Insight into the Deprotonation at the Half-Equivalence for (Thio)Amido–Benzimidazoles in the presence of Anions

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Contents

Details of the X–ray crystal structures

Crystallographic data of all compounds were collected with a MM007 R-Axis Rapid Rigaku diffractometer with rotating anode and monochromatic Cu-Kα radiation (λ = 1.54187 Å) and a curved image plate as detector.

The unit cell determination and data reduction were performed using the Crystal Clear program suite[1] on the full set of data. The structure was solved by direct methods and refined using Shelx suite of programs[2] in the integrated WinGX system[3]. The positions of most of the H atoms were deduced from coordinates of the non-H atoms and confirmed by Fourier synthesis. They were included for structure factor calculations but not refined. The non-H atoms were refined with anisotropic temperature parameters. The coordinates of some H atoms brought by nitrogen atoms were refined.

Figures were obtained using Mercury 3.8 software. All crystallographic data have been deposited in the Cambridge Crystallographic Data Centre. The CCDC number is indicated in the corresponding table of crystallographic data.

These crystallographic data have benefited from the facilities and expertises of the Biophysical and Structural Chemistry plateform (BPCS) at IECB, CNRS UMS3033, Inserm US001, Bordeaux University,
http://www.iecb.ubordeaux.fr/index.php/fr/plateformestechnologiques

Compounds **1a**–**b** and **2a**–**b** were synthesized according to the previous reported procedure.[4] All tetrabutylammoniums salts were dried prior use. Acetonitrile was dried over calcium hydride and freshly distilled. UV-Visible absorption spectra were recorded at 298K using a Varian Cary 100 spectrophotometer and a quartz cuvette (path length: 1 cm).

Single crystals were grown by slow evaporation of a dichloromethane/ethanol solution containing HBD receptors **1**–**2** and TBAX (X: F, $PhCO_2$) in a (1:1) stoichiometry.

Table S1. Crystal Data and structure Refinement for [**(1a–H$^+$).(*n*Bu$_4$N$^+$)**]

Empirical formula	$C_{33}H_{52}N_4O_2$	
Formula weight	536.79	
Temperature	213(2) K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 47.563(3) Å	α= 90°.
	b = 7.5976(4) Å	β= 94.075(4)°
	c = 17.5514(8) Å	γ = 90°
Volume	6326.4(6) Å^3	
Z	8	
Density (calculated)	1.127 Mg/m^3	
Absorption coefficient	0.544 mm^{-1}	
F(000)	2352	
Crystal size	0.09 x 0.06 x 0.03 mm^3	
Theta range for data collection	7.02 to 71.99°.	
Index ranges	-58≤ h≤ 58, -5≤ k ≤ 8, -21≤ l ≤ 21	
Reflections collected	37061	
Independent reflections	5894 [R(int) = 0.0328]	
Completeness to theta = 68.25°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9839 and 0.9527	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5894 / 0 / 360	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1232	
R indices (all data)	R1 = 0.0578, wR2 = 0.1347	
Largest diff. peak and hole	0.216 and -0.160 e.Å^{-3}	
CCDC Number	1545903	

Table S2. Crystal Data and structure Refinement for [(**1b**).(**1b**–H^+).(n**Bu**$_4$$N^+$)]

Empirical formula	C50 H69 N7 O2 S2	
Formula weight	864.24	
Temperature	213(2) K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	Pna21	
Unit cell dimensions	a = 21.9302(15) Å	α= 90°
	b = 8.3467(6) Å	β= 90°
	c = 26.7797(14) Å	γ = 90°
Volume	4901.9(5) Å^3	
Z	4	
Density (calculated)	1.171 Mg/m^3	
Absorption coefficient	1.330 mm^{-1}	
F(000)	1864	
Crystal size	0.10 x 0.06 x 0.04 mm^3	
Theta range for data collection	6.57 to 68.24°	
Index ranges	$-20 \le h \le 26$, $-9 \le k \le 9$, $-32 \le l \le 32$	
Reflections collected	47965	
Independent reflections	8679 [R(int) = 0.0666]	
Completeness to theta = 68.24°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9487 and 0.8785	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8679 / 3 / 560	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1399	
R indices (all data)	R1 = 0.0723, wR2 = 0.1535	
Absolute structure parameter	0.51(4)	
Largest diff. peak and hole	0.499 and -0.239 e. Å^3	
CCDC Number	1545901	

