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

Partitioning of interaction-induced nonlinear optical properties of molecular complexes. II. Halogen-bonded systems

SUPPORTING INFORMATION

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Table S1: Electronic (hyper)polarizabilities of HCN$\cdots$II complex computed using the MP2 method. All values are given in au.

basis set	α_{zz}	β_{zzz}	γ_{zzzz}
aug-cc-pVTZ-PP	143.89	-450.6	71750
aug-cc-pVQZ-PP	143.75	-471.4	73849

Table S2: Comparison of interaction-induced electric properties determined using the MP2 and SCS-MP2 methods and the aug-cc-pVTZ-PP basis set. All values are given in au.

	$\Delta\alpha^{\mathrm{el}}$		$\Delta\alpha^{\mathrm{nr}}$		$\Delta\beta^{\mathrm{el}}$		$\Delta\beta^{\mathrm{nr}}$		$\Delta\gamma^{\mathrm{el}}$	
	MP2	SCS-MP2	MP2	SCS-MP2	MP2	SCS-MP2	MP2	SCS-MP2	MP2	SCS-MP2
HCN···BrF	17.04	15.28	33.92	29.36	-73.3	-107.6	-3652.8	-3309.7	14463	12866
HCN···IBr	23.45	21.17	39.07	34.64	-333.3	-348.8	-6222.6	-5370.8	35421	31490
HCN···II	23.57	21.20	32.43	29.30	-476.1	-460.6	-5538.0	-4679.0	45019	39725

Table S3: Intermolecular interaction energy decomposition performed at the MP2/aug-cc-pVTZ-PP level of theory and CCSD(T) binding energies$^{(a)}$. All values are given in kcal/mol.

	$\varepsilon_{\mathrm{el}}^{(10)}$	$\Delta E_{\mathrm{ex}}^{\mathrm{HL}}$	$\Delta E_{\mathrm{del}}^{\mathrm{HF}}$	ΔE^{HF}	$\varepsilon_{\mathrm{el,r}}^{(12)}$	$\varepsilon_{\mathrm{disp}}^{(20)}$	$\Delta E_{\mathrm{ex}}^{(2)}$	ΔE^{MP2}	CCSD(T)$^{(a)}$
HCN$\cdots$BrBr	-8.293	13.062	-4.096	0.673	-0.653	-6.126	2.188	-3.918	-3.63
HCN$\cdots$BrCl	-10.286	15.380	-5.209	-0.115	-0.662	-6.682	2.617	-4.842	-4.47
HCN$\cdots$BrF	-19.967	30.438	-12.829	-2.358	-1.013	-9.772	4.921	-8.223	-7.61
HCN$\cdots$BrH	-2.220	3.430	-0.751	0.459	-0.242	-2.569	0.853	-1.498	-1.41
HCN$\cdots$IBr	-12.651	18.657	-6.782	-0.776	-0.729	-7.822	3.617	-5.711	-5.31
HCN$\cdots$ICl	-15.016	21.658	-8.381	-1.740	-0.802	-8.480	4.214	-6.808	-6.31
HCN$\cdots$IF	-23.610	34.649	-15.484	-4.445	-1.180	-10.999	6.505	-10.120	-9.45
HCN$\cdots$IH	-3.781	5.010	-1.268	-0.039	-0.228	-3.366	1.260	-2.373	-2.24
HCN$\cdots$II	-9.309	14.138	-4.675	0.153	-0.640	-6.669	2.732	-4.424	-4.03

(a) The values are taken from ref. [J. Chem. Theory Comput. 2013, 9, 1918–1931] and correspond to the binding energies. The geometries were calculated at the CCSD(T)/aug-cc-pVQZ level and the energies at CCSD(T)/CBS.

Table S4: The A-X bond lengths in an isolated donor and in the corresponding AX$\cdots$B complex (in Å), X·B bond lengths (in Å), vibrational frequencies of the corresponding stretching modes (in cm^{-1}) and natural charges (q_X) on the halogen atom X in an isolated XB donor obtained at the MP2/aug-cc-pVTZ(PP) level of theory.
Note that q_A = -q_X.

