Supporting Information

"Anti-electrostatic" halogen bonding in solution

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Details of the UV-Vis measurements and evaluation of equilibrium constant K.

Formation constants (K), of the XB complexes [**1**, X^-] between 1,2-bis(dicyanomethylene)-3-iodo-cyclopropanide anion (**1**) (taken as salt with tris(dimethylamino)cyclopropenium counter-ions) and halide anions (X = Cl, Br, I) were established via UV-Vis measurements of the acetonitrile or dichloromethane solutions containing mixtures of these reactants . The measurements were carried out under argon atmosphere (in a Teflon-capped 1 mm-cuvette equipped with a sidearm) on a CARY 500 spectrophoto-meter at 22 °C. For each [**1**, X^-] complex, the values of K were established based on the UV-Vis measurements of 3 - 5 series of solutions. Each series included 10 - 18 solutions. The concentrations of **1** (about 1 mM) were kept constant in each series and the concentrations of halides varied from 0 to 0.25 M. (Halides were taken as salts with tetra-*n*-butyl- or tetra-*n*-propylammonium cations, Bu_4NX or Pr_4NX, measurements with both cations afforded the same - within accuracy limit - formation constants). The ionic strength of the solutions was kept constant with Bu_4NPF_6.

In a typical series of measurements, stock solutions of individual **1** (10.0 mL, ~2.0 mM), Bu_4NX (5.00 mL, 0.50 M) and Bu_4NPF_6 (5.00 mL, 0.50 M) in CH_3CN (or CH_2Cl_2) were prepared in Schlenk tubes under Ar atmosphere. (The solvents were freshly distilled over P_2O_5 under argon.) Then, 0.500 mL of the solution of **1** were mixed in Teflon-capped (1 mm) cuvettes with x mL of stock solution of Bu_4NX and (0.500-x) mL of 0.50 M solution of Bu_4NPF_6 (where x typically were 0.500, 0.400, 0.330, 0.250, 0.200, 0.160, 0.130, 0.100, 0.080, 0.065, 0.050, 0.035, 0.020 or similar numbers) using gas-tight micro syringes with capacities from 0.050 mL to 0.500 mL. The UV-vis spectra were measured immediately after mixing. (Control experiments taken 5 – 20 min after mixing showed no substantial changes of absorption of the solutions containing **1** and I^- or Br^- anions. However, small spectral changes were observed in solutions with Cl^- anions if measurements were repeated 10 – 20 min after mixing.) Alternatively, series of UV-Vis measurements with I^- or Br^- anions were done by mixing 0.250 mL of the stock solution of **1** (prepared as described above) with 0.250 mL of the stock solution of Bu_4NX in Teflon-capped (1 mm) cuvettes equipped with a sidearm (solution A). Separately, 5.0 mL of the stock solution of **1** was mixed with 5.0 mL of a 0.50 M-solution of Bu_4NPF_6 in acetonitrile (solution B with the same concentration of **1** and ionic strength as solution A). After measuring the UV-Vis spectrum of solution A, x ml portions of the diluted solution B (where x = 0.125, 0.150, 0.200, 0.250, 0.300, 0.400, 0.500, 0.600, 0.750, 0.900, 1.000, 1.500, 2.000 or similar number) were added progressively and the spectra were measured after each addition. Since the concentration of **1** and the ionic strength of solution B are the same as solution A, an addition of B to A decreased concentration of iodide in the mixture, but kept the concentration of **1** and the ionic strength constant. Thus, regardless of the method of preparation of the solutions for the UV-Vis measurements, the concentrations of **1** and the ionic strength were kept constant, and the concentrations of Bu_4NX varied in a series of measurements; and the values of

formation constants derived from both types of the UV-Vis experiments were the same within the accuracy limit, except for the studies of interaction of **1** with Cl^-. Since slow side reactions were observed in the solutions containing mixtures of **1** and Cl^-, UV-Vis measurements of the interaction of Cl^- with **1** were done only using the first method, i.e. each measurement was done immediately after mixing of the reactants.

