Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information Available for

Structural preferences in strong anion-π and halogen-bonded complexes: π- and σ-holes vs frontier orbitals interaction

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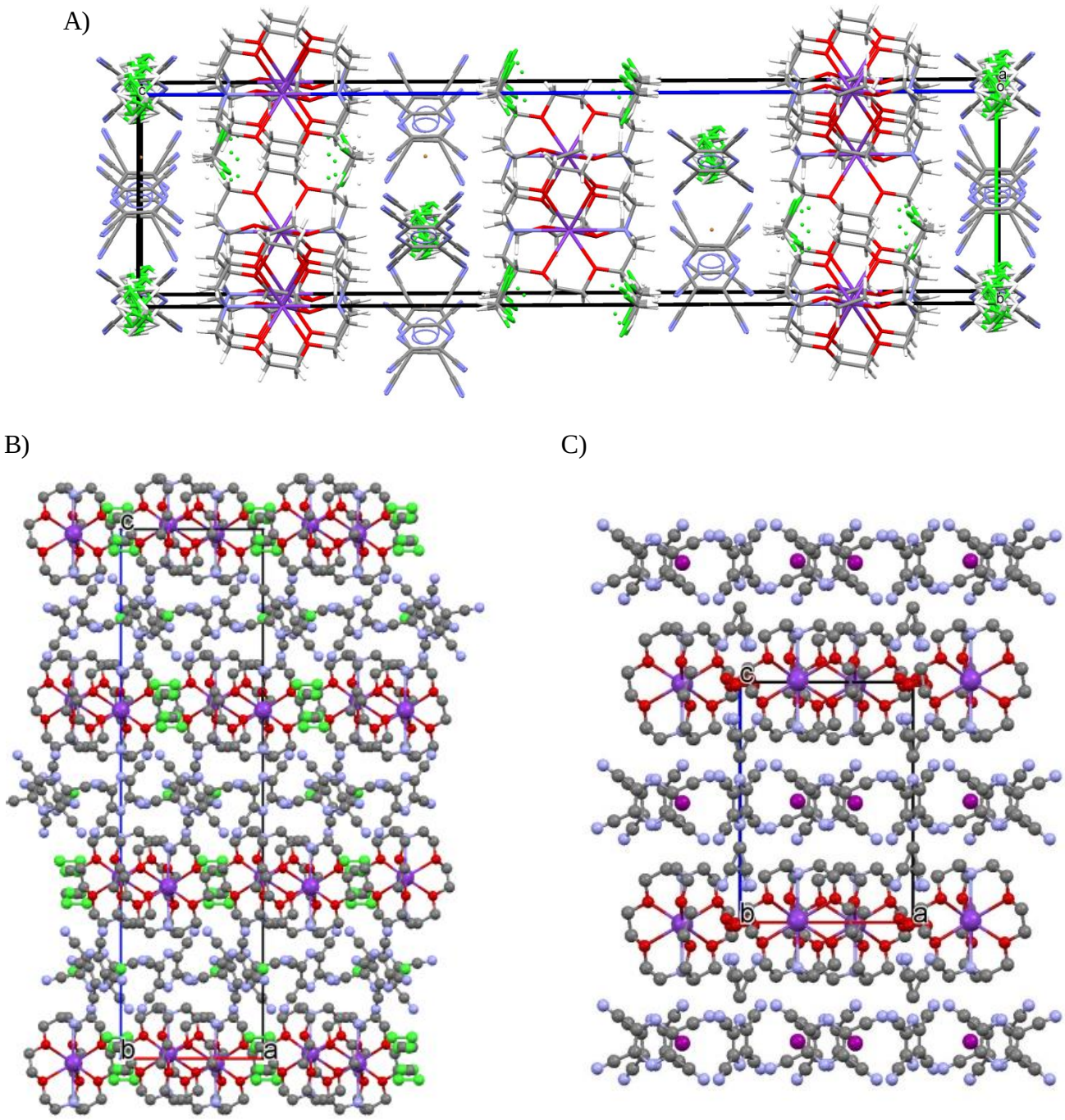