	$d(\text{A-X})_\text{A}$	$d(\text{A-X})_\text{AB}$	$\Delta d(\text{A-X})$	$d(\text{X}\cdots\text{B})_\text{AB}$	$\nu(\text{A-X})_\text{A}$	$\nu(\text{A-X})_\text{AB}$	$\Delta\nu(\text{A-X})$	$\nu(\text{X}\cdots\text{B})_\text{AB}$	q_X
HCN$\cdots$BrBr	2.271	2.287	0.016	2.698	343.5	329.5	-14.0	111.4	0.00
HCN$\cdots$BrCl	2.132	2.153	0.021	2.631	463.9	441.4	-22.5	121.8	0.12
HCN$\cdots$BrF	1.754	1.784	0.030	2.386	697.6	645.4	-52.2	162.5	0.49
HCN$\cdots$BrH	1.400	1.403	0.003	3.105	2768.9	2750.0	-18.9	79.7	-0.18
HCN$\cdots$IBr	2.462	2.485	0.023	2.734	286.5	272.2	-14.4	118.8	0.16
HCN$\cdots$ICl	2.318	2.347	0.028	2.670	406.5	382.9	-23.6	127.9	0.28
HCN$\cdots$IF	1.915	1.944	0.029	2.484	639.3	597.8	-41.6	166.3	0.60
HCN$\cdots$IH	1.596	1.601	0.005	3.167	2426.4	2407.7	-18.7	87.8	-0.06
HCN$\cdots$II	2.662	2.680	0.018	2.847	230.8	222.5	-8.3	106.6	0.00

Table S5: Electronic dipole moment (in au) at equilibrium geometries corresponding to the MP2 method.

	μ_z^e
HCN$\cdots$BrBr	-1.82
HCN$\cdots$BrCl	-2.06
HCN$\cdots$BrF	-2.57
HCN$\cdots$BrH	-1.06
HCN$\cdots$IBr	-2.33
HCN$\cdots$ICl	-2.55
HCN$\cdots$IF	-2.90
HCN$\cdots$IH	-1.31
HCN$\cdots$II	-2.01

Table S6: Interaction-induced electronic dipole moment computed at the MP2/aug-cc-pVTZ-PP level of theory. All values are given in au.

	$\Delta\mu_{\mathrm{el}}^{(10)}$	$\Delta\mu_{\mathrm{ex}}^{\mathrm{HL}}$	$\Delta\mu_{\mathrm{del}}^{\mathrm{HF}}$	$\Delta\mu^{\mathrm{HF}}$	$\Delta\mu_{\mathrm{el,r}}^{(12)}$	$\Delta\mu_{\mathrm{disp}}^{(20)}$	$\Delta\mu_{\mathrm{ex}}^{(2)}$	$\Delta\mu^{\mathrm{MP2}}$
HCN$\cdots$BrBr	-0.40	-0.08	-0.17	-0.66	0.01	0.03	-0.02	-0.64
HCN$\cdots$BrCl	-0.42	-0.06	-0.20	-0.68	0.01	0.03	-0.02	-0.66
HCN$\cdots$BrF	-0.54	0.05	-0.32	-0.81	0.01	0.02	-0.02	-0.80
HCN$\cdots$BrH	-0.17	0.00	-0.03	-0.20	-0.01	0.00	0.01	-0.19
HCN$\cdots$IBr	-0.50	-0.19	-0.25	-0.94	0.02	0.06	-0.04	-0.89
HCN$\cdots$ICl	-0.52	-0.16	-0.27	-0.95	0.02	0.06	-0.04	-0.91
HCN$\cdots$IF	-0.61	-0.03	-0.33	-0.97	0.03	0.04	-0.04	-0.94
HCN$\cdots$IH	-0.24	-0.02	-0.05	-0.31	0.00	0.01	-0.00	-0.30
HCN$\cdots$II	-0.47	-0.21	-0.20	-0.88	0.02	0.06	-0.03	-0.82

Table S7: Electronic and nuclear relaxation longitudinal polarizability (given in a.u.) and their percentage contributions.