Formation constants of complexes [**1**, X^-], K in Table 1 were established via regression analysis of the UV-Vis data. An addition of X^- anions to the solutions of **1** leads to the formation of XB complexes

$$1 + X^- \underset{}{\overset{K}{\rightleftharpoons}} [1, X^-] \quad \text{(S1)}$$

The formation constant of the complex, K, is expressed as

$$K = C_{com} / ((C^o_{\mathbf{1}} - C_{com})(C^o_{\mathbf{X}} - C_{com})) \quad \text{(S2)}$$

where C_{com}, C^o_1 and C^o_X are equilibrium concentration of complex and initial concentrations of **1** and halide in the mixture. Solving equation S2 leads to expression for concentration of complex as:

$$C_{com} = \{(C^o_1+C^o_X+1/K) - ((C^o_1+C^o_X+1/K)^2 - 4C^o_1C^o_X)^{0.5}\}/2 \quad \text{(S3)}$$

The changes of absorption intensity at a certain wavelength upon formation of complex are

$$\Delta Abs = (\varepsilon_{com} \times C_{com} + \varepsilon_1 \times (C^o_{\mathbf{1}} - C_{com}) + \varepsilon_X \times (C^o_{\mathbf{x}} - C_{com})) - (\varepsilon_1 \times C^o_{\mathbf{1}} + \varepsilon_X \times C^o_x))l \quad \text{(S4)}$$

where ε_{com}, ε_1, and ε_X are extinction coefficients of complex, 1 and X^- at this wavelength and *l* is length of the UV-Vis cuvette. Since the extinction coefficients of the halide salts (and their absorption) were negligible in the spectral range which was used in the analysis, ΔAbs can be expressed as:

$$\Delta Abs = \Delta\varepsilon l \times C_{com} \quad \text{(S5)}$$

where Δε is a difference in extinction coefficients of complex and **1**. Thus, values of ΔAbs measured in a series of solutions with the same concentration of **1** and variable concentration of X^- can be expressed as:

$$\Delta Abs = \Delta\varepsilon l \times C_{com} = \varepsilon l \times \{(C^o_1+C^o_X+1/K) - ((C^o_1+C^o_X+1/K)^2 - 4C^o_1C^o_X)^{0.5}\}/2 \quad \text{(S6)}$$

Fittings of the results of the UV-Vis titrations to eq. S6 was done using Origin Pro 2016 (with ΔAbs and C^o_X as dependent and independent variables y and x, respectively, C^o_1 as a constant and Δε and K as adjustable parameters). Such fittings (illustrated in Figures S1-S4) produced values of K and Δε in Table 1.

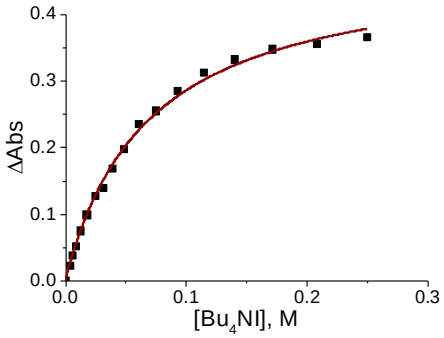

Figure S1. Dependence of differential absorbance ΔAbs (obtained by subtraction of absorption of components from the absorption of the mixture) on the concentration of Bu_4I in the acetonitrile solutions containing 0.8 mM of **1** and Bu_4NI (ionic strength was kept constant with Bu_4NIPF_6).

