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

Supporting Information Available for

From charge transfer to electron transfer in halogen-bonded complexes of electrophilic bromocarbons with halide anions

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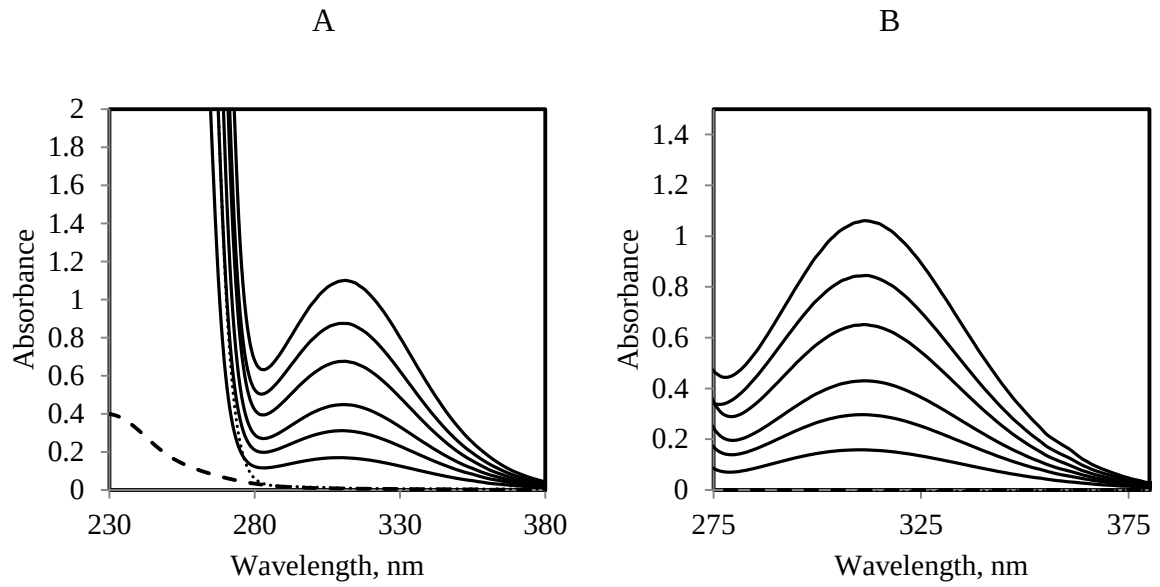


Figure S1. (A) Spectral changes resulting from the addition of $(Bu_4N)I$ to a 2.5 mM solution of CBr_3F in CH_3CN (19 ^oC). Concentration of $(Bu_4N)I$ (solid lines, in mM): 29, 57, 87, 157, 214 and 285. Dot and dashed line correspond to the separate solutions of $(Bu_4N)I$ and CBr_3F, respectively. B) Spectra of the $[CFBr_3,I^-]$ complex after subtraction of the absorption of components.

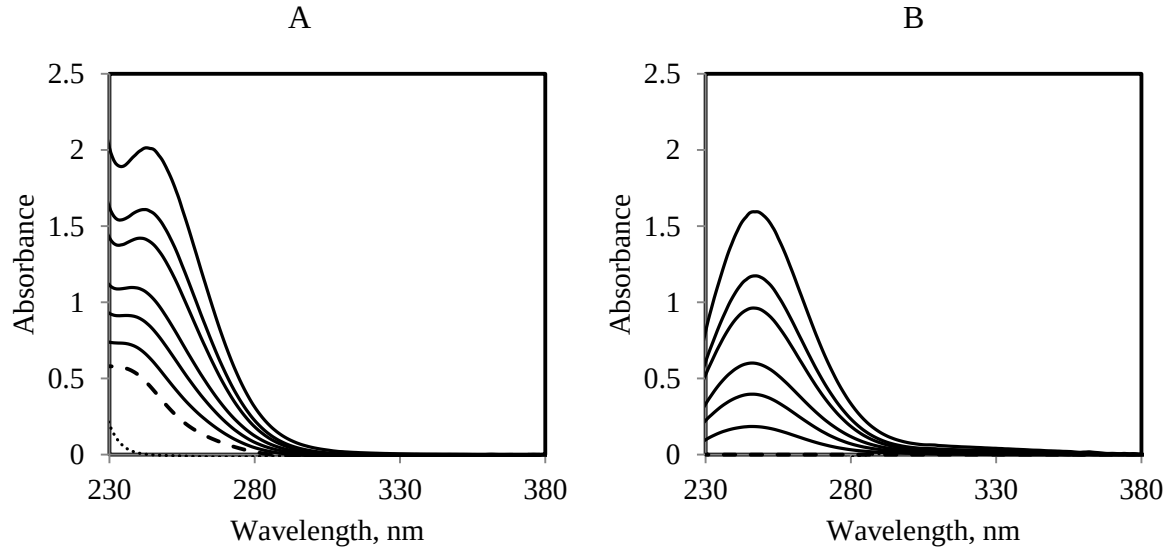


Figure S2. (A) Spectral changes resulting from the addition of $(Bu_4N)Cl$ to a 4.1 mM solution of CBr_3F (CH_2Cl_2, 19 ^oC). Concentration of $(Bu_4N)Cl$ (solid lines from the bottom to the top, in mM): 26, 54, 87, 139,189 and 272. Dashed line and dot line correspond to the separate solutions of CBr_3F and $(Bu_4N)Cl$, respectively. (B) Spectra of the $[CFBr_3,Cl^-]$ complex after subtraction of the absorption of components.