	α_{zz}^{e}	α_{zz}^{nr}	$\alpha_{zz}^{e} + \alpha_{zz}^{nr}$	$\alpha_{zz}^{e}/(\alpha_{zz}^{e} + \alpha_{zz}^{nr})$	$\alpha_{zz}^{nr}/(\alpha_{zz}^{e} + \alpha_{zz}^{nr})$
HCN···BrBr	102.02	24.08	126.10	81%	19%
HCN···BrCl	91.22	25.30	116.52	78%	22%
HCN···BrF	68.04	27.07	95.10	72%	28%
HCN···BrH	52.68	2.59	55.27	95%	5%
HCN···IBr	123.87	39.34	163.21	76%	24%
HCN···ICl	110.37	39.08	149.44	74%	26%
HCN···IF	80.76	26.39	107.14	75%	25%
HCN···IH	67.30	4.76	72.06	93%	7%
HCN···II	143.89	35.60	179.50	80%	20%

Table S8: Electronic and nuclear relaxation polarizability and first hyperpolarizability (given in a.u.) at equilibrium geometries corresponding to the MP2 method. The “RR error” accounts for the numerical uncertainty of the reported values determined with the Romberg-Rutishauser (RR) procedure.

	α^{e}_{zz}	RR error	α^{nr}_{zz}	$\alpha^{e}_{zz} + \alpha^{nr}_{zz}$	RR error
HCN$\cdots$BrBr	102.02	0.000008	24.08	126.10	0.014383
HCN$\cdots$BrCl	91.22	0.000020	25.30	116.52	0.000057
HCN$\cdots$BrF	68.04	0.000004	27.07	95.10	0.001261
HCN$\cdots$BrH	52.68	0.000001	2.59	55.27	0.006009
HCN$\cdots$IBr	123.87	0.000011	39.34	163.21	0.009534
HCN$\cdots$ICl	110.37	0.000041	39.08	149.44	0.003946
HCN$\cdots$IF	80.76	0.000002	26.39	107.14	0.002512
HCN$\cdots$IH	67.30	0.000001	4.76	72.06	0.000003
HCN$\cdots$II	143.89	0.000013	35.60	179.50	0.016504
	β^{e}_{zzz}	RR error	β^{nr}_{zzz}	$\beta^{e}_{zzz} + \beta^{nr}_{zzz}$	RR error
HCN$\cdots$BrBr	-355.5	0.030226	-3266.2	-3621.7	1.893596
HCN$\cdots$BrCl	-245.2	0.003635	-3204.1	-3449.3	2.271960
HCN$\cdots$BrF	-15.6	0.042520	-2235.0	-2250.6	2.266631
HCN$\cdots$BrH	-56.4	0.006631	-189.6	-246.0	5.055323
HCN$\cdots$IBr	-262.6	0.002156	-4780.0	-5042.5	5.376264
HCN$\cdots$ICl	-92.8	0.044897	-4076.0	-4168.8	5.964590
HCN$\cdots$IF	190.5	0.013282	-1479.8	-1289.3	7.245777
HCN$\cdots$IH	-74.0	0.000977	-383.4	-457.4	2.005613
HCN$\cdots$II	-450.6	0.003152	-5207.9	-5658.6	37.860313
	γ^{e}_{zzzz}	RR error	γ^{nr}_{zzzz}	$\gamma^{e}_{zzzz} + \gamma^{nr}_{zzzz}$	RR error
HCN$\cdots$BrBr	44278	43	393142	437420	21068
HCN$\cdots$BrCl	34550	30	366530	401080	83
HCN$\cdots$BrF	18745	5	73858	92603	9234
HCN$\cdots$BrH	10224	2	11874	22098	1931
HCN$\cdots$IBr	53409	72	329321	382730	49404
HCN$\cdots$ICl	42423	66	185267	227690	7647
HCN$\cdots$IF	29266	13	-10825	18441	13231
HCN$\cdots$IH	17385	6	626045	643430	365
HCN$\cdots$II	71750	83	602380	674130	93743

Table S9: Interaction-induced electronic polarizability computed at the MP2/aug-cc-pVTZ-PP level of theory. All values are given in au.