Figure S1 X-ray structures of K(crp)Br·TCP (A), K(crp)Cl·TCP (B) and K(crp)I·TCP (C) co-crystals

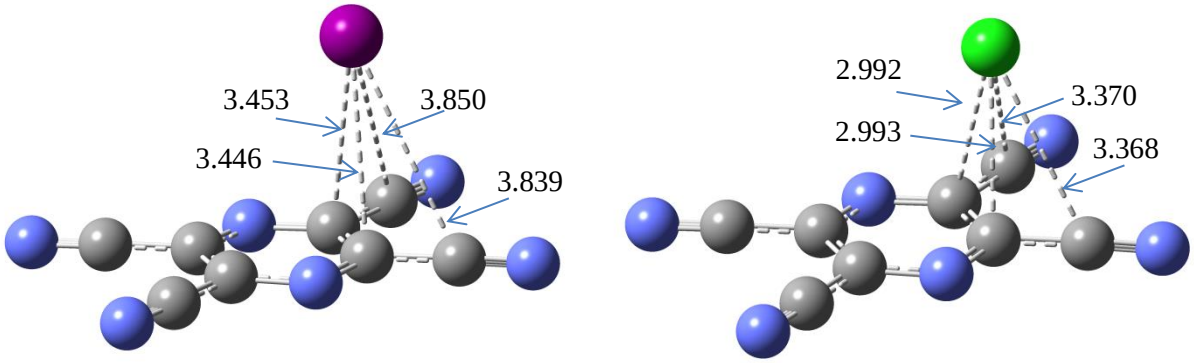

Figure S2. Calculated structures of TCP•I^- (left) and TCP•Cl^- (right) complexes (M062X/def2tzvpp computations in CH_2Cl_2, numbers indicate interatomic distances in Å).

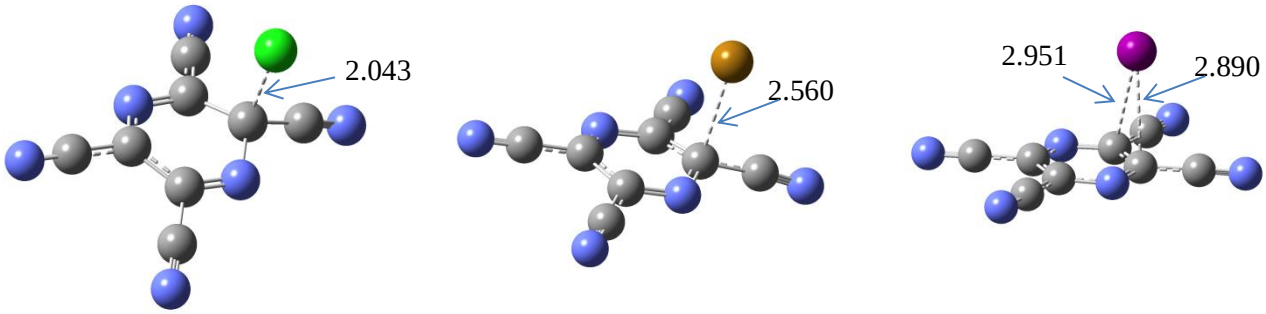

Figure S3. Calculated structures of TCP•Cl^- (left) and TCP•Br^- (center) and TCP•I^- (right) complexes (M062X/def2tzvpp computations in the gas phase, numbers indicate interatomic distances in Å).

