	1.657	1.657	0.038	0.52	23.85	-0.89	3.312	1.657	1.657	0.038	0.54	16.69	-0.90	3.287	1.644	1.644	0.047	0.46	0.94	-0.96	-1.24
AA2	O2	N7															3.333	1.634	1.766	0.034	0.46	1.04	-0.76	-1.03
AA3	H5	O2															2.798	1.376	1.590	0.034	0.55	1.80	-0.86	-1.00
AA3	H6	O2	2.311	0.952	1.401	0.082	0.98	0.32	-2.22	2.311	0.968	1.370	0.078	1.24	0.35	-2.41	2.292	0.941	1.383	0.094	1.06	0.05	-2.62	-3.19
AA4	N7	C5	3.433	1.690	1.800	0.029	0.39	0.67	-0.63	3.433	1.711	1.731	0.028	0.38	1.15	-0.60	3.350	1.672	1.681	0.040	0.39	0.48	-0.78	-0.85
AA5	N7	N1	3.765	1.903	1.926	0.010	0.17	3.24	-0.22	3.765	1.896	1.897	0.012	0.20	1.43	-0.26								
AA6	H6	C5	2.998	1.315	1.784	0.031	0.24	0.10	-0.49	2.998	1.261	1.797	0.024	0.28	0.75	-0.45	2.953	1.239	1.771	0.027	0.34	0.43	-0.55	-0.58
AB1	H7B	Cl1	2.365	0.885	1.496	0.151	0.86	0.04	-4.13	2.365			0.120	1.07	0.10	-3.34	2.300	0.809	1.535	0.142	1.28	0.00	-4.27	-3.66
AB1	H5	Cl1	2.544	0.929	1.629	0.091	0.97	0.28	-2.43	2.544	0.928	1.627	0.089	1.01	0.20	-2.42	2.580	0.965	1.645	0.088	0.89	0.04	-2.26	-2.46
AB2	N7	Cl1	3.308	1.574	1.739	0.052	0.75	0.56	-1.36	3.308	1.626	1.746	0.054	0.76	0.86	-1.40	3.329	1.797	1.803	0.047	0.65	0.86	-1.17	-1.34
AB3	C2	Cl1	3.340	1.573	1.772	0.054	0.57	0.31	-1.19	3.340	1.581	1.786	0.053	0.54	2.18	-1.14								
AB3	N3	Cl1															3.402	1.652	1.804	0.054	0.55	2.76	-1.18	-1.32
AB4	H3	Cl1	2.024	0.702	1.329	0.327	1.20	0.05	-12.91	2.024	0.630	1.398	0.232	1.96	0.01	-8.68	1.994	0.659	1.376	0.277	2.19	0.00	-11.16	-8.79
AB4	H7A	Cl1	2.621	0.959	1.698	0.069	0.78	0.43	-1.72	2.621	0.948	1.696	0.069	0.76	0.33	-1.69	2.686	1.008	1.721	0.067	0.68	0.11	-1.57	-1.87
AB5	C6	Cl1	3.729	1.956	1.961	0.023	0.34	0.39	-0.51															
AB5	H6	Cl1								3.210	1.577	1.924	0.026	0.38	0.82	-0.58	3.173	1.366	1.928	0.034	0.39	0.52	-0.68	-0.71
AB6	C6	Cl1	3.690	1.822	1.953	0.025	0.30	0.41	-0.48	3.690	1.756	1.956	0.025	0.29	0.20	-0.48	3.692	1.697	2.005	0.027	0.29	0.39	-0.50	-0.56
BB1	Cl1	Cl1															4.098	2.050	2.050	0.027	0.24	3.86	-0.44	-0.53
Adeninium chloride hemihydrate (ACH)																								
AA1	H10A	N7	1.943	0.727	1.228	0.241	0.99	0.02	-8.05	1.943	0.688	1.264	0.184	1.94	0.06	-6.56	1.874	0.677	1.243	0.236	2.43	0.05	-9.39	-7.16
AA1	N7	N7	3.796	1.957	1.957	0.016	0.24	1.30	-0.34															
AA2	H2	N3	2.720	1.389	1.574	0.047	0.76	0.44	-1.28	2.720	1.268	1.572	0.040	0.70	0.63	-1.11	2.737	1.166	1.628	0.047	0.58	0.28	-1.09	-1.35