A

B

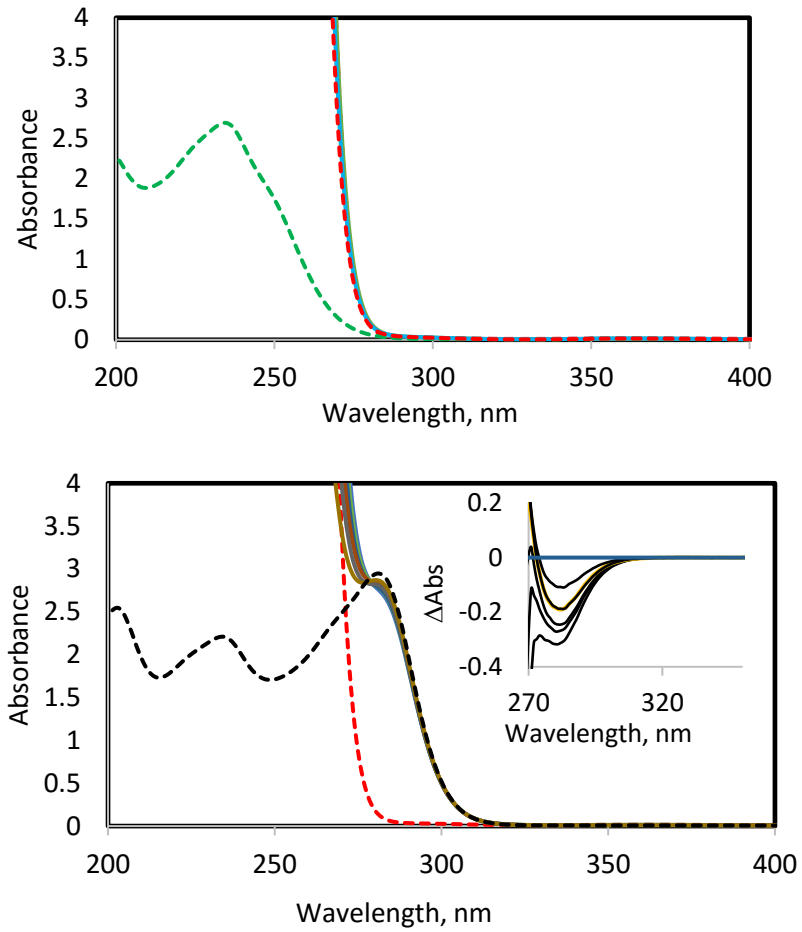

Figure S2. (A) Spectra of acetonitrile solutions of 1.5 mM **TDACl** (green dashed line), 250 mM Bu_4NI (red dashed line) and their mixtures (solid line) with the same concentrations of components. (B) Spectra of acetonitrile solutions with constant concentration of **2TDA** (2.0 mM) and various concentrations of Bu_4NI (from 0 to 250 mM). Dashed lines show spectra of the individual solutions of 2.0 mM **2TDA** (black) and of 250 mM Bu_4NI (red). Ionic strength was maintained with Bu_4NPF_6. Insert: Differential spectra of the solutions obtained by subtraction of the absorption of components from the spectra of their mixtures.