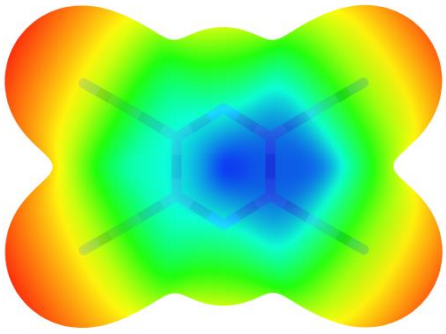

Figure S4. ESPs of the TCP molecule in the presence of the negative (-1) point charge located at the positions of the Br^- anion in the optimized (in dichloromethane) TCP•Br^- complex.

Table S1. Interatomic distances in the TCP•X^- co-crystals.[a]

X	Counter-ion	$d_{X\cdots C(Ar)}$, Å[b]		$d_{X\cdots C(cyano)}$, Å[c]	
Br	K^+(crp)	3.265	3.259	3.437	3.454
Br	Bu_4N^+	3.169	3.411	3.253	3.578
Br[d]	Pr_4N^+	3.149	3.458	3.222	3.692
Br[d]	Et_4N^+	3.154	3.235	3.372	3.510
I	K^+(crp)	3.425	3.444	3.739	3.793
I[d]	Et_4N^+	3.517	3.659	3.647	3.818
I[d]	Bu_4N^+	3.477	3.640	3.907	4.216
Cl	K^+(crp)	3.147	3.161	3.255	3.278
Cl	Pr_4N^+	3.055	3.411	3.105	3.677
Cl[d]	Bu_4N^+	3.066	3.363	3.114	3.568

a) The sums of the van der Waals radii for Cl···C, Br···C and I···C contacts are 3.45 Å, 3.55 Å and 3.68 Å respectively.[17] b) Distance from the halide to the aromatic ring carbons. c) Distance from the halide to the cyano-group carbons. d) Y. Rosokha, S. Lindeman, S. Rosokha and J. Kochi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4650.

Table S2. Halogen bond geometries in the R-Br•X^- co-crystals.[a]

Co-crystals (ref. code)	Contact	D(Z-X…Y), Å	∠(Z-X…Y), deg	∠X-X…Br), deg	R_{XY}
$(Pr_4N)N_3{\cdot}CBr_4$	Br3…N1	2.875(3)	167.66(12)	99.3(2)	0.85
(POCZAK)	Br2…N1	2.806 (3)	176.90(11)	108.2(2)	0.83
	Br4…N1	3.216(4)	160.48(18)	79.0 (2)	0.95
$(Pr_4N)NCO{\cdot}CBr_4$	Br2…N1	2.823(3)	176.39(12)	109.7(3)	0.83
(PODDAP)	Br4…N1	2.937(3)	167.40(12)	96.5(2)	0.86
	Br3…N1	3.188(3)	173.74(12)	79.8(2)	0.94
$(Pr_4N)NCO{\cdot}CBr_3NO_2$	Br2…N3	3.004(3)	167.74(9)	94.4(2)	0.88
(POCZEO)	Br1…N3	2.763(3)	176.06(9)	112.9(2)	0.81
	Br3…N3	3.212(3)	173.50(9)	80.3(2)	0.94
$2((Pr_4N)NCS){\cdot}CBr_4$	Br4…S1	3.2309(11)	171.76(11)	93.23(13)	0.92
(PODCUI)	Br1…S1	3.2147(11)	170.15(11)	108.83(13)	0.91
	Br3…N1	3.013(3)	167.07(13)	139.2(3)	0.89
	Br2…N2	2.897(4)	172.74(13)	136.5(3)	0.85
$2((Pr_4N)NCS){\cdot}CBr_3CONH_2$	Br2…S2	3.2294(6)	174.50(6)	96.21(8)	0.88
(POTDET)	Br3…S1	3.3377(6)	178.02(6)	79.13(8)	0.91
	Br1…S1	3.5286(6)	151.85(7)	123.56(8)	0.95

a) S. Rosokha, C. Stern, A. Swartz and R. Stewart, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12968. b) $R_{XY} = D_{X\cdots Y}/(r_X + r_Y)$, where $D_{X\cdots Y}$ is the intermolecular separation between X and Y, and r_X and r_Y are their van der Waals radii, i.e. 1.85Å for bromine, 1.55 Å for nitrogen and 1.80 Å for sulfur.