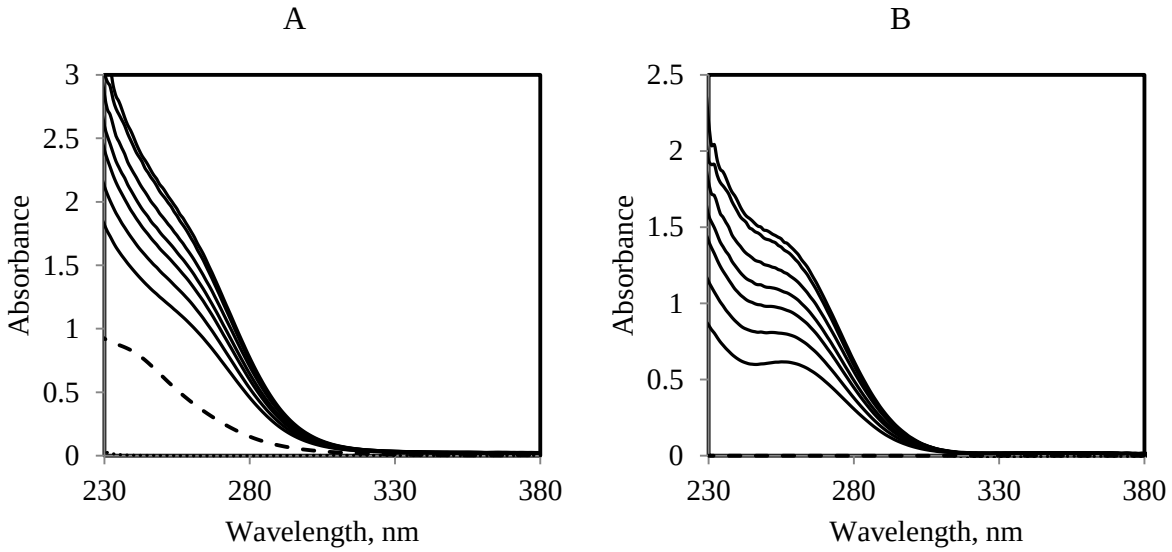


Figure S3. (A) Spectral changes resulting from the addition of $(Bu_4N)Cl$ to a 3.1 mM solution of CBr_3CN (CH_2Cl_2, 19 ^oC). Concentration of $(Bu_4N)Cl$ (solid lines, in mM): 59, 84, 118, 147, 196, 245, 294 and 493. Dashed line and dot-dashed line correspond to the separate solutions of $(Bu_4N)Cl$ and CBr_3CN, respectively. (B) Spectra of the $[CBr_3CN,Cl^-]$ complex after subtraction of the absorption of components.

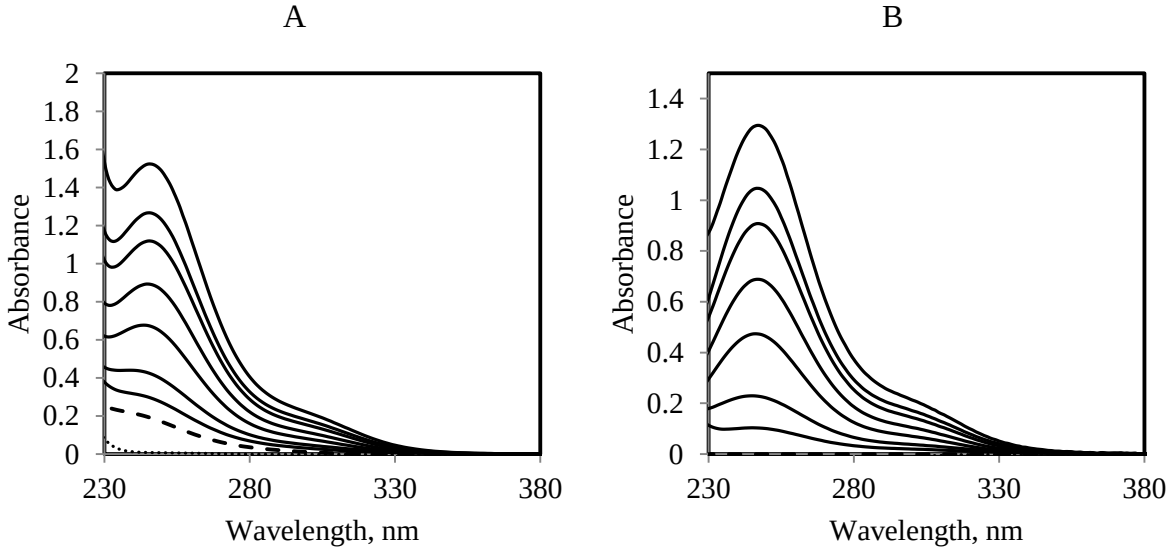


Figure S4. Spectral changes resulting from the addition of $(Bu_4N)Cl$ to a 1.25 mM solution of CBr_3NO_2 (CH_2Cl_2, 19 ^oC). Concentration of $(Bu_4N)Cl$ (solid lines, in mM): 9.7, 19.1, 56, 105, 176, 236 and 317. Dashed line and dot-dashed line correspond to the separate solutions of $(Bu_4N)Cl$ and CBr_3NO_2, respectively. (B) Spectra of the $[CBr_3NO_2,Cl^-]$ complex after subtraction of the absorption of components.