AA2	N3	N3	3.150	1.586	1.586	0.043	0.68	0.61	-1.13	3.150	1.581	1.581	0.040	0.65	0.40	-1.06	3.147	1.581	1.581	0.047	0.55	0.21	-1.06	-1.46
AA3	N3	N3	3.204	1.604	1.604	0.051	0.64	2.67	-1.22	3.204	1.604	1.604	0.048	0.66	7.99	-1.19	3.217	1.609	1.609	0.047	0.51	2.17	-1.01	-1.26
AA4	N3	N7	3.217	1.612	1.615	0.043	0.58	0.44	-1.02	3.217	1.611	1.614	0.041	0.57	0.65	-0.99	3.218	1.605	1.620	0.047	0.48	0.62	-0.98	-1.24
AA4	C2	N10	3.438	1.715	2.110	0.031	0.38	11.22	-0.64															
AA4	N1	N10															3.401	1.941	1.729	0.034	0.36	4.24	-0.66	-0.80
AA5	C2	C6								3.447	1.717	2.394	0.034	0.37	17.60	-0.67								
AA5	N7	C6	3.287	1.618	1.769	0.046	0.49	0.50	-0.97															
AA5	N7	N10								3.340	1.650	1.808	0.041	0.52	4.05	-0.93	3.364	1.662	1.737	0.040	0.46	1.23	-0.85	-1.17
AB1	H10B	Cl1	2.258	0.809	1.465	0.157	0.91	0.02	-4.40	2.258	0.760	1.510	0.148	1.40	0.12	-4.61	2.214	0.766	1.490	0.169	1.59	0.01	-5.58	-4.71
AB2	H8	Cl1	2.601	0.953	1.664	0.078	0.62	0.10	-1.74	2.601	0.950	1.657	0.083	0.80	0.09	-2.05	2.548	0.935	1.645	0.094	0.84	0.00	-2.38	-2.46
AB3	H9	Cl1	2.104	0.713	1.398	0.224	0.86	0.04	-7.11	2.104	0.669	1.439	0.198	1.67	0.02	-6.84	2.099	0.710	1.433	0.209	1.88	0.01	-7.55	-5.94
AB4	H2	Cl1	2.705	1.021	1.694	0.061	0.55	0.04	-1.30	2.705	1.007	1.704	0.069	0.65	0.06	-1.58	2.676	1.004	1.705	0.074	0.67	0.02	-1.71	-1.89
AB5	N1	Cl1	3.570	1.714	1.872	0.028	0.39	0.27	-0.62	3.570	1.698	1.883	0.031	0.43	0.37	-0.70	3.612	1.688	1.933	0.034	0.36	0.61	-0.66	-0.79
AB6	C8	Cl1	3.950	1.911	2.099	0.011	0.16	0.43	-0.21	3.950	1.977	2.074	0.015	0.21	0.83	-0.29	3.909	2.040	2.090	0.020	0.22	1.41	-0.35	-0.36
AB7	N9	Cl1	3.826	1.886	2.009	0.017	0.22	1.17	-0.32	3.826	1.836	2.028	0.018	0.25	2.49	-0.36	3.829	1.866	2.047	0.020	0.24	1.44	-0.37	-0.52
AW1	H1	O1	1.830	0.693	1.139	0.294	1.53	0.00	-11.38	1.830	0.631	1.204	0.209	2.38	0.02	-8.09	1.762	0.637	1.169	0.277	3.01	0.03	-12.05	-9.51
BW1	H1A	Cl1	2.120	0.668	1.462	0.174	1.66	0.00	-5.86	2.120	0.681	1.442	0.191	1.80	0.02	-6.69	2.090	0.710	1.432	0.216	1.95	0.01	-7.93	-6.27
BW2	O1	Cl1	3.608	1.678	1.939	0.022	0.33	0.79	-0.49	3.608	1.662	1.949	0.024	0.35	0.39	-0.52	3.633	1.661	1.982	0.027	0.34	0.80	-0.55	-0.71
BB1	Cl1	Cl1	4.261	2.133	2.133	0.011	0.14	0.22	-0.19	4.261	2.131	2.131	0.013	0.16	0.03	-0.23	4.220	2.110	2.110	0.020	0.19	0.12	-0.32	-0.40
Guaninium chloride (GDC)																								