Table S3 Values of electrostatic potential (in a.u.) on the surface (0.001density) of the pseudohalide anions[a] X^- in the absence and in the presence of point charges (PC)

X^-	PC	-V (N_{top})	-V (N_{perp})	-V (S_{perp})
NCS^-	No PC	0.204	0.200	0.191
	PC-N_{top}	0.211	0.204	0.189
	PC-N_{perp}	0.210	0.207	0.190
	PC-S_{perp}	0.202	0.201	0.198
N_3^-	No PC	0.216	0.209	
	PC-N_{top}	0.223	0.211	
	PC-N_{perp}	0.220	0.215	
NCO^-	No PC	0.229	0.224	
	PC-N_{top}	0.234	0.225	
	PC-N_{perp}	0.233	0.229	

a) $V(N_{top})$, $V(N_{perp})$, $V(S_{perp})$ - ESP at the top of the nitrogen atom along the extension of C-N or N-N bond, on the surface of the nitrogen atom perpendicular to C-N or N-N bond and on the surface of the sulfur atom perpendicular to C-S bond (see below). PC-N_{top}, PC-N_{perp}, PC-S_{perp} - values of ESPs calculated with the point charge (0.17) placed along the extension of C-N or N-N bond, perpendicular to C-N or N-N bond or perpendicular to C-S bond (see below)

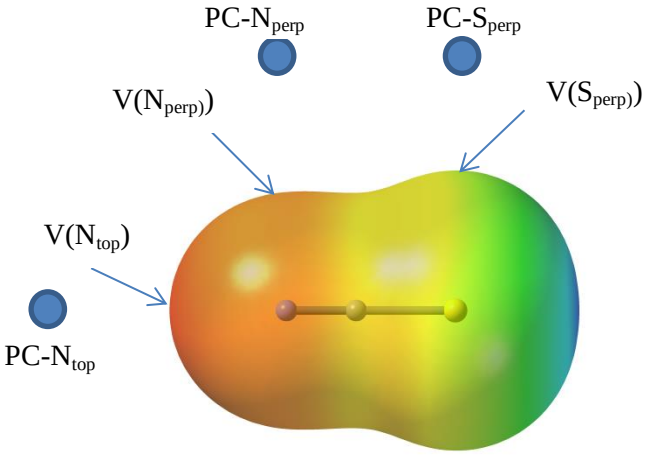

Table S4. Interaction energies, ΔE*, (in kcal/mol) in the calculated R-Br•X^- complexes [a]

R-Br	X	C-Br…S[b]	C-Br…N[b]	C-Br…N[c]
CBr_3F	NCS^-	-3.625	-3.092	-2.984
CBr_4	NCS^-	-3.889	-3.249	-3.213
CBr_4	NCO^-		-4.651	-4.260
CBr_3F	N_3^-		-4.878	-3.208
CBr_4	N_3^-		-5.225	-3.583

a) $\Delta E^* = E_{comp} - (E_{R\text{-}Br} + E_X)$, where E_{comp}, $E_{R\text{-}Br}$ and E_X are electronic energies of the complex, R-Br and X^- anion (from M062X/def2tzvpp computations in CH_2Cl_2.) b) Fully-optimized minimum with S…N or Br…N halogen bonding. c) Pairs resulted from constrained optimization with linear C-N…Br or N-N…Br angle.

