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

Tracing Absorption and Emission Characteristics of Halogen-bonded Ion Pairs Involving Halogenated Imidazolium Species

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Supporting Information

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Table S1: 2-Iodo-imidazolium · OTf: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in vacuum at the ADC(2)/def2-TZVPP level.

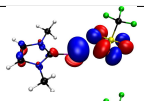
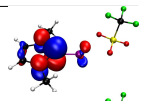
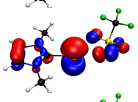
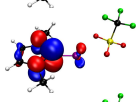
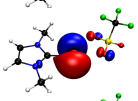
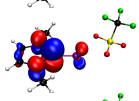
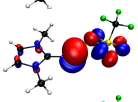
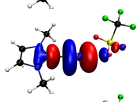
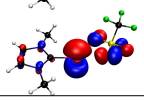
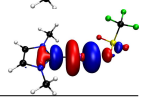
State	ω	f	occ	vir
1	5.22	0.104		
2	5.33	0.221		
3	5.59	0.000		
4	6.06	0.131		
5	6.17	0.136		

Table S2: 2-Iodo-imidazolium cation: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

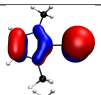
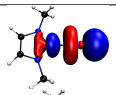
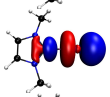
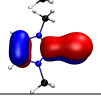
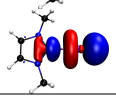
State	ω	f	occ	vir
1	5.06	0.000		
2	5.59	0.388		
3	5.83	0.001		
4	6.72	0.000		
5	6.95	0.000		

Table S3: 2-Iodo-imidazolium cation: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the S_1 equilibrium structure (S_1-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

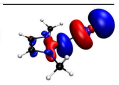
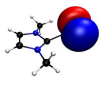
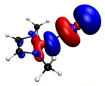
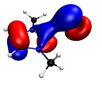
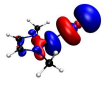
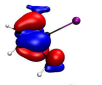
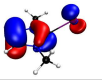
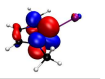
State	ω	occ	vir
1	2.58		
2	2.96		
3	3.54		
4	4.38		
5	5.98		

Table S4: 2-Iodo-benzimidazolium · OTf: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in vacuum at the ADC(2)/def2-TZVPP level.

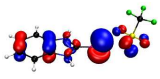
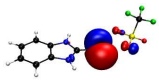
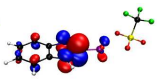
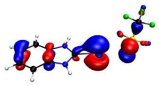
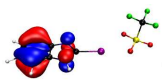
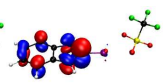
State	ω	f	occ	vir
1	4.55	0.411		
2	4.67	0.073		
3	5.15	0.000		
4	5.33	0.024		
5	5.44	0.061		

Table S5: 2-Iodo-benzimidazolium cation: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

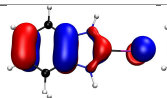
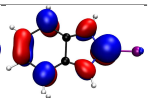
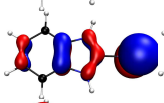
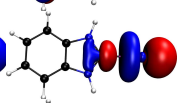
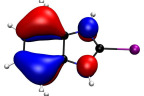
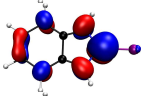
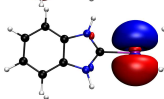
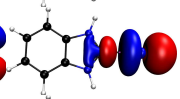
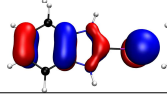
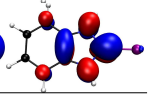
State	ω	f	occ	vir
1	4.73	0.445		
2	5.10	0.000		
3	5.14	0.093		
4	5.71	0.001		
5	5.82	0.429		

Table S6: 2-Iodo-benzimidazolium cation: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the S_1 equilibrium structure (S_1-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