	$\Delta\alpha_{\text{el}}^{(10)}$	$\Delta\alpha_{\text{ex}}^{\text{HL}}$	$\Delta\alpha_{\text{del}}^{\text{HF}}$	$\Delta\alpha^{\text{HF}}$	$\Delta\alpha_{\text{el,r}}^{(12)}$	$\Delta\alpha_{\text{disp}}^{(20)}$	$\Delta\alpha_{\text{ex}}^{(2)}$	$\Delta\alpha^{\text{MP2}}$	$(\Delta\alpha/\alpha)^{(a)}$
HCN···BrBr	15.02	-7.53	8.88	16.37	0.01	1.36	0.91	18.65	0.18
HCN···BrCl	13.95	-7.57	8.77	15.14	0.45	1.32	1.01	17.94	0.20
HCN···BrF	12.35	-8.97	9.98	13.36	1.30	1.31	1.07	17.04	0.25
HCN···BrH	6.00	-2.16	1.54	5.39	0.38	0.54	-0.56	5.75	0.11
HCN···IBr	19.21	-12.01	12.43	19.63	0.53	2.10	1.19	23.45	0.19
HCN···ICl	17.72	-11.68	12.05	18.08	1.09	2.01	1.02	22.20	0.20
HCN···IF	14.74	-11.26	12.09	15.57	1.97	1.71	0.38	19.63	0.24
HCN···IH	8.39	-3.40	2.68	7.68	0.48	0.83	-0.73	8.25	0.12
HCN···II	20.60	-11.73	12.09	20.95	-0.15	2.17	0.59	23.57	0.16

(a) The ratio of the excess electronic polarizability ($\Delta\alpha^{\text{el}}$) and total electronic (α^{el}) value computed using the MP2 method.

Table S10: Interaction-induced electronic first hyperpolarizability computed at the MP2/aug-cc-pVTZ-PP level of theory. All values are given in au.

	$\Delta\beta_{\mathrm{el}}^{(10)}$	$\Delta\beta_{\mathrm{ex}}^{\mathrm{HL}}$	$\Delta\beta_{\mathrm{del}}^{\mathrm{HF}}$	$\Delta\beta^{\mathrm{HF}}$	$\Delta\beta_{\mathrm{el,r}}^{(12)}$	$\Delta\beta_{\mathrm{disp}}^{(20)}$	$\Delta\beta_{\mathrm{ex}}^{(2)}$	$\Delta\beta^{\mathrm{MP2}}$
HCN···BrBr	31.4	-88.2	-155.0	-211.9	-40.4	28.2	-141.5	-370.2
HCN···BrCl	23.0	-57.3	-124.3	-158.2	-46.3	17.2	-101.2	-288.5
HCN···BrF	-10.6	27.8	-51.9	-39.5	-51.2	4.0	14.4	-73.3
HCN···BrH	-23.2	7.9	-18.9	-34.3	-18.3	1.1	2.0	-49.5
HCN···IBr	121.8	-214.8	-91.5	-184.3	-64.9	47.4	-131.4	-333.3
HCN···ICl	93.5	-155.2	-57.4	-118.7	-56.4	37.6	-66.7	-203.9
HCN···IF	10.9	-22.5	33.0	21.4	-38.9	16.1	62.9	61.5
HCN···IH	-12.3	-24.0	-21.2	-57.6	-18.4	10.5	-13.0	-78.2
HCN···II	146.7	-285.1	-136.0	-275.7	-48.8	63.7	-214.7	-476.1

Table S11: Interaction-induced electronic second hyperpolarizability computed at the MP2/aug-cc-pVTZ-PP level of theory. All values are given in au.

	$\Delta\gamma_{\mathrm{el}}^{(10)}$	$\Delta\gamma_{\mathrm{ex}}^{\mathrm{HL}}$	$\Delta\gamma_{\mathrm{del}}^{\mathrm{HF}}$	$\Delta\gamma^{\mathrm{HF}}$	$\Delta\gamma_{\mathrm{el,r}}^{(12)}$	$\Delta\gamma_{\mathrm{disp}}^{(20)}$	$\Delta\gamma_{\mathrm{ex}}^{(2)}$	$\Delta\gamma^{\mathrm{MP2}}$
HCN···BrBr	8211	-10840	18086	15491	3982	2120	10215	31814
HCN···BrCl	7030	-9574	15148	12826	3073	1691	7630	25221
HCN···BrF	4836	-7713	10989	8040	1791	1096	3563	14463
HCN···BrH	3278	-3247	2827	2829	1612	685	-340	4784
HCN···IBr	12714	-18684	24535	18533	4543	3498	8844	35421
HCN···ICl	10748	-16139	21353	16162	3251	2800	7530	29685
HCN···IF	6540	-11447	17589	12486	2480	1692	6617	23180
HCN···IH	5269	-5971	5971	5217	2306	1237	-105	8383
HCN···II	15899	-24868	29985	21241	7564	4722	11514	45019

Table S12: Interaction-induced nuclear-relaxation polarizability computed at the MP2/aug-cc-pVTZ-PP level of theory. All values are given in au.