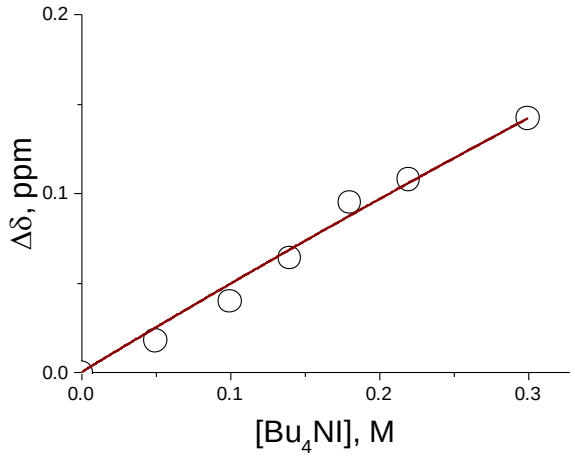

Figure S3. Dependence NMR shifts of the protons of **2** on the concentration of I^- anions in the solutions with constant initial concentration of 2 of 11 mM (as compared to the chemical shift of the individual **2**, in CD_3CN, 22°C, ionic strength was maintained with Bu_4NPF_6) Solid line represent a fit of the data to the expression $\Delta\delta=\Delta\delta_\infty C_{com}/C^o_2=(\Delta\delta_\infty/C^o_2)\times\{(C^o_2+C^o_X+1/K)-((C^o_2+C^o_X+1/K)^2-4C^o_2C^o_X)^{0.5}\}/2$, where C_{com} is an equilibrium concentration of complex in solution, C^o_2 and C^o_X are initial concentrations of **2** and halide in the mixture, and $\Delta\delta_\infty$ is a limiting shift (when all **2** are hydrogen-bonded with iodide). This fitting produced value of K = 0.22. Note that the dependence of Δδ on [Bu_4NI] is almost linear (since only a very small fraction of 2 are hydrogen bonded with iodides in the accessible concentration range of Bu_4NI). Therefore the value of $\Delta\delta_\infty$ = 2.23 ppm were taken from the calculated chemical shifts of the protons of **2** (8.11 ppm) and its hydrogen-bonded complex with iodide [2,I^-] (10.34 ppm) (GIAO ^1H NMR calculations at the M062X/def2trzvpp level in CH_3CN as a medium). \

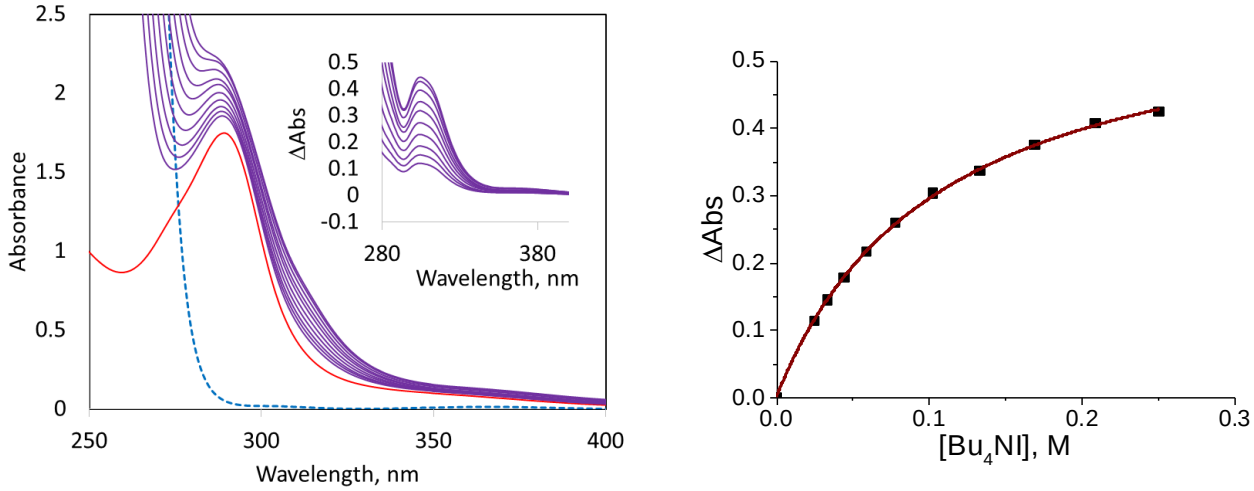

Figure S4. Left: Spectra of dichloromethane solutions with constant concentration of **1** (0.85 mM) and various concentrations of Bu_4NI (solid lines from the bottom to the top). Dashed lines show spectra of the individual solutions of 0.80 mM **1** (red) and of 250 mM Bu_4NI (blue). Ionic strength was maintained with Bu_4NPF_6. Insert: Differential spectra of the solutions obtained by subtraction of the absorption of components from the spectra of their mixtures. (Right) Dependence of differential absorbance ΔAbs (obtained by subtraction of absorption of components from the absorption of the mixture) on the concentration of Bu_4NI in these solutions.