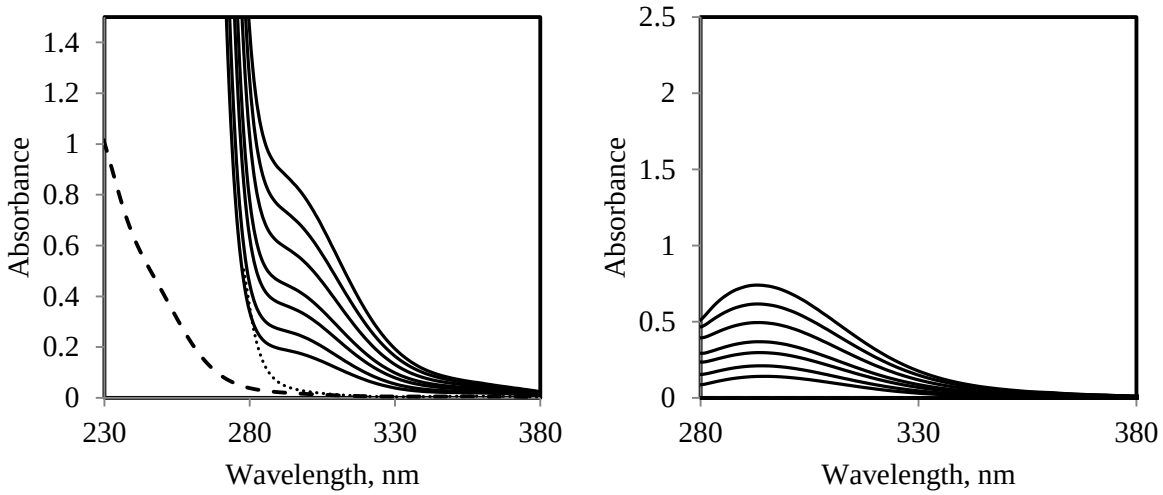


Figure S5. Spectral changes resulting from the addition of $(Bu_4N)I$ to a 5.1 mM solution of CBr_3H (CH_2Cl_2, 19 ^oC). Concentration of $(Bu_4N)I$ (solid lines, in mM): 72, 103, 145, 181, 241, 301, and 361 mM. Dot-line and dashed line correspond to the separate solutions of $(Bu_4N)I$ and $CHBr_3$, respectively. (B) Spectra of the $[CHBr_3,I^-]$ complex after subtraction of the absorption of components.

Table S1. Spectral characteristics and formation constants of the [R-Br, X^-] complexes in CH_3CN.[a]

	[R-Br, Cl^-]		[R-Br, I^-]	
R-Br	λ_{max}, nm (ε, 10^4 $M^{-1}cm^{-1}$)	K, M^{-1}	λ_{max}, nm (ε, 10^4 $M^{-1}cm^{-1}$)	K, M^{-1}
CBr_3H	<230 [d]	-	292(2.7)	0.7
CBr_3F	247(1.4)	2.1	312 (1.2)	1.9
CBr_3CN	260 (0.7)	10.7	reaction	-
CBr_4	265		344 (1.5)	3.0
CBr_3NO_2	247, 300sh	7.5	reaction	-

A) at 292 K.

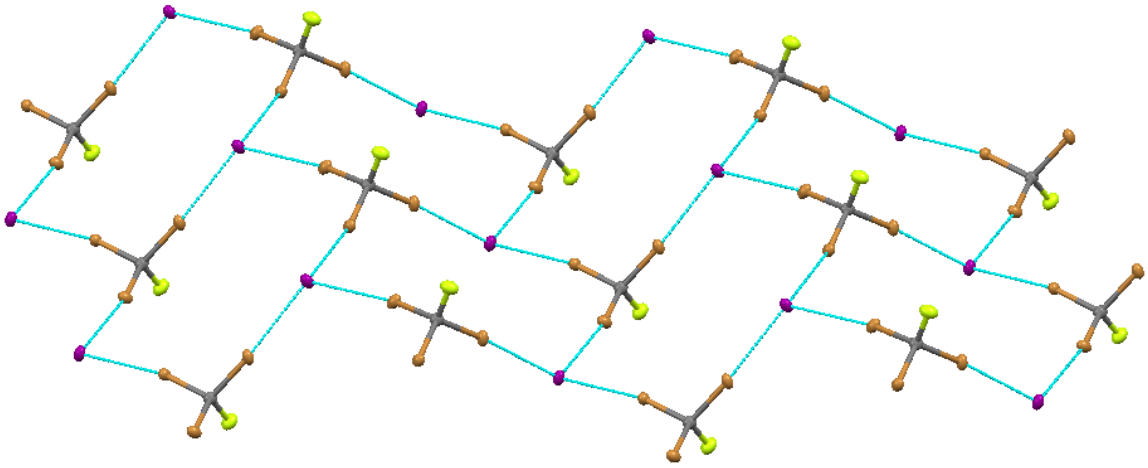


Figure S6. Infinite networks formed by halogen bonding of CBr_3F electrophile and I^- anions (in the $(Pr_4N)I{\cdot}CBr_3F$ co-crystals. Halogen Br…I bonds are shown as light blue lines. Tetrapropylammonium counterions are omitted, for clarity.

Table S2. Characteristics of short crystallographically-independent contacts (distances, ion Å and angles, in deg) in the X-ray structures of $(Pr_4N)X \cdot$R-Br co-crystals.

$(Pr_4N)Cl \cdot CB_3NO_2$			
Br1…Cl2	3.124	C1Br1Cl2	170.9
Br2…Cl1	3.044	C1Br2Cl1	174.1
Br3…Cl2	2.986	C1Br3Cl2	173.4
Br5…Cl2	3.084	C2Br5Cl2	176.2
Br4…Cl1	3.269	C2Br4Cl1	169.1
Br6…Cl1	2.987	C2Br6Cl1	174.9
$(Pr_4N)I \cdot CB_3F$			
Br2…I1	3.372	C1Br2I1	175.3
Br3…I1	3.443	C1Br3I1	166.2
Br5…I2	3.394	C2Br5I2	175.7
Br4…I2	3.498	C2Br4I2	166.6
Br6…I2	3.462	C2Br6I2	170.1
$(Pr_4N)I{\cdot}CB_3CN$ I			
Br1…I1	3.356	C1Br1I1	177.1
Br2…I1	3.316	C1Br2I1	175.2
Br3…I1	3.539	C1Br3I1	162.9

Table S3. Intramolecular C-Br bond lengths and energies of the R-Br· X^- associates together with the bond lengths in separate R-Br electrophiles.