Table S5. Energies (in Hartree) of the calculated complexes and their components.[a]

		E	E+ZPE
TCP	Br^-	-3207.64518	-3207.574147
TCP	Cl^-	-1093.64031	-1093.569207
TCP	I^-	-931.08558	-931.014411
-	Br^-	-2574.36766	-2574.36766
-	Cl^-	-460.36033	-460.36033
-	I^-	-297.81015	-297.81015
TCP	-	-633.26413	-633.193537
CBr_3F	NCS^- (Br…S)	-8351.712653	-8351.693552
	NCS^- (Br…N)	-8351.711804	-8351.692605
CBr_4	NCS^- (Br…S)	-10826.04745	-8351.693552
	NCS^- (Br…N)	-10826.04643	-10826.029467
CBr_3F	NCO^-	-8028.748971	-8028.727624
CBr_4	NCO^-	-10503.08372	-10503.064649
CBr_3F	N_3^-	-8024.84389	-8024.822074
CBr_4	N_3^-	-10499.17882	-10499.159546
-	NCS^-	-491.1918022	-491.182954
-	NCO^-	-168.2268634	-168.21582
-	N_3^-	-164.3210425	-164.309706
CBr_3F	-	-7860.515074	-7860.505479
CBr_4	-	-10334.84945	-10334.8422

a) From M062X/def2tzvpp computations in CH_2Cl_2.

Atomic coordinates of the calculated complexes (M062X/def2tzvpp computations in CH_2Cl_2).

TCP	Br^-	N	-0.62855500	-0.62616300	1.44406700
		C	-1.69409800	-0.29960100	0.72359100
		C	-1.69830300	-0.40669000	-0.66955700
		N	-0.63679100	-0.84031600	-1.33769800
		C	0.43596700	-1.11523400	-0.62684900
		C	0.44022600	-1.00664900	0.77688700
		C	1.61369200	-1.55983500	-1.32944600
		N	2.54636700	-1.94783400	-1.86853500
		C	1.62184200	-1.33998100	1.53203300
		N	2.55632500	-1.64283700	2.12041900
		C	-2.86619100	0.14808200	1.43188200
		N	-3.81105600	0.50075500	1.97438000
		C	-2.87332900	-0.06900600	-1.43187900
		N	-3.81909500	0.20126300	-2.01840200
		Br	1.61916500	1.83941100	-0.132560001
TCP	Cl^-	N	-0.28578500	-1.39616700	-0.44114100
		C	-1.40108500	-0.69781600	-0.25519500
		C	-1.40097100	0.69726500	-0.25626900
		N	-0.28548900	1.39513200	-0.44300600
		C	0.82486000	0.70435000	-0.57177600
		C	0.82469800	-0.70580500	-0.57098900
		C	2.05559600	1.43416600	-0.74970000
		N	3.03403200	1.99941200	-0.93461500
		C	2.05523500	-1.43603800	-0.74861300
		N	3.03355500	-2.00155600	-0.93331800
		C	-2.62655000	-1.43412900	-0.07724600
		N	-3.61382600	-1.99767500	0.06161800
		C	-2.62628000	1.43417500	-0.07972300
		N	-3.61339300	1.99826700	0.05808800
		Cl	1.52254800	0.00241800	2.25198100
TCP	I^-	N	1.02321700	0.85834100	1.40371200
		C	1.98287600	0.26924900	0.70418600
		C	1.98810200	0.28670400	-0.69477900
		N	1.03308300	0.89255400	-1.38646200
		C	0.05123100	1.42959100	-0.69167000
		C	0.04618200	1.41225700	0.71525900
		C	-1.02005800	2.06313800	-1.41880100
		N	-1.86629400	2.59644200	-1.97630300
		C	-1.02984100	2.02908000	1.44976900
		N	-1.87903300	2.55091600	2.01359400
		C	3.04474800	-0.37474500	1.43487900
		N	3.90213500	-0.89041500	1.99209300
		C	3.05638900	-0.33720900	-1.43347000
		N	3.91887200	-0.83729400	-1.99696900
		I	-1.72908700	-1.45023000	-0.01396000