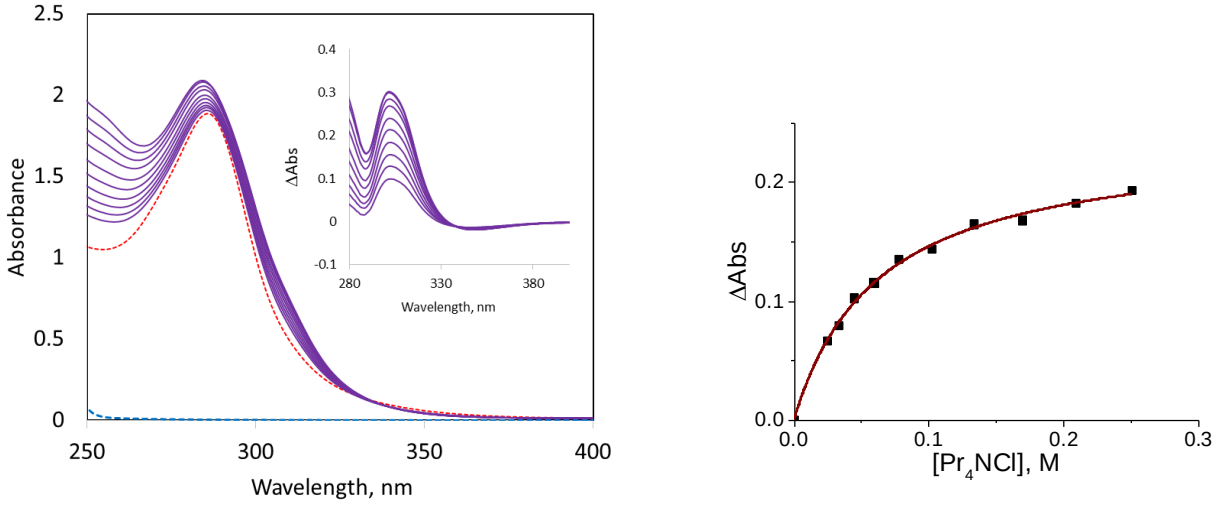

Figure S5. Left: Spectra of acetonitrile solutions with constant concentration of **1** (0.80 mM) and various concentrations of Bu_4NBr (solid lines from the bottom to the top). Dashed lines show spectra of the individual solutions of 0.80 mM **1** (red) and of 250 mM Bu_4NBr (blue). Ionic strength was maintained with Bu_4NPF_6. Insert: Differential spectra of the solutions obtained by subtraction of the absorption of components from the spectra of their mixtures. Right: Dependence of differential absorbance ΔAbs (obtained by subtraction of absorption of components from the absorption of the mixture) on the concentration of Bu_4NBr in these solutions containing.