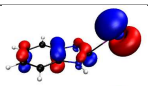
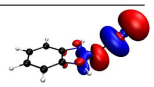
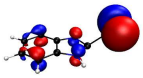
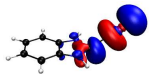
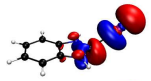
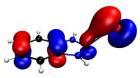
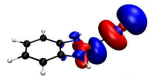
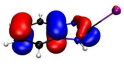
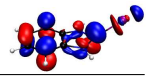
State	ω	occ	vir
1	2.58		
2	2.86		
3	3.17		
4	3.39		
5	5.05		

Table S7: 2-Bromo-benzimidazolium · OTf: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

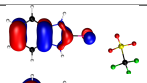
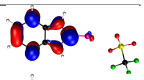
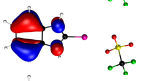
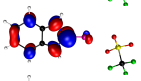
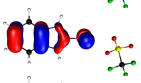
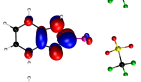
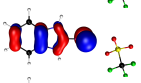
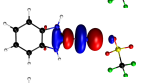
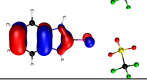
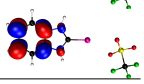
State	ω	f	Occ	Vir
1	4.84	0.381		
2	5.27	0.124		
3	5.95	0.574		
4	6.60	0.000		
5	6.73	0.046		

Table S8: 2-Bromo-benzimidazolium · OTf: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the S_1 equilibrium structure (S_1-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

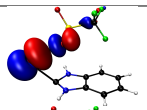
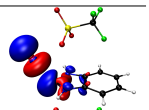
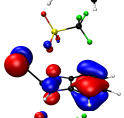
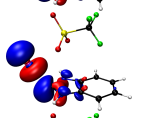
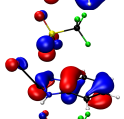
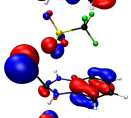
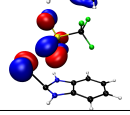
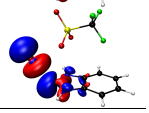
State	ω	f	Occ	Vir
1	0.89	0.001		
2	2.33	0.006		
3	2.63	0.157		
4	2.73	0.049		
5	2.90	0.013		

Table S9: 2-Bromo-benzimidazolium cation: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

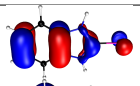
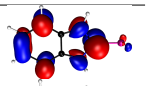
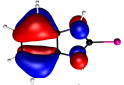
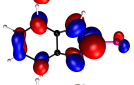
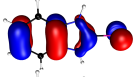
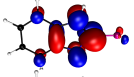
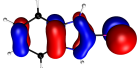
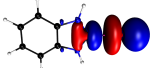
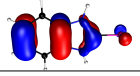
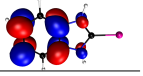
State	ω	f	Occ	Vir
1	4.84	0.350		
2	5.22	0.121		
3	5.95	0.496		
4	6.18	0.000		
5	6.73	0.019		

Table S10: 2-Bromo-benzimidazolium cation: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the S_1 equilibrium structure (S_1-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

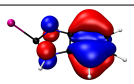
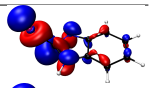
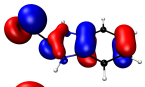
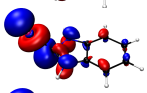
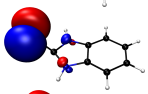
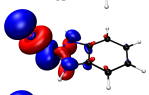
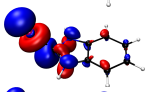
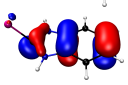
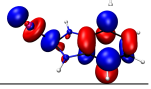
State	ω	f	Occ	Vir
1	2.55	0.036		
2	3.05	0.298		
3	4.08	0.002		
4	4.24	0.065		
5	5.43	0.021		

Table S11: Bis(2-Iodo-benzimidazolium) · Cl: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in vacuum at the ADC(2)/def2-TZVPP level.