R-Br	E, Hartree	C-Br, Å				∠CBrX, deg
		R-Br· Cl^- (gas-phase)				
CBr_3H	-8221.479576	1.9398	1.9597	1.9597		175.1
CBr_3F	-8320.717525	1.9560	1.9709	1.9709		176.9
CBr_4	-10795.03904	1.9903	1.9644	1.9648	1.9648	179.9
CBr_3CN	-8313.708157	2.0310	1.9603	1.9603		179.7
CBr_3NO_2	-8425.956093	2.0376	1.9338	1.9337		179.0
		R-Br· Cl^- (in dichloromethane)				
CBr_3H	-8221.56622	1.9300	1.9407	1.9407		176.7
CBr_3F	-8320.798866	1.9352	1.9455	1.9455		177.6
CBr_4	-10795.11943	1.9451	1.9494	1.9501	1.9495	179.9
CBr_3CN	-8313.785172	1.9546	1.9483	1.9483		179.6
CBr_3NO_2	-8426.03284	1.9472	1.9222	1.9222		178.4
		R-Br· I^- (gas-phase)				
CBr_3H	-14681.21979	1.9392	1.9555	1.9555		174.5
CBr_3F	-14780.45696	1.9577	1.9660	1.9660		176.7
CBr_4	-17254.77846	1.9937	1.9614	1.9618	1.9628	180.0
CBr_3CN	-14773.44686	2.0436	1.9575	1.9575		179.7
CBr_3NO_2	-14885.69479	2.0556	1.9298	1.9298		179.2
		R-Br· I^- (in dichloromethane)				
CBr_3H	-14681.29811	1.9342	1.9384	1.9384		175.8
CBr_3F	-14780.53047	1.9411	1.9432	1.9432		177.2
CBr_4	-17254.85115	1.9514	1.9493	1.9480	1.9467	179.8
CBr_3CN	-14773.51684	1.9614	1.9458	1.9458		179.4
CBr_3NO_2	-14885.76437	1.9540	1.9204	1.9206		179.3
		R-Br· (gas-phase)[a]				
CBr_3H		1.9308	1.9310	1.9310		
CBr_3F		1.9381	1.9372	1.9371		
CBr_4		1.9430	1.9422	1.9420	1.9424	
CBr_3CN		1.9450	1.9430	1.9434		
CBr_3NO_2		1.9281	1.9117	1.9281		
		R-Br· (in dichloromethane)[a]				
CBr_3H		1.9327	1.9324	1.9320		
CBr_3F		1.9364	1.9373	1.9374		
CBr_4		1.9429	1.9425	1.9433	1.9433	
CBr_3CN		1.9422	1.9440	1.9423		
CBr_3NO_2		1.9317	1.9151	1.9184		

a) From ref. 10.

Table S4. Charge transfer and intermolecular separations in [R-Br, Br^-] complexes.[a]

	Gas-phase		CH_2Cl_2	
R-Br	Δq, e	$d_{Br\cdots Br}$	Δq, e	$d_{Br\cdots Br}$
		2.884		3.268
CBr4	0.236		0.058	
		3.068		3.363
CHBr3	0.131		0.038	
		2.774		3.189
CBr3NO2	0.320		0.078	
		2.803		3.203
CBr3CN	0.293		0.074	
		3.03		3.223
BrCN	0.121		0.053	
		2.914		3.29
CBr3COOH	0.218		0.053	
		2.972		3.292
CFBr3	0.177		0.051	
		3.014		3.309
CBr3CONH2	0.154		0.047	
		3.008		3.295
C3Br2F6	0.150		0.047	
		2.784		3.261
CBr3COCBr3	0.318		0.057	

a) Resulted from M062X/6-311+G(dp) computations (from ref. 10).

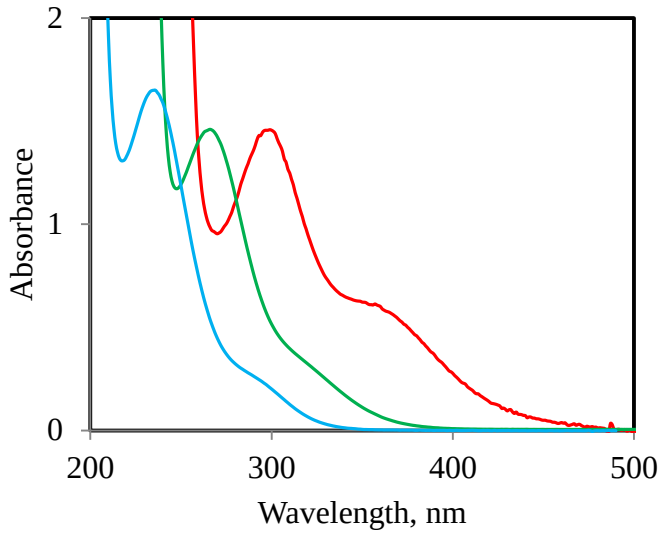


Figure S7.Absorption spectra of complex [CBr_3NO_2,I^-] (red) obtained by mixing of dichloromethane solutions of CBr_3NO_2 and(Bu_4N)I at -90°C in comparison with the spectra of [CBr_3NO_2,Br^-] (green) and [CBr_3NO_2,Cl^-] (blue).