AA1	H8	O10	2.252	1.198	1.321	0.083	1.75	0.30	-3.07	2.252	1.102	1.304	0.103	1.71	0.37	-3.55	2.201	0.976	1.303	0.115	1.61	0.25	-3.78	-4.24
AA1	H9	O10															2.216	1.019	1.326	0.101	1.42	0.32	-3.19	-3.89
AA1	O10	N9	2.759	1.329	1.617	0.083	1.70	1.40	-3.02	2.759	1.321	1.769	0.094	1.64	0.59	-3.23								
AA2	N11	O10	3.418	1.715	1.720	0.021	0.36	0.99	-0.51	3.418	1.710	1.733	0.022	0.34	0.97	-0.50	3.417	1.695	1.734	0.027	0.34	0.24	-0.55	-0.73
AA2	N7	N1	3.783	1.879	1.916	0.011	0.18	3.25	-0.24															
AA3	N3	N9	3.786	1.884	1.918	0.011	0.18	1.13	-0.24	3.786	1.897	1.907	0.013	0.19	5.60	-0.26								
AB1	H11B	Cl1	2.097	0.720	1.394	0.221	0.50	0.02	-6.59	2.097	0.673	1.431	0.204	1.79	0.08	-7.23	2.065	0.703	1.405	0.229	2.07	0.00	-8.68	-7.17
AB1	H3	Cl1	2.301	0.836	1.484	0.138	0.97	0.07	-3.81	2.301	0.775	1.546	0.126	1.33	0.23	-3.81	2.317	0.813	1.545	0.142	1.25	0.00	-4.24	-3.66
AB2	H1	Cl1	2.035	0.690	1.349	0.275	1.32	0.02	-10.12	2.035	0.624	1.412	0.220	1.82	0.00	-7.97	2.007	0.667	1.383	0.263	2.14	0.01	-10.41	-8.09
AB3	H8	Cl1	2.824	1.103	1.740	0.056	0.26	0.04	-0.89	2.824	1.054	1.775	0.053	0.47	0.07	-1.07	2.764	1.030	1.771	0.054	0.53	0.04	-1.15	-1.43
AB4	H3	Cl2	2.952	1.223	1.831	0.033	0.36	0.71	-0.64	2.952	1.143	1.871	0.034	0.46	1.92	-0.76	2.982	1.155	1.877	0.040	0.43	0.52	-0.83	-0.99
AB4	H9	Cl2	2.219	0.779	1.455	0.166	1.09	0.06	-4.93	2.219	0.737	1.500	0.151	1.54	0.16	-4.87	2.203	0.758	1.489	0.169	1.57	0.00	-5.55	-4.69
AB5	H7	Cl2	2.074	0.706	1.371	0.252	0.82	0.01	-8.41	2.074	0.647	1.430	0.205	1.74	0.02	-7.22	2.043	0.677	1.410	0.250	1.98	0.02	-9.55	-7.23
AB6	H11A	Cl2	2.291	0.810	1.511	0.138	0.65	0.08	-3.46	2.291	0.777	1.530	0.135	1.36	0.19	-4.13	2.212	0.767	1.488	0.169	1.59	0.01	-5.58	-4.66
AB7	C8	Cl1	3.255	1.520	1.744	0.049	0.57	0.08	-1.11	3.255	1.528	1.727	0.065	0.64	0.11	-1.48	3.265	1.492	1.776	0.061	0.63	0.27	-1.38	-1.31
AB8	C2	Cl2								3.424	1.663	1.799	0.049	0.54	1.18	-1.08								
AB8	Cl2	C4	3.546	1.836	2.139	0.035	0.41	4.23	-0.73	3.546	1.811	1.849	0.040	0.46	2.27	-0.84	3.540	1.885	1.969	0.040	0.43	7.37	-0.83	-0.95
AB8	N1	Cl2	3.483	1.720	1.819	0.035	0.49	8.85	-0.81								3.491	1.691	1.850	0.047	0.51	3.09	-1.01	-1.20
AB8	N3	Cl2	3.466	1.690	1.800	0.038	0.53	2.49	-0.90								3.463	1.636	1.841	0.047	0.51	1.58	-1.01	-1.27
BB1	Cl2	Cl1	3.692	1.843	1.850	0.032	0.43	0.92	-0.70	3.692	1.845	1.847	0.039	0.48	0.31	-0.85								