	$\Delta\alpha_{\mathrm{el}}^{(10)}$	$\Delta\alpha_{\mathrm{ex}}^{\mathrm{HL}}$	$\Delta\alpha_{\mathrm{del}}^{\mathrm{HF}}$	$\Delta\alpha^{\mathrm{HF}}$	$\Delta\alpha_{\mathrm{el,r}}^{(12)}$	$\Delta\alpha_{\mathrm{disp}}^{(20)}$	$\Delta\alpha_{\mathrm{ex}}^{(2)}$	$\Delta\alpha^{\mathrm{MP2}}$
HCN···BrBr	98.48	-181.25	83.93	1.16	6.43	34.34	-20.10	21.83
HCN···BrCl	107.19	-197.10	96.56	6.65	6.53	34.74	-22.31	25.62
HCN···BrF	99.55	-182.54	112.13	29.13	4.63	22.79	-22.63	33.92
HCN···BrH	8.75	-12.45	3.68	-0.07	0.84	3.39	-2.36	1.79
HCN···IBr	153.17	-272.85	145.66	25.81	9.56	44.10	-40.88	39.07
HCN···ICl	140.82	-246.91	140.93	34.86	8.05	35.60	-35.84	42.51
HCN···IF	58.09	-87.61	65.07	35.55	1.23	6.60	-12.31	31.06
HCN···IH	14.63	-19.97	7.37	2.09	1.05	4.87	-3.74	4.25
HCN···II	142.57	-253.61	122.85	11.91	9.60	48.72	-37.81	32.43

Table S13: Interaction-induced nuclear-relaxation first hyperpolarizability computed at the MP2/aug-cc-pVTZ-PP level of theory. All values are given in au.

	$\Delta\beta_{\text{el}}^{(10)}$	$\Delta\beta_{\text{ex}}^{\text{HL}}$	$\Delta\beta_{\text{del}}^{\text{HF}}$	$\Delta\beta^{\text{HF}}$	$\Delta\beta_{\text{el,r}}^{(12)}$	$\Delta\beta_{\text{disp}}^{(20)}$	$\Delta\beta_{\text{ex}}^{(2)}$	$\Delta\beta^{\text{MP2}}$
HCN$\cdots$BrBr	-12937.8	24693.1	-13605.1	-1956.0	-653.3	-3711.7	2304.4	-3861.2
HCN$\cdots$BrCl	-13095.3	24968.6	-14563.0	-2690.0	-631.6	-3452.2	2588.9	-4234.7
HCN$\cdots$BrF	-5306.8	9478.4	-8500.6	-4324.3	-108.4	-539.7	1330.6	-3652.8
HCN$\cdots$BrH	-609.0	835.3	-326.2	-106.2	-62.1	-134.6	129.1	-171.5
HCN$\cdots$IBr	-14167.1	25432.5	-18377.7	-7112.5	-610.0	-1998.7	3257.3	-6222.6
HCN$\cdots$ICl	-8556.8	14235.4	-13170.9	-7492.7	-193.0	-275.2	1891.5	-6020.2
HCN$\cdots$IF	-25.5	-1468.1	-1356.8	-2855.0	162.8	633.2	-209.4	-2265.6
HCN$\cdots$IH	-1097.5	1536.8	-708.2	-268.8	-92.6	-261.9	245.0	-378.6
HCN$\cdots$II	-19380.6	35696.7	-20923.7	-4603.8	-1064.4	-4824.2	4953.6	-5538.0

Table S14: Curvature contributions to electric properties (in au). The corresponding numerical errors are shown in parentheses.