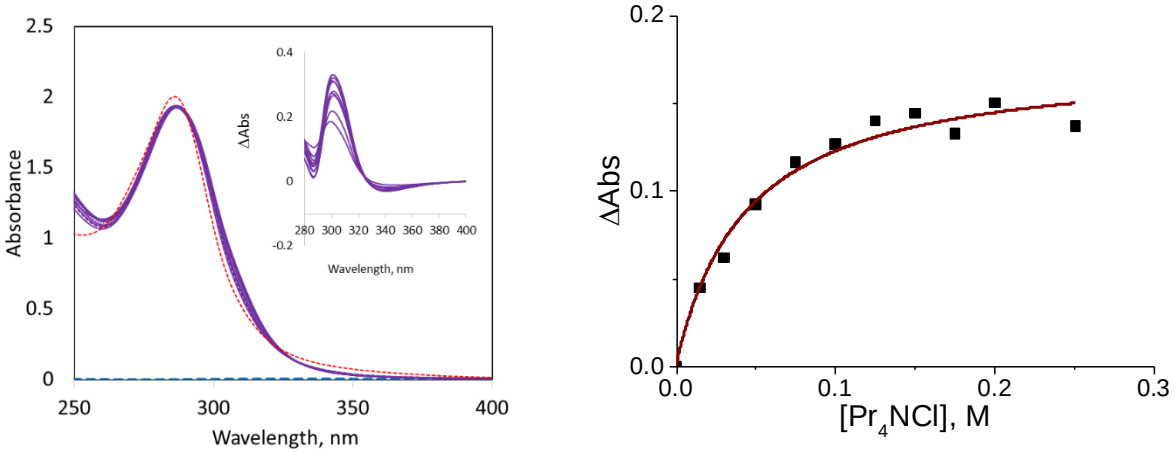

Figure S6. Left: Spectra of acetonitrile solutions with constant concentration of **1** (0.80 mM) and various concentrations of Pr_4NCl (solid lines from the bottom to the top). Dashed lines show spectra of the individual solutions of 0.80 mM **1** (red) and of 250 mM Pr_4NCl (blue). Ionic strength was maintained with Pr_4NPF_6. Insert: Differential spectra of the solutions obtained by subtraction of the absorption of components from the spectra of their mixtures. Right: Dependence of differential absorbance ΔAbs (obtained by subtraction of absorption of components from the absorption of the mixture) on the concentration of Pr_4NCl in these solutions.

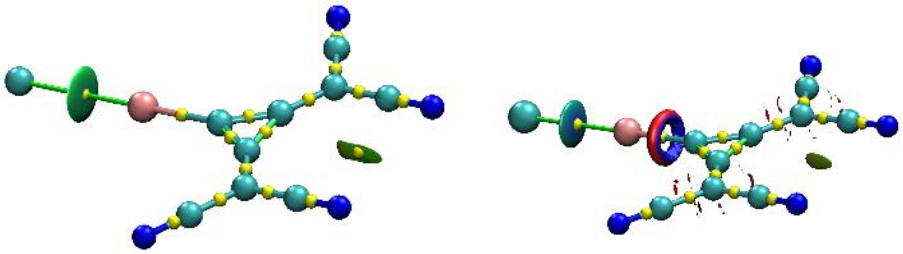

Figure S7. Optimized geometries of the [**1**, Br^-] (left) and [**1**, Cl^-] complexes with (3, -1) critical points (yellow spheres) and bond paths (green line) from AIM analysis and the blue-green disc indicating intermolecular attractive interactions resulting from the NCI treatments (s = 0.4 au isosurfaces, a color scale of -0.035 (blue) < ρ < 0.02 (red) au).

Table S1. Characteristics of the (3,-1) bond critical points along $I\cdots X^-$ halogen bonds (in a.u.)

Complex	ρ (density)	H(Energy density)	$\nabla^2\rho$ (Laplacian of electron density)
[**1**, I^-]	1.49E-02	4.68E-04	3.46E-02
[**1**, Br^-]	1.79E-02	4.53E-04	4.60E-02
[**1**, Cl^-]	2.21E-02	4.37E-04	6.15E-02