Table S2. A list of symmetry operation defining selected dimers in the CC, ACH and GDC structures. To build a given dimer symmetry card assigned to it should be applied to the second molecule in the dimer represented by the second letter in the dimer name (A nucleobase cation, B chloride anion, W water molecule).

Dimer	Symmetry card
Cytosinium chloride (CC)	
AA1	-x, -y+2, -z+1
AA2	-x, -y+1, -z+1
AA3	x+0.5, -y+1.5, z+0.5
AA4	-x+1, -y+1, -z+1
AA5	x, y-1, z
AA6	-x+0.5, y+0.5, -z+1.5
AA7	-x,+1, -y, -z+1
AB1	x, y, z
AB2	-x+1, -y, -z+1
AB3	-x+1, -y+1, -z+1
AB4	x-0.5, -y+0.5, z-0.5
AB5	x, y+1, z
AB6	-x+0.5, +y+0.5, -z+1.5
BB1	-x+1, -y, -z+1
Adeninium chloride hemihydrate (ACH)	
AA1	-x, -y, -z+1
AA2	-x+1, -y+2, -z+1
AA3	-x+1, -y+1, -z+1
AA4	x, y+1, z
AA5	-x, -y+1, -z+1
AA6	-x+0.5, y, -z+1.5
AB1	x-0.5, -y+1, z+0.5
AB2	-x+0.5, y-1, -z+0.5
AB3	x, y, z
AB4	-x+1, -y+2, -z+1
AB5	-x+1, -y+1, -z+1
AB6	x, y-1, z
AB7	-x+0.5, y, -z+0.5
AW1	x, y, z
BW1	x+0.5, -y+2, z-0.5
BW2	-x+1, -y+1, -z+1
BB1	-x+0.5, y, -z+0.5
Guaninium dichloride (GDC)	
AA1	x+0.5, -y+1.5, -z+1.5
AA2	-x+1.5, -y+1, z+0.5
AA3	-x+2, y-0.5, -z+1
AA4	x, y-1, z
AA5	x, y, z-1
AB1	x+0.5, -y+1.5, -z+0.5
AB2	x, y, z
AB3	x+0.5, -y+1.5, -z+1.5
AB4	x+0.5, -y+1.5, -z+1.5
AB5	x, y, z
AB6	x, y, z-1
AB7	-x+1.5, -y+1, z+0.5
AB8	-x+1.5, -y+1, z-0.5
AB9	-x+1, y+0.5, -z+1
BB1	x, y, z-1