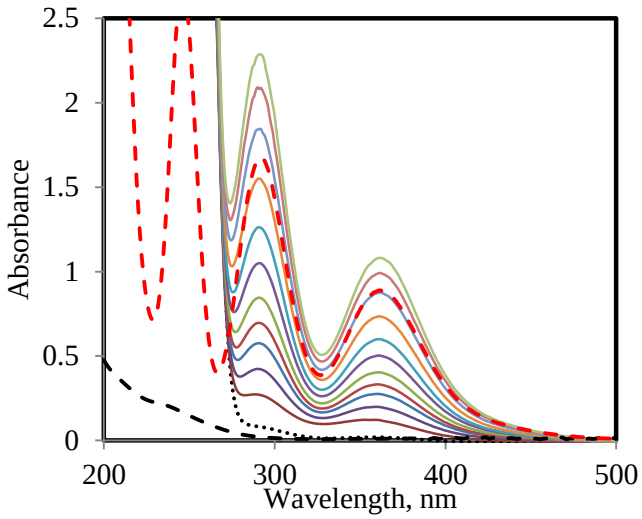


Figure S8. Time-dependent absorption spectra (solid lines, from the bottom to the top) of the solution containing 0.025 mM of CBr_3CN and 4 mM iodide in acetonitrile at 22°C showing rise of the absorption of the triiodide anion. Black dot- and dashed-line correspond to the separate solutions of $(Bu_4N)I$ and CHr_3CN, respectively, and red dashed-line represent triiodide produced by addition of I_2 to solution of $(Bu_4N)I$.

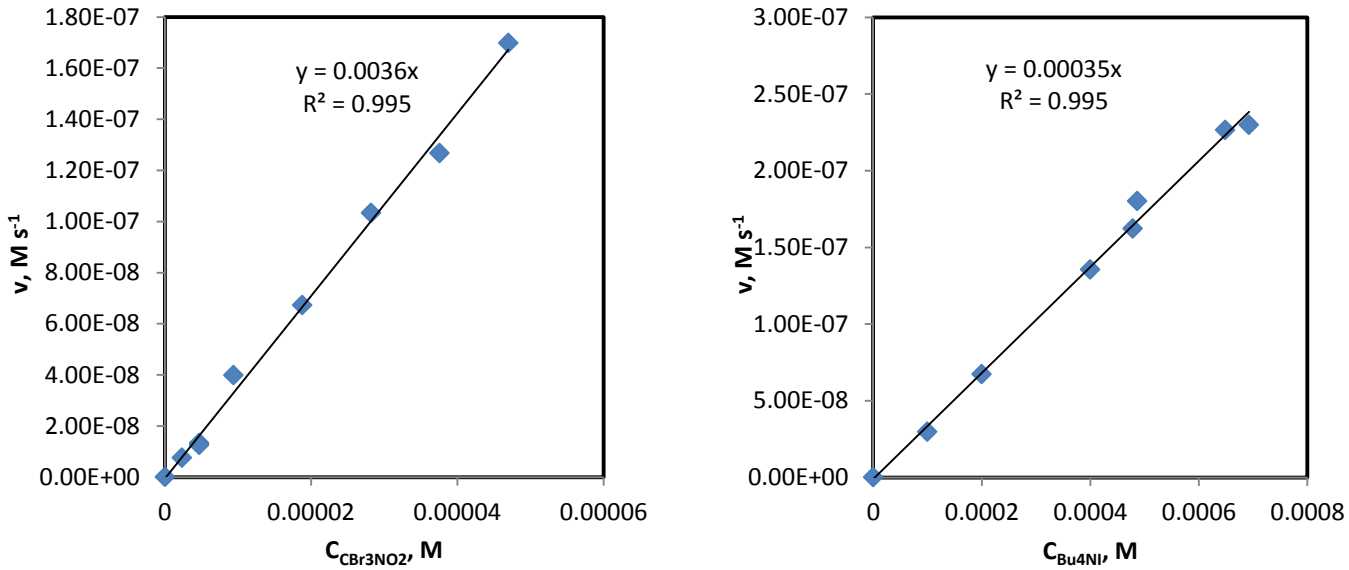


Figure S9. Dependence of the initial rates of the formation of I_3^- in the acetonitrile solutions containing $(Bu_4N)I$ and CHr_3NO_2 on initial concentrations of reactants (22°C). (A) Variations of rates with concentration of CHr_3NO_2 at $[(Bu_4N)I] = 0.2$mM; (B) Variation of rates with concentration of $(Bu_4N)I$ at $[CHr_3NO_2] = 0.019$ mM.

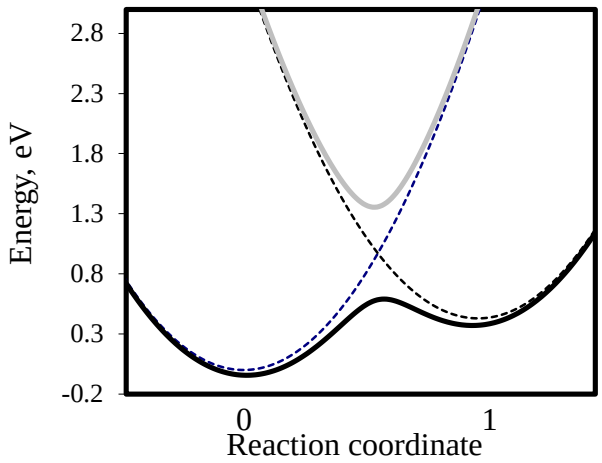


Figure S10. Potential energy diagram 7 for the inner-sphere ET in the CBr_3NO_2/I^- dyad in which energies of the initial and final diabatic states (shown as dashed lines) were calculated at each point along the ET reaction coordinate (from X= 0 to X = 1) as $H_{aa} = \lambda X^2$ and $H_{bb} = \Delta G_{ET}^{o} + \lambda(X-1)^2$ using λ = 68.3 kcal/mol (2.96 eV), G^{o}_{IS} = 9.9 kcal/mol (0.43 eV). Adiabatic ground and exited state energies (solid black and grey lines) were calculated as $E_{GS}= (H_{aa}+ H_{bb})/2 - ((H_{bb} - H_{aa})^2+ 4H_{ab}^2)^{1/2}/2$ and $E_{ES}= (H_{aa}+ H_{bb})/2 + ((H_{bb} - H_{aa})^2+ 4H_{ab}^2)^{1/2}/2$ based on the energies of the diabatic states and H_{ab} = 8.9 kcal/mol (0.39eV).