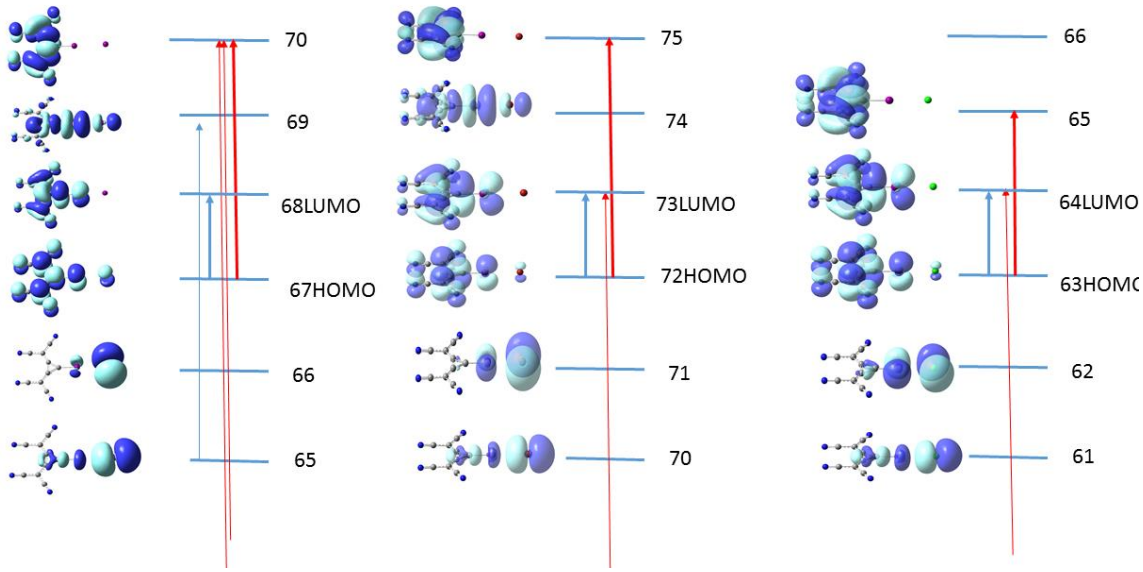

Figure S8. MO shapes and energies for [**1**, I^-] (left), [**1**, Br^-] (center) and [**1**, Cl^-] (right). Blue and red arrows represent components of the transitions responsible for the appearance of the lowest-energy absorption bands in the complexes (see details from the output files of TD DFT computations below, note that oscillators strengths of exited state **1** in each case are essentially negligible, and they are not shown).

Excitation energies and oscillator strengths calculated for [**1**, I^-]:
Excited State 1: Singlet-A 4.7537 eV 260.82 nm f=0.0051 <S**2>=0.000
61 -> 69 0.17095
67 -> 69 0.66012
67 -> 71 0.10259
Excited State 2: Singlet-A 4.8580 eV 255.22 nm f=0.6738 <S**2>=0.000
65 -> 69 -0.15352
67 -> 68 0.67137
Excited State 3: Singlet-A 4.9441 eV 250.77 nm f=0.7223 <S**2>=0.000
63 -> 68 -0.11512
64 -> 70 0.11454
67 -> 70 0.67911

Excitation energies and oscillator strengths calculated for [**1**, Br^-]:
Excited State 1: Singlet-A 4.8664 eV 254.77 nm f=0.0075 <S**2>=0.000
66 -> 74 0.13754
68 -> 77 0.14542
72 -> 74 0.58566
72 -> 76 0.30052
Excited State 2: Singlet-A 4.8866 eV 253.72 nm f=0.5213 <S**2>=0.000
72 -> 73 0.69240
Excited State 3: Singlet-A 4.9458 eV 250.69 nm f=0.7170 <S**2>=0.000
68 -> 73 -0.11416
72 -> 75 0.68518

Excitation energies and oscillator strengths for [1, Cl^-]:
Excited State 1: Singlet-A 4.9035 eV 252.85 nm f=0.0210 <S**2>=0.000
59 -> 68 -0.26929
63 -> 64 -0.11527
63 -> 66 0.29147
63 -> 67 0.53349
Excited State 2: Singlet-A 4.9066 eV 252.69 nm f=0.4459 <S**2>=0.000
63 -> 64 0.68575
Excited State 3: Singlet-A 4.9479 eV 250.58 nm f=0.7169 <S**2>=0.000
59 -> 64 -0.11330
63 -> 65 0.68017

Table S2. Energies and HOMO/LUMO energies of the complexes and individual reactants (M06-2X/def2tzvpp calculations, PCM model)

	Solvent	E, Hartree	E+ZPE, Hartree	E(HOMO), eV	E(LUMO), eV
[**1**, I^-]	CH_3CN	-1157.451835	-1157.387045	-0.25026	0.00922
[**1**, Br^-]	CH_3CN	-3434.011928	-3433.946936	-0.24975	0.01048
[**1**, Cl^-]	CH_3CN	-1320.007332	-1319.942294	-0.24873	0.01217
[**1**, I^-]	CH_2Cl_2	-1157.433215	-1157.368343	-0.23414	0.02483
1	CH_3CN	-859.6273823	-859.562732	-0.25604	-0.00746
I^-	CH_3CN	-297.818415	-297.818415	-0.26435	0.21877
B^-	CH_3CN	-2574.37678	-2574.37678	-0.27940	0.31332
Cl^-	CH_3CN	-460.370291	-460.370291	-0.28893	0.43374
I^-	CH_2Cl_2	-297.810083	-297.810083	-0.24750	0.23449

Table S3. Calculated characteristics of the hypothetical anion-π [**1**, X^-] complexes.[a]

Complex	ΔE, kJ mol^{-1}	λ_{max}, nm	$10^{-4}\varepsilon$, $M^{-1}cm^{-1}$
1·I^-	0.7	252	3.76
1·Br^-	4.6	252	3.46
1·Cl^-	6.9	251	3.80

a) From M06-2X/def2tzvpp calculations, In CH_3CN, PCM model.