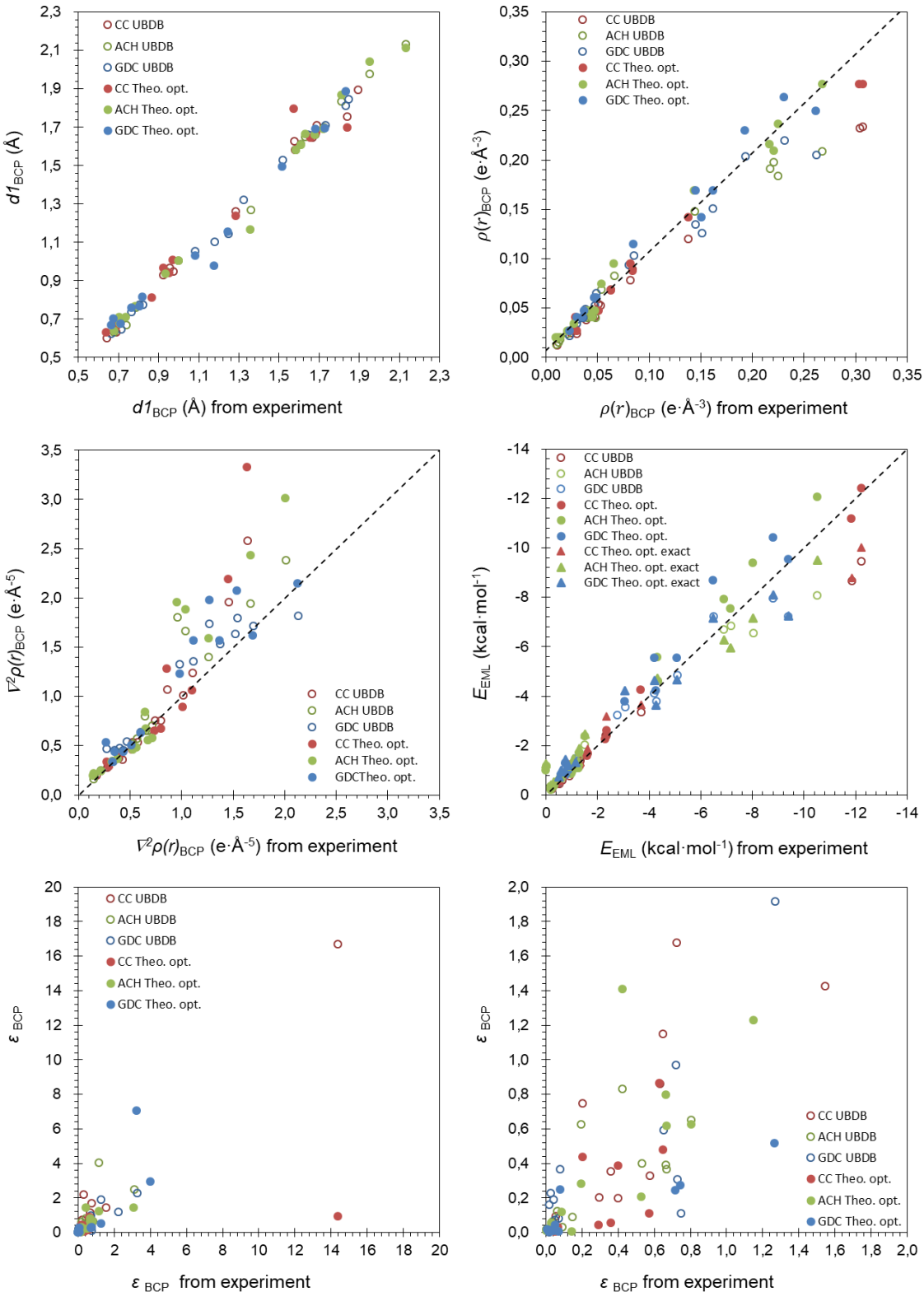

Figure S4

Selected QTAIM parameters of intermolecular interactions at BCPs detected in the experimental electron densities (HC model) of the CC, ACH and GDC crystals related to parameters at BCPs detected in the electron densities (HC model) from the UBDB models (UBDB) or from the periodic theoretical calculations (without HC model) done for relaxed geometry (Theo. opt.). $d1_{BPL}$ - path lengths (Å) from the first atom to the BCP; $\rho(r)_{BCP}$ - electron density (eÅ^{-3}) at BCP; $\nabla^2\rho(r)_{BCP}$ - Laplacian of electron density (eÅ^{-5}) at BCP; ε - ellipticity at BCP, E_{EML} - interaction energy (kcal mol^{-1}) estimated from Espinosa-Molins-Lecomte approach computed on the basis of the Abramov approximation (UBDB, Theo. opt.) or of the exact values of the virial density $V(r)_{BCP}$ (Theo. opt. exact).