Atomic coordinates resulting from the M062X/6-311+G(dp) computations of R-Br·X^- pairs in the gas phase and in dichloromethane

$CHBr_3 \cdot I^-$ (Gas-Phase)

C	1.69682900	0.00000000	0.54481300
H	1.86203400	0.00002100	1.61432000
Br	-0.21150200	0.00068100	0.20013400
Br	2.60416700	1.60198700	-0.11424000
Br	2.60312000	-1.60263000	-0.11410700
I	-3.52633000	-0.00002600	-0.07350400

$CHBr_3 \cdot I^-$ (Gas-Phase)

C	1.80670200	0.00001400	0.55939200
H	1.96681000	0.00006500	1.62934800
Br	-0.10164200	0.00008300	0.24430000
Br	2.65549300	1.59994300	-0.13129200
Br	2.65524400	-1.60005700	-0.13126900
I	-3.68161000	0.00001700	-0.08201100

$CHBr_3 \cdot Cl^-$ (Gas-Phase)

C	0.59295300	-0.58969000	0.00000000
H	1.67386000	-0.64529700	0.00000000
Br	0.03899700	1.26927700	0.00000000
Br	0.03899700	-1.57259500	-1.60226700
Br	0.03899700	-1.57259500	1.60226700
Cl	-0.54860200	4.10828000	0.00000000

$CHBr_3 \cdot Cl^-$ (Dichloromethane)

C	-0.71001800	0.00000500	0.55697000
H	-0.84889800	0.00000900	1.62983400
Br	1.18546900	0.00067100	0.19372300
Br	-1.58011000	-1.60016700	-0.11293000
Br	-1.58107500	1.59954800	-0.11306300
Cl	4.36818100	-0.00010800	-0.22601400

$CBr_4 \cdot I^-$ (Gas-Phase)

C	1.34835700	-0.00009200	-0.00082400
Br	2.04303600	-1.19260400	-1.39456600
Br	2.03905100	-0.61342800	1.72987800
Br	-0.64530900	0.00046400	-0.00119800
Br	2.04219200	1.80563800	-0.33340600
I	-3.77083200	-0.00003600	-0.00037400

$CBr_4 \cdot I^-$(Dichloromethane)

C	-1.55565900	0.00002400	0.13239100
Br	-2.29322200	-1.58469700	-0.66302400
Br	0.39742200	0.00041300	0.07325600
Br	-2.29412800	1.58457300	-0.66285300
N	-1.89664100	-0.00032100	1.66596500
O	-1.97700400	1.07256700	2.20079500
O	-1.97856500	-1.07359700	2.19981100
I	3.79061300	0.00000400	-0.07206000

$CBr_4 \cdot Cl^-$ (Gas-Phase)

C	-0.46618700	-0.00040400	0.00752700
Br	-1.19211200	1.14789200	-1.41190700
Br	-1.13777100	0.66798400	1.72875300
Br	1.52385000	-0.00228800	-0.02653700
Br	-1.17650800	-1.81272700	-0.25698400
Cl	4.24623900	-0.00163100	-0.07126800

$CBr_4 \cdot Cl^-$ (Dichloromethane)

C	0.51939700	-0.00031600	-0.00015900
Br	1.18667200	0.84927000	-1.62282600
Br	1.18190600	-1.83276600	0.07760300
Br	-1.42568200	0.00050600	-0.00185600
Br	1.18223600	0.98250600	1.54751800
Cl	-4.55858900	0.00110800	-0.00084900

$CBr_3NO_2 \cdot I^-$ (Gas-Phase)

C	-1.48664200	-0.00002900	0.15571500
Br	-2.22422000	-1.58454400	-0.66242000
Br	0.56755900	-0.00009500	0.07915200
Br	-2.22369500	1.58487200	-0.66210100
N	-1.84266800	-0.00019800	1.65201100
O	-1.92258300	1.07358700	2.19667600
O	-1.92197800	-1.07413900	2.19644100
I	3.55448000	-0.00004100	-0.07651700

$CBr_3NO_2 \cdot I^-$(Dichloromethane)

C	-1.55565900	0.00002400	0.13239100
Br	-2.29322200	-1.58469700	-0.66302400
Br	0.39742200	0.00041300	0.07325600
Br	-2.29412800	1.58457300	-0.66285300
N	-1.89664100	-0.00032100	1.66596500
O	-1.97700400	1.07256700	2.20079500
O	-1.97856500	-1.07359700	2.19981100
I	3.79061300	0.00000400	-0.07206000

$CBr_3NO_2 \cdot Cl^-$ (Gas-Phase)

C	-0.57947000	-0.00002100	0.15798300
Br	-1.35387300	-1.58426000	-0.63574900
Br	1.45282200	0.00081100	0.01052900
Br	-1.35508800	1.58328900	-0.63629900
N	-0.89806500	0.00020200	1.66562200
O	-0.96491400	1.07370700	2.21226300
O	-0.96364800	-1.07307500	2.21286100
Cl	4.06803600	-0.00004300	-0.22676800