Table S3. Crystal Data and structure Refinement for (**1b–H$^+$**).(***n*Bu$_4$N$^+$**)

Empirical formula	C33 H52 N4 O S	
Formula weight	552.85	
Temperature	153(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 46.4589(8) Å	α= 90°
	b = 7.76490(10) Å	β= 93.435(7) °
	c = 18.0818(13) Å	γ = 90°
Volume	6511.3(5) Å^3	
Z	8	
Density (calculated)	1.128 Mg/m^3	
Absorption coefficient	1.102 mm^{-1}	
F(000)	2416	
Crystal size	0.20 x 0.12 x 0.05 mm^3	
Theta range for data collection	6.77 to 68.25°	
Index ranges	$-55 \leq h \leq 50$, $-6 \leq k \leq 9$, $-21 \leq l \leq 21$	
Reflections collected	23276	
Independent reflections	5861 [R(int) = 0.0393]	
Completeness to theta = 68.25°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9470 and 0.8097	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5861 / 0 / 359	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1270	
R indices (all data)	R1 = 0.0562, wR2 = 0.1462	
Extinction coefficient	0.00039(5)	
Largest diff. peak and hole	0.210 and -0.244 e.Å^{-3}	
CCDC Number	1545904	

Table S4. Crystal Data and structure Refinement for (**2a–H$^+$**).(***n*Bu$_4$N$^+$**)

Empirical formula	C26 H30.50 F6 N3.50 O	
Formula weight	522.04	
Temperature	153(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 10.42800(10) Å	α= 90°
	b = 8.66040(10) Å	β= 99.054(6) °
	c = 30.374(2) Å	γ = 90°
Volume	2708.94(18) Å^3	
Z	4	
Density (calculated)	1.280 Mg/m^3	
Absorption coefficient	0.924 mm^{-1}	
F(000)	1092	
Crystal size	0.20 x 0.15 x 0.04 mm^3	
Theta range for data collection	6.64 to 70.08°	
Index ranges	$-12 \le h \le 8$, $-10 \le k \le 9$, $-36 \le l \le 36$	
Reflections collected	22353	
Independent reflections	5100 [R(int) = 0.0237]	
Completeness to theta = 70.08°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9640 and 0.8368	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5100 / 57 / 415	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1391	
R indices (all data)	R1 = 0.0787, wR2 = 0.1607	
Extinction coefficient	0.0044(4)	
Largest diff. peak and hole	0.295 and -0.180 e. Å^{-3}	
CCDC Number	1545905	

Table S5. Crystal Data and structure Refinement for (**2a).**MeOH

Empirical formula	C19 H17 F6 N3 O2	
Formula weight	433.36	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 4.8277(2) Å	α= 90°
	b = 24.7394(9) Å	β= 94.129(2) °
	c = 16.4158(9) Å	γ = 90°
Volume	1955.52(15) $Å^3$	
Z	4	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	1.193 mm^{-1}	
F(000)	888	
Crystal size	0.20 x 0.08 x 0.05 mm^3	
Theta range for data collection	3.24 to 72.49°	
Index ranges	$-3 \leq h \leq 5, -30 \leq k \leq 30, -17 \leq l \leq 20$	
Reflections collected	10772	
Independent reflections	3513 [R(int) = 0.0525]	
Completeness to theta = 72.49°	91.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9427 and 0.7963	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3513 / 3 / 340	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.1578	
R indices (all data)	R1 = 0.1050, wR2 = 0.1823	
Extinction coefficient	0.0024(3)	
Largest diff. peak and hole	0.238 and -0.168 $e.Å^{-3}$	
CCDC Number	1545902	