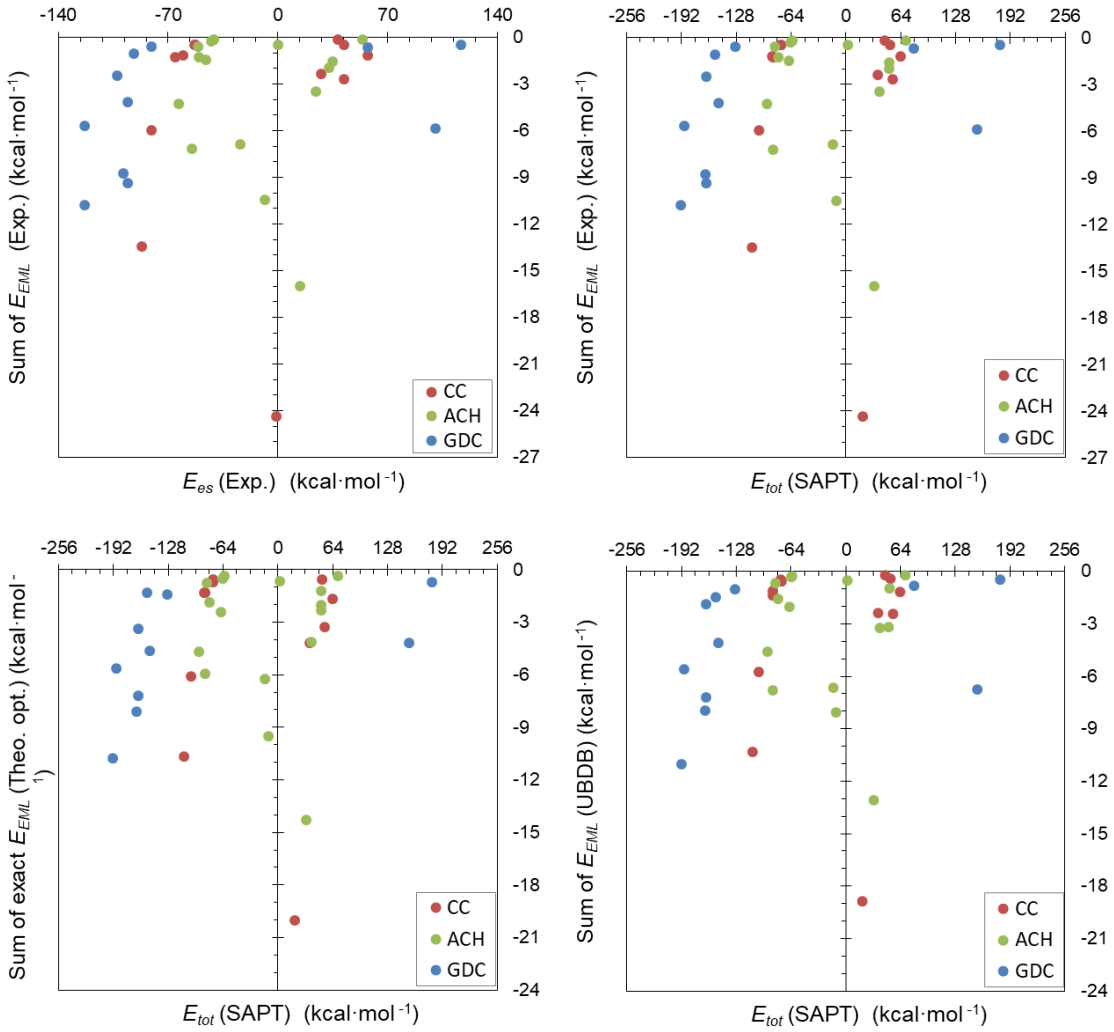

Figure S5

Correlation between the E_{EML} interaction energies (kcal mol^{-1}) summed over all intermolecular BCPs found in particular dimer and the electrostatic interaction energies of dimers (Ees) from experimental charge densities (Exp) or the total interaction energies (E_{tot}) from the SAPT. The E_{EML} energies were estimated from the Espinosa-Molins-Lecomte approach and the Abramov expression on the basis of experimental densities (Exp.), UBDB (UBDB) densities, or from the Espinosa-Molins-Lecomte approach and exact values of $V(r)_{BCP}$ (not approximated by Abramov expression) on the basis of periodic DFT electron densities from geometry optimization (Theo. opt.).