$CBr_3NO_2 \cdot Cl^-$(Dichloromethane)

C	0.60309200	-0.00009500	0.13549000
Br	1.36279000	1.58423300	-0.64390400
Br	-1.34108300	-0.00074600	0.02710200
Br	1.36426900	-1.58388400	-0.64367200
N	0.91377700	0.00048000	1.67556000
O	0.98404800	-1.07221700	2.21242000
O	0.98541200	1.07372300	2.21114200
Cl	-4.36940100	-0.00005400	-0.2243380

$CBr_3CN \cdot I^-$ (Gas-Phase)

C	0.68698600	-1.45440200	0.00000000
Br	0.06261900	-2.38985600	1.60208900
Br	0.06261900	0.49147400	0.00000000
Br	0.06261900	-2.38985600	-1.60208900
C	2.13369700	-1.50853200	0.00000000
N	3.28434200	-1.52129400	0.00000000
I	-0.87715900	3.36820700	0.00000000

$CBr_3\ CN \cdot I^-$(Dichloromethane)

C	1.43448300	-0.88460200	0.00000000
Br	1.43448300	-1.99182400	1.60010000
Br	-0.09520100	0.34310400	0.00000000
Br	1.43448300	-1.99182400	-1.60010000
C	2.65899100	-0.10245600	0.00000000
N	3.62144500	0.52482000	0.00000000
I	-2.77344900	2.44656000	0.00000000

$CBr_3\ CN \cdot Cl^-$ (Gas-Phase)

C	0.44169300	0.54610200	0.00000000
Br	1.49073700	0.12538400	1.60162000
Br	-1.32856800	-0.44950300	0.00000000
Br	1.49073700	0.12538400	-1.60162000
C	0.21230100	1.97604200	0.00000000
N	0.00000000	3.10708500	0.00000000
Cl	-3.63391800	-1.76040900	0.00000000

$CBr_3CN \cdot Cl^-$(Dichloromethane)

C	0.47603700	0.54540200	0.00000000
Br	1.50742700	0.13183600	1.60029000
Br	-1.23167300	-0.40557800	0.00000000
Br	1.50742700	0.13183600	-1.60029000
C	0.21478600	1.97496900	0.00000000
N	0.00000000	3.10344200	0.00000000
Cl	-3.91504600	-1.87526900	0.00000000

$CBr_3F \cdot I^-$ (Gas-Phase)

C	1.60470900	0.00001500	0.45504000
Br	2.47093700	-1.60182100	-0.28593400
Br	2.47133300	1.60159600	-0.28598800
Br	-0.33330100	0.00024100	0.17830700
F	1.87554400	-0.00004800	1.76958700
I	-3.54381300	-0.00000400	-0.09207500

$CBr_3F \cdot I^-$(Dichloromethane)

C	0.00000000	1.76588000	0.00000000
Br	0.92784400	2.36635700	1.59830800
Br	0.92784400	2.36635700	-1.59830800
Br	-0.24538200	-0.15965600	0.00000000
F	-1.20973500	2.34439400	0.00000000
I	-0.85798800	-3.61799300	0.00000000

$CBr_3F \cdot Cl^-$ (Gas-Phase)

C	0.59992400	0.00000900	0.45167300
Br	1.50117600	-1.60211100	-0.25932700
Br	1.50169200	1.60182400	-0.25938800
Br	-1.32491400	0.00028500	0.10392600
F	0.83400900	-0.00001400	1.77521100
Cl	-4.10788400	0.00000800	-0.24525400

$CBr_3F \cdot Cl^-$(Dichloromethane)

C	0.66592900	0.00000000	0.44704600
Br	1.51168400	-1.59820800	-0.27097000
Br	1.51117700	1.59849500	-0.27090700
Br	-1.24324100	-0.00029500	0.13093400
F	0.88004400	0.00003400	1.77205800
Cl	-4.36486400	-0.00000100	-0.24987100

Table S5. Frontier orbital energies of X^- anions and R-Br electrophiles.

	E, Hartree			
	MP2/SCI[a]	M062X[b]	ωB97XD[b]	MP2[b]
		E_{LUMO}		
CBr_3H	0.07564	-0.04371	-0.00800	0.04851
CBR_3F	0.06130	-0.05720	-0.02117	0.03984
CBr_4	0.04652	-0.07101	-0.03502	0.02618
CBr_3CN	0.05593	-0.06229	-0.02705	0.03454
CBr_3NO_2	0.04731	-0.07120	-0.04398	0.02719
		E_{HOMO}		
Cl^-	-0.31396	-0.28173	-0.30647	-0.35277
Br^-	-0.29131	-0.26601	-0.29212	-0.32780
I^-	-0.26925	-0.24984	-0.27560	-0.29999

a) Single-point MP2 calculations with 6-311G* basis set and Self-Consistent Isodensity PCM (SCIPCM) model using structures for structures optimized at MP2/6-311+G(d,p) level. b) Computations with 6-311+G(dp) basis set for all atoms except iodine for which 6-311G* basis set was downloaded from EMSL Basis Set Exchange Library. Solvent effect was taken into account using Polarizable Continuum Model (PCM), which is the default SCRF method in Gaussian 09.