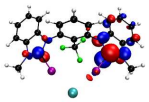
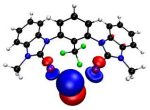
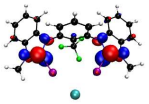
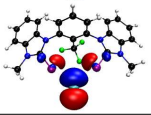
State	ω	f	occ	vir
1	4.30	0.189		
2	4.31	0.197		
3	4.45	0.012		
4	4.48	0.024		
5	4.54	0.003		

Table S12: Bis(2-Iodo-benzimidazolium) dication: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the ground state equilibrium structure (S_0-eq) in acetonirile solution at the COSMO-ADC(2)/def2-TZVPP(post-SCF) level.

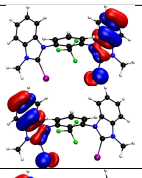
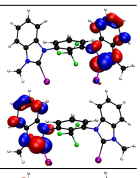
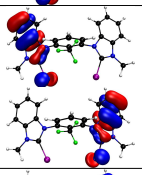
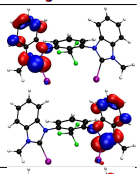
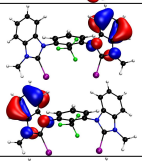
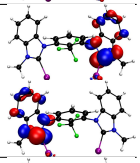
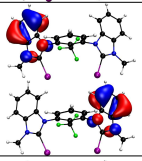
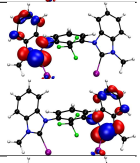
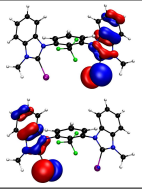
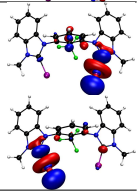
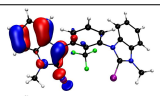
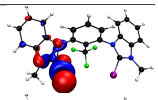
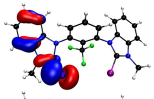
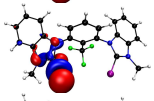
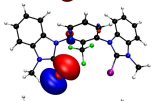
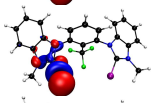
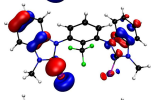
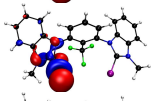
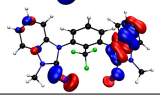
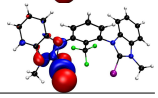
State	ω	f	occ	vir
1	4.54	0.120		
2	4.58	0.605		
3	4.81	0.302		
4	4.83	0.059		
5	5.00	0.004		

Table S13: Bis(2-Iodo-benzimidazolium) dication: Vertical excitation energies (ω), oscillator strengths (f) and NTOs for the S_1 equilibrium structure (S_1-eq) in acetonitrile solution at the COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) level.

State	ω	f	occ	vir
1	2.30	0.061		
2	2.83	0.115		
3	3.25	0.012		
4	3.62	0.087		
5	3.73	0.028		