	μ_z^{curv}	$\alpha_{zz}^{\text{curv}}$	$\beta_{zzz}^{\text{curv}}$	$\gamma_{zzzz}^{\text{curv}}$
HCN$\cdots$BrBr	0.06 (0.000)	1.15 (0.001)	351.0 (6)	101650 (2630)
HCN$\cdots$BrCl	0.06 (0.000)	1.32 (0.000)	346.1 (5)	123100 (1800)
HCN$\cdots$BrF	0.05 (0.000)	1.45 (0.000)	34.7 (2.0)	29796 (369)
HCN$\cdots$BrH	0.06 (0.000)	1.77 (0.001)	345.3 (6.1)	123292 (2715)
HCN$\cdots$IBr	−0.07 (0.000)	0.57 (0.003)	−379.0 (4.7)	192527 (16427)
HCN$\cdots$ICl	0.06 (0.000)	1.13 (0.000)	214.1 (2.2)	158458 (3158)
HCN$\cdots$IF	0.05 (0.000)	1.92 (0.000)	6.9 (0.0)	17434 (1)
HCN$\cdots$IH	0.05 (0.000)	2.11 (0.000)	325.6 (28.0)	140286 (10206)
HCN$\cdots$II	0.07 (0.000)	1.09 (0.001)	790.1 (4.5)	167756 (17549)

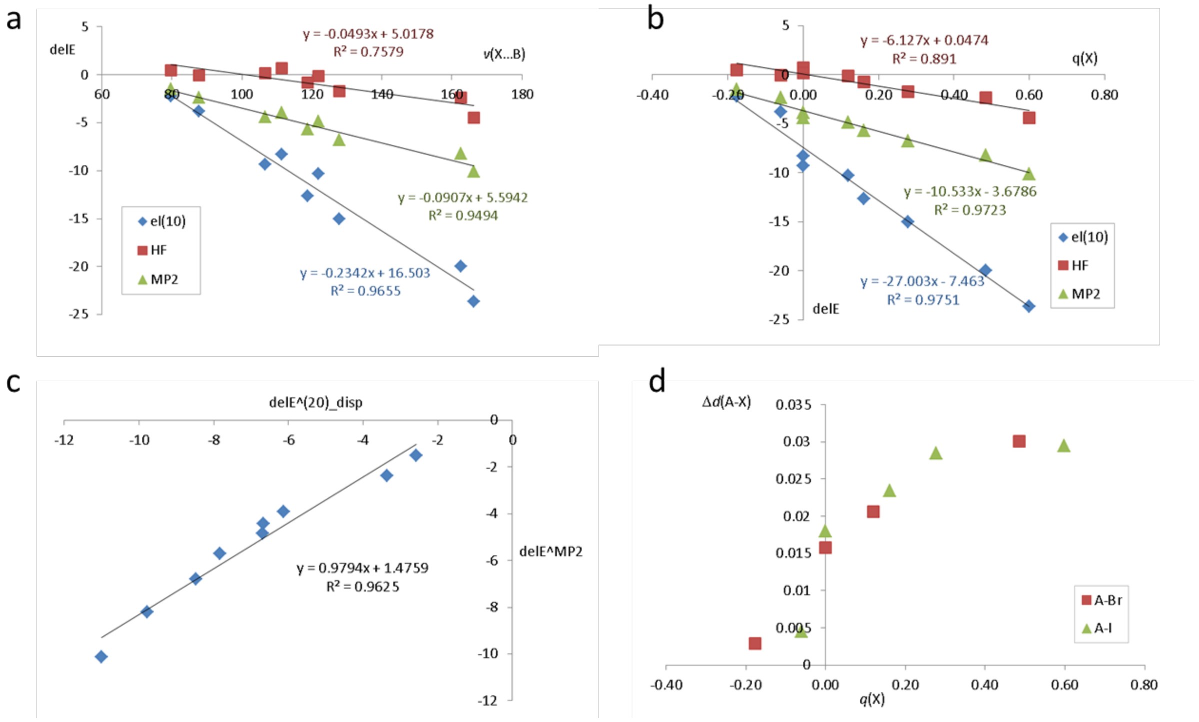

Figure S1 Linear regression analysis of the ΔE^{MP2} (green), ΔE^{HF} (red), and $\Delta\varepsilon_{\mathrm{el}}^{(10)}$ (blue) values on (a) the vibrational frequencies of the X…B stretching mode and (b) the natural partial charge on the X atom (q_X) in an isolated XB donor molecule. (c) The linear regression between the ΔE^{MP2} and $\Delta\varepsilon_{\mathrm{disp}}^{(20)}$ values for the whole set of XB complexes. (d) The linear regression between the change of the A–X bond length (Δd(A–X)) and the natural partial charge on the X atom (q_X). The red and green points correspond to bromine- and iodine-bonded complexes, respectively.