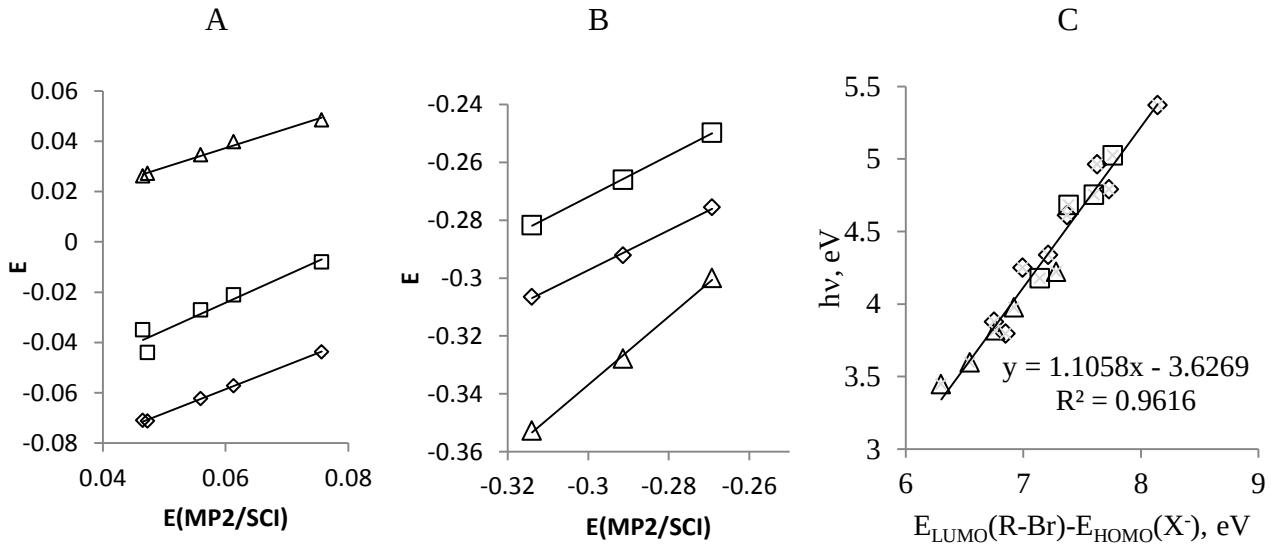
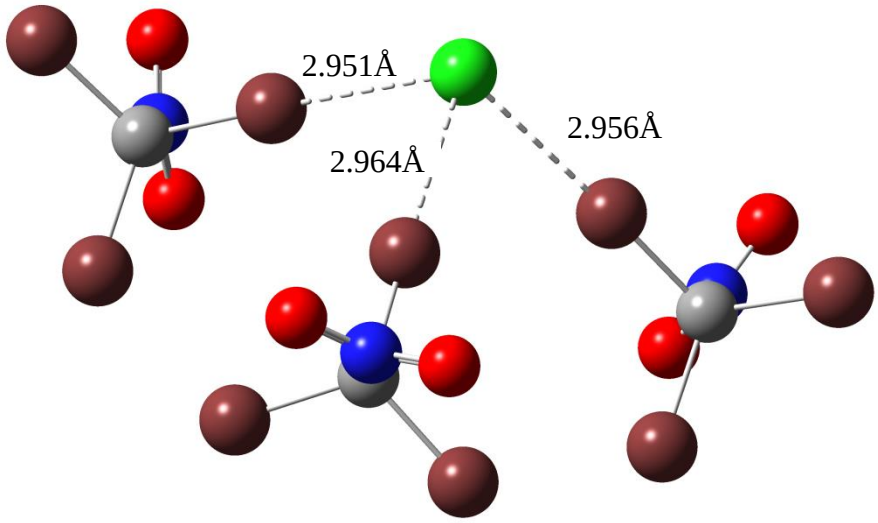


Figure S11. Correlations between orbital energies resulted from MP2 computations with SCI solvation model and the same energies calculated using MP2 (Δ) , M062X(□) and ωB97XD (◊) calculations in Table S5 for R-Br electrophiles (A) and halide anions (B) . (C) Correlation between energies of the absorption bands in [R-Br, X^-] complexes and frontier orbital gaps calculated with ωB97XD functional and PCM model .

A)



B)

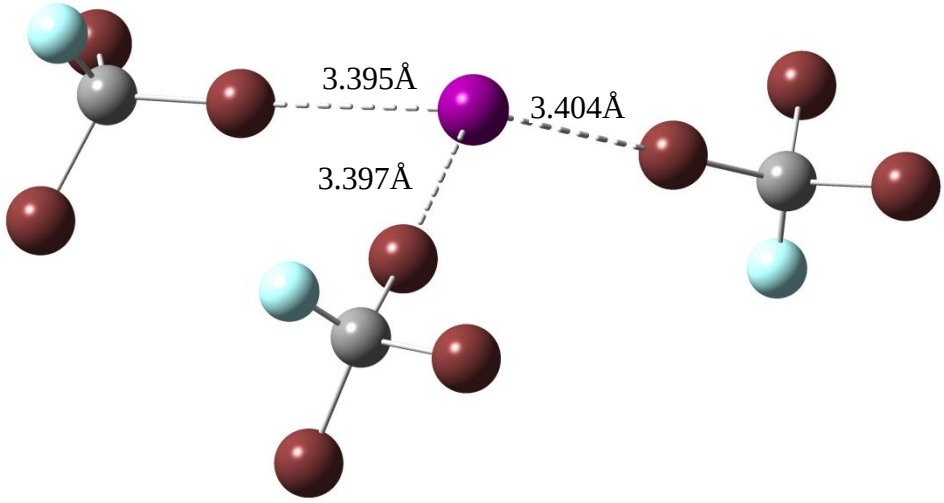


Figure S12. 3 CBr_3NO_2/Cl^- (A) and 3CBrF/I^- (B) clusters resulted from the M062X/6-311+G(dp) computations in the gas-phase (starting from the geometries taken form the X-ray structures).