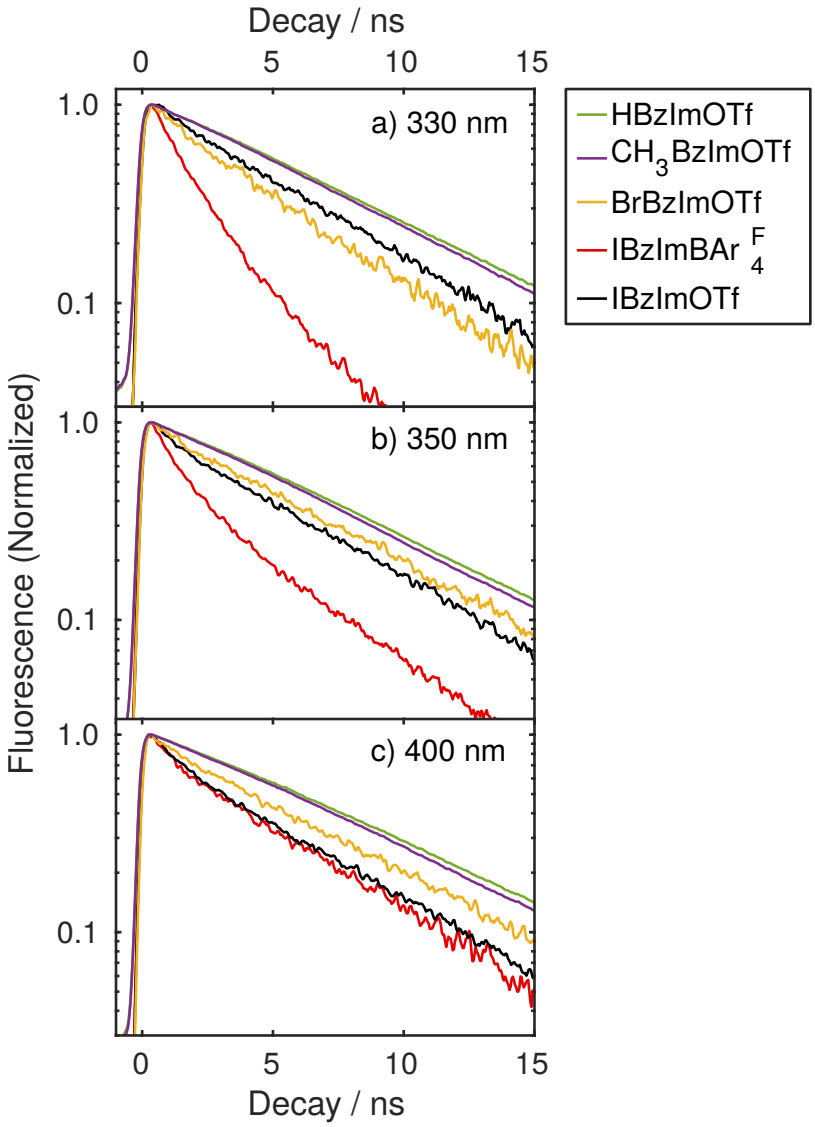


Figure S1: Normalized transient fluorescence decays at 330 nm (**a**), 350 nm (**b**), and 400 nm (**c**) for the five $BzIm^+$ compounds in acetonitrile solution (390 μM) after 266 nm excitation.

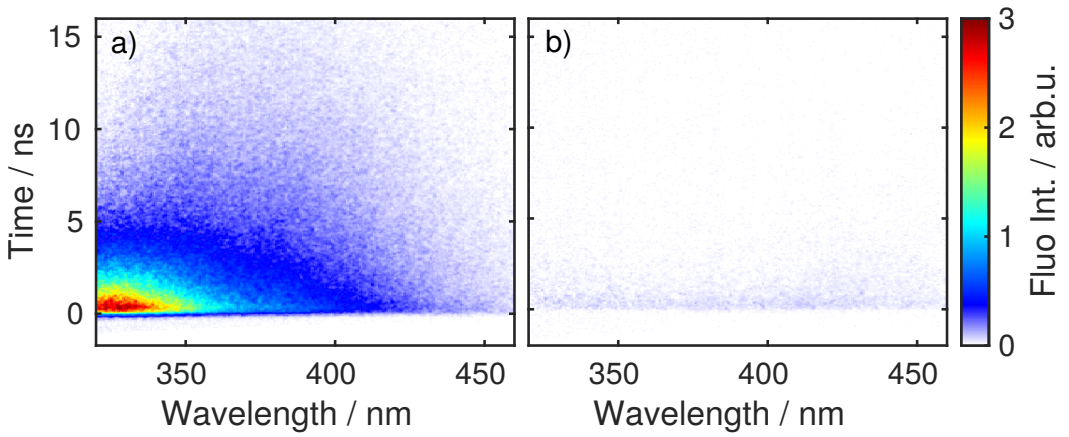


Figure S2: Impact study of the counterion $[BAr_4^F]^-$, time-resolved fluorescence streak images of $IBzImBAr_4^F$ (**a**) and $NaBAr_4^F$ (**b**) in acetonitrile solution (390 μM) excited at 266 nm.