Atomic coordinates of the optimized AEXB complexes

[1, I^-] CH_3CN

I	0.74561200	-0.04678700	-0.01608500
N	-1.77282400	4.10762300	-0.00658700
C	-1.30316400	-0.01995800	-0.01162700
N	-5.68510000	2.04487600	0.02168800
C	-2.48905700	-0.69742000	-0.00384000
C	-2.38275200	3.12932000	-0.00292200
C	-3.12129500	1.92169900	0.00144000
N	-5.78229600	-1.85968500	0.01984900
C	-2.45625900	0.71128200	-0.00407200
N	-1.98151800	-4.12524600	-0.00401800
C	-4.53377700	1.98535600	0.01237800
C	-3.21506300	-1.87256300	0.00202500
C	-2.54019600	-3.11680200	-0.00126800
C	-4.62932000	-1.86217900	0.01176900
I	4.28415200	0.00442100	0.01156000

[1, Br^-] CH_3CN

I	1.25029400	-0.00020500	-0.00001400
N	-1.37232600	4.11671800	-0.02427500
C	-0.80107500	-0.00017200	-0.00000300
N	-5.23235800	1.95630000	0.04622300
C	-1.97189400	-0.70396400	0.00017400
C	-1.95792500	3.12363400	-0.01190200
C	-2.66638900	1.89839300	0.00115100
N	-5.23287700	-1.95519300	-0.04618800
C	-1.97173900	0.70388500	-0.00015600
N	-1.37308200	-4.11676400	0.02422400
C	-4.07990700	1.92697300	0.02396600
C	-2.66687900	-1.89829000	-0.00114600
C	-1.95879200	-3.12374500	0.01189500
C	-4.08040900	-1.92644300	-0.02393300
Br	4.54682800	0.00005100	0.00001700

[1, I^-] CH_2Cl_2

I	-0.75284700	-0.07080700	0.04252100
N	1.72847800	4.10777500	0.01823500
C	1.29824800	-0.03179400	0.03164900
N	5.65467500	2.09642100	-0.05634500
C	2.49297600	-0.69483100	0.01078700
C	2.34314800	3.13246400	0.00850400
C	3.09339000	1.93163800	-0.00292600
N	5.80492900	-1.80665600	-0.05564300
C	2.44303600	0.71321800	0.01167500
N	2.05285600	-4.13716100	0.01117500
C	4.50492300	2.01510500	-0.03202400
C	3.23800000	-1.85829900	-0.00542200
C	2.58745700	-3.11573100	0.00330000
C	4.65225900	-1.82484000	-0.03248700
I	-4.27747700	0.00619900	-0.03082800

[1, Cl^-] CH_3CN

I	1.81581100	-0.06615900	0.00073900
N	-0.74975400	4.10492700	0.01712400
C	-0.23997900	-0.02303700	0.00163500
N	-4.64064000	2.00224700	-0.03381900
C	-1.42373100	-0.70626700	0.00145800
C	-1.34957100	3.12018800	0.00860700
C	-2.07588000	1.90574100	-0.00034600
N	-4.70361800	-1.91179700	0.03327600
C	-1.40001300	0.69963400	0.00125000
N	-0.87347300	-4.12680700	-0.01438400
C	-3.48857100	1.95571100	-0.01726900
C	-2.13683300	-1.89083000	0.00251900
C	-1.44595900	-3.12592700	-0.00613200
C	-3.55058800	-1.89919300	0.01805700
Cl	4.89393300	-0.16076300	-0.00330100