CBr_3	NCS^-	Br	-0.82275300	-0.29796700	-0.03557000
	(Br…S)	Br	2.16951500	-1.42746200	-0.02200800
		Br	1.66047300	1.69342700	-0.40727800
		C	1.01959400	0.06742500	0.43958400
		F	1.09380300	0.24296200	1.76481200
		C	-4.32290200	0.46023900	0.27119700
		S	-3.94996500	-0.87611700	-0.64050100
		N	-4.58259400	1.39789800	0.91000100
	NCS^-	Br	0.63987400	-0.40512600	-0.01962400
	(Br…N)	Br	-1.68847800	1.77783600	-0.25740700
		Br	-2.41841900	-1.31991400	-0.17387900
		C	-1.17769900	0.04041600	0.44594500
		N	3.39335000	-1.09540800	-0.54381300
		F	-1.27775300	0.10117200	1.78008100
		C	4.32175400	-0.45087700	-0.25522600
		S	5.63923700	0.46076600	0.15147100
CBr_4	NCS^-	Br	1.41839600	-0.55925500	1.77850000
	(Br…S)	Br	1.87918600	1.55904700	-0.52605900
		Br	1.22152400	-1.44997400	-1.25343900
		Br	-1.03791600	0.40732200	0.00060700
		C	0.86357300	-0.01033200	0.00005700
		S	-4.15673400	1.05445000	-0.00211600
		N	-4.77188600	-1.70189400	0.00498100
		C	-4.51869300	-0.56597200	0.00205900
	NCS^-	Br	1.51116300	1.71662700	-0.81617100
	(Br…N)	Br	1.71951900	-0.00903900	1.82922300
		Br	-0.85366600	-0.24364700	-0.01417900
		Br	1.93063200	-1.41591300	-0.99690400
		C	1.06325100	0.00852200	-0.00143900
		S	-6.40014300	0.22861900	0.00550600
		N	-3.69526500	-0.56728700	-0.01563900
		C	-4.81301200	-0.23650000	-0.00648300
CBr_3	NCO^-	Br	1.03610000	-0.36152400	-0.02553700
		Br	-1.36445300	1.75071200	-0.25716900
		Br	-2.00269500	-1.36799300	-0.17477600
		C	-0.79743200	0.02828100	0.44353500
		N	3.71512600	-0.93872000	-0.58541500
		F	-0.90284200	0.08597200	1.77895900
		C	4.45674600	-0.12607100	-0.15115600
		O	5.21881200	0.70527700	0.29310800
CBr_4	NCO^-	Br	-1.56687500	-0.92800100	-1.43936500
		Br	-0.89831300	1.92340800	-0.24233300
		Br	-1.44590200	-0.51709300	1.69658100
		Br	1.23497600	-0.43097300	-0.01354000
		C	-0.65467300	0.00939600	-0.00202900
		N	3.93527500	-1.10935600	-0.00601300
		C	4.60841200	-0.13644600	-0.00186800
		O	5.29932100	0.85885600	0.00230800

CBr_3	N_3^-	Br	1.08284800	-0.00041100	0.59363600
		Br	-1.50853400	1.59441100	-0.41826600
		Br	-1.50908500	-1.59397900	-0.41880600
		C	-0.85282100	-0.00004200	0.48266100
		N	4.05557400	0.00004300	-0.47392000
		N	3.86045200	-0.00072500	0.68337200
		N	4.24035300	0.00080700	-1.62120500
		F	-1.36230500	-0.00015200	1.72295000
CBr_4	N_3^-	Br	-1.13220000	-0.64193600	1.76449700
		Br	1.25522300	0.52801100	0.00184600
		Br	-1.74132600	1.51023500	-0.47465700
		Br	-0.90142900	-1.42953100	-1.29246000
		C	-0.61961300	-0.00507100	-0.00099500
		N	4.38031400	0.05356700	0.00156100
		N	3.91287700	1.13086000	0.00367000
		N	4.83657000	-1.01397300	-0.00050800