Table S14: 2-Bromo-1,3-dimethylbenzimidazolium and 2-Bromo-1,3-dimethylbenzimidazolium · MeCN: Ground state and S_1 equilibrium structures in acetonitrile solution obtained with COSMO-RI-MP2/def2-TZVPP(post-SCF) for ground states and COSMO-RI-ADC(2)/def2-TZVPP(post-SCF) for excited states.

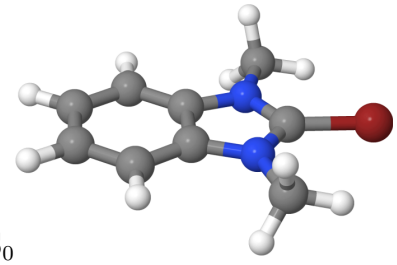
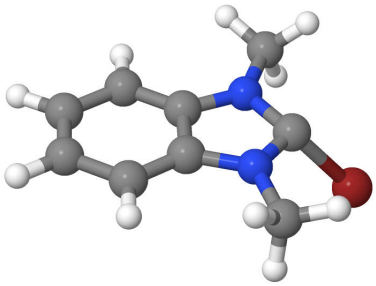
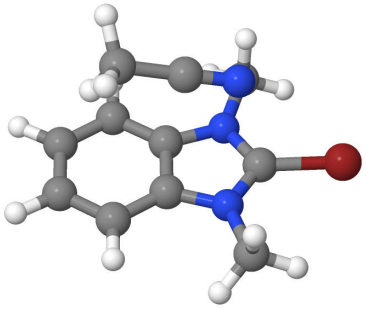
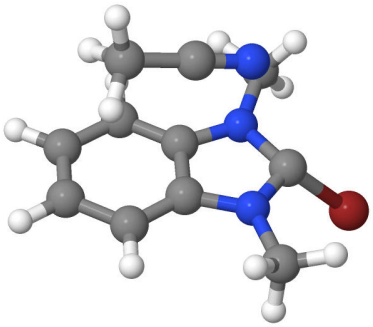
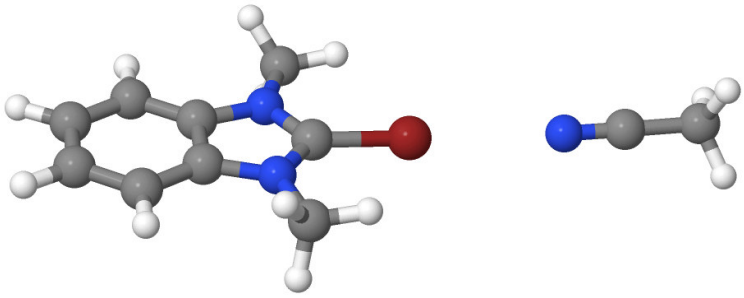
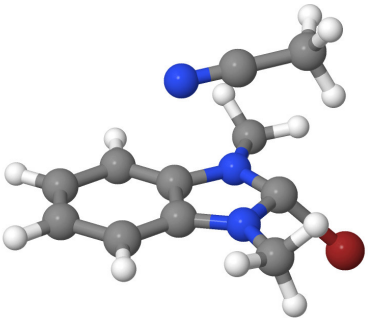
S_0	S_1
 S_0	 S_1
 S_0(A)	 S_1(A)
 S_0(B)	 S_1(B)

Table S15: 2-Bromo-1,3-dimethylbenzimidazolium and 2-Bromo-1,3-dimethylbenzimidazolium · MeCN: Ground state and S_1 energies (in eV) relative to ground state energy at the S_0 and S_0(A) structure for, respectively 2-Bromo-imadazolium and the complexes with one explicit MeCN molecule. All results obtained with COSMO-RI-MP2/def2-TZVPP (S_0) and COSMO-RI-ADC(2)/def2-TZVPP (S_1).

structure	S_0	S_1	ΔE
S_0	0.00	4.79	4.79
S_1	1.54	3.82	2.28
S_0(A)	0.00	4.78	4.78
S_1(A)	1.56	3.85	2.29
S_0(B)	0.18	4.96	4.79
S_1(B)	1.52	3.83	2.31