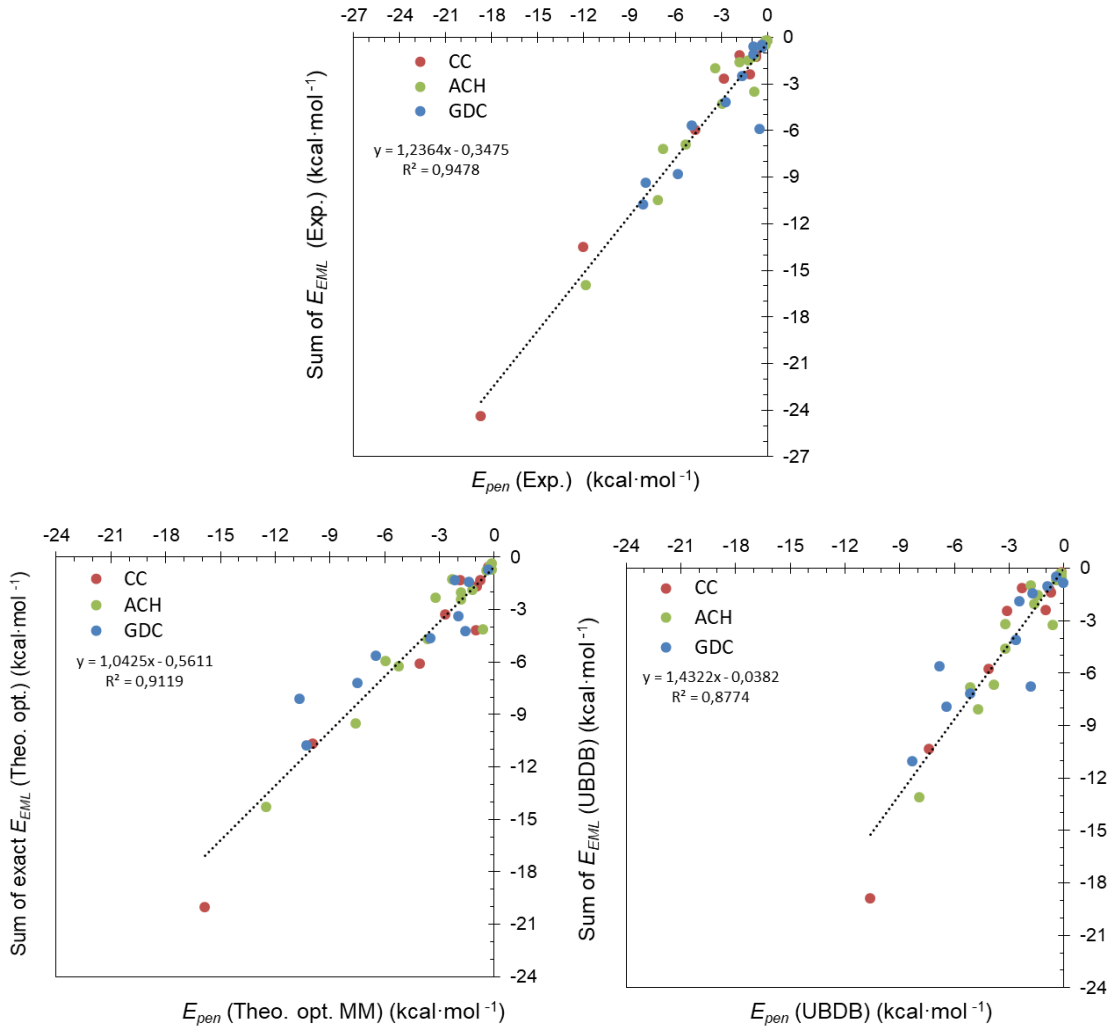

Figure S6

Correlation between the E_{EML} interaction energies (kcal mol^{-1}) summed over all intermolecular BCPs found in particular dimer and the charge penetration contributions (E_{pen}) to E_{es} computed from MM model of experimental charge densities (Exp.), of periodic DFT charge densities (Theo. opt. MM) or build from UBDB (UBDB). The E_{EML} energies were estimated from the Espinosa-Molins-Lecomte approach and the Abramov expression on the basis of experimental densities (Exp.), UBDB (UBDB) densities, or from the Espinosa-Molins-Lecomte approach and exact values of $V(r)_{BCP}$ (not approximated by Abramov expression) on the basis of periodic DFT electron densities from geometry optimization (Theo. opt.).

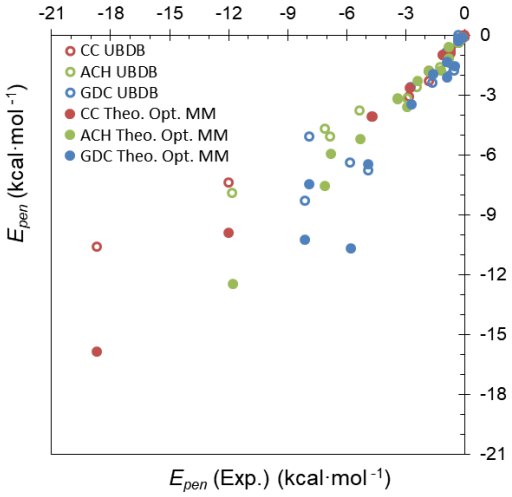

Figure S7

Correlation between the E_{pen} energies (kcal mol^{-1}) computed from MM model of experimental charge densities (Exp.) and E_{pen} energies (kcal mol^{-1}) computed from MM model of periodic DFT charge densities (Theo. opt. MM) or build from UBDB (UBDB).