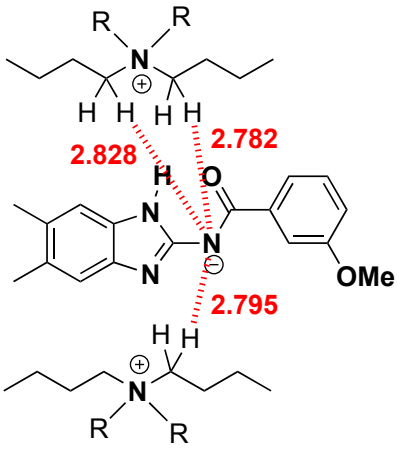
Table S6. Crystal Data and structure Refinement for $(\mathbf{2a})_2$

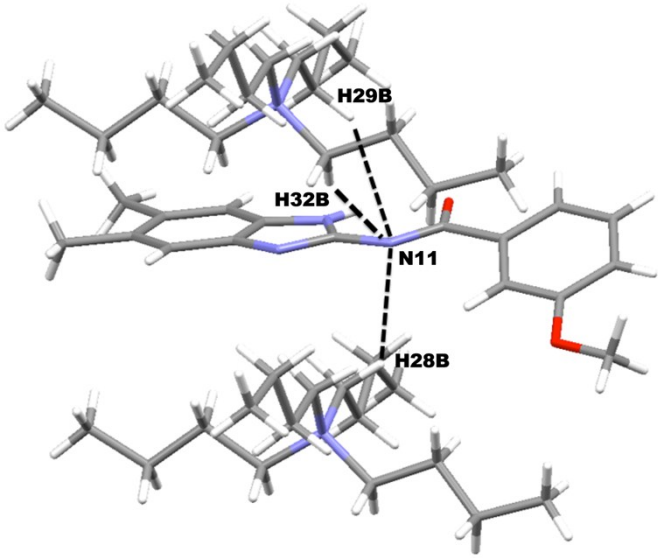
Empirical formula	C36 H26 F12 N6 O2	
Formula weight	802.63	
Temperature	253(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8669(12) Å	α= 94.509(5)°
	b = 11.6783(13) Å	β= 90.153(4) °
	c = 16.7989(19) Å	γ = 99.505(5) °
Volume	1903.0(4) $Å^3$	
Z	2	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	1.143 mm^{-1}	
F(000)	816	
Crystal size	0.20 x 0.15 x 0.04 mm^3	
Theta range for data collection	2.64 to 72.06°	
Index ranges	$-7 \leq h \leq 11$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$	
Reflections collected	27444	
Independent reflections	7106 [R(int) = 0.0229]	
Completeness to theta = 72.06°	95.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9557 and 0.8036	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7106 / 24 / 537	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1770	
R indices (all data)	R1 = 0.0962, wR2 = 0.1920	
Extinction coefficient	0.0060(3)	
Largest diff. peak and hole	0.800 and -0.489 $e.Å^{-3}$	
CCDC Number	1545906	

Table S7. Crystal Data and structure Refinement for (**2b**).(**2b–H**$^+$).(***n*Bu$_4$N**$^+$)

Empirical formula	C53 H65 F12 N7 O S2	
Formula weight	1108.24	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 30.8271(17) Å	α= 90°
	b = 8.5867(4) Å	β= 108.296(3) °
	c = 22.1213(16) Å	γ = 90°
Volume	5559.6(6) Å^3	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	1.600 mm^{-1}	
F(000)	2320	
Crystal size	0.12 x 0.08 x 0.02 mm^3	
Theta range for data collection	6.53 to 68.22°	
Index ranges	$-36 \leq h \leq 36$, $-9 \leq k \leq 10$, $-20 \leq l \leq 26$	
Reflections collected	12807	
Independent reflections	7503 [R(int) = 0.0465]	
Completeness to theta = 68.22°	96.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9687 and 0.8312	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7503 / 30 / 692	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0703, wR2 = 0.1652	
R indices (all data)	R1 = 0.1022, wR2 = 0.1751	
Largest diff. peak and hole	0.270 and -0.232 e.Å^{-3}	
CCDC Number	1545907	

Table S8-A. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of **(1a – H^+).*n*Bu_4N^+**, obtained in the presence of ***n*Bu_4N^+.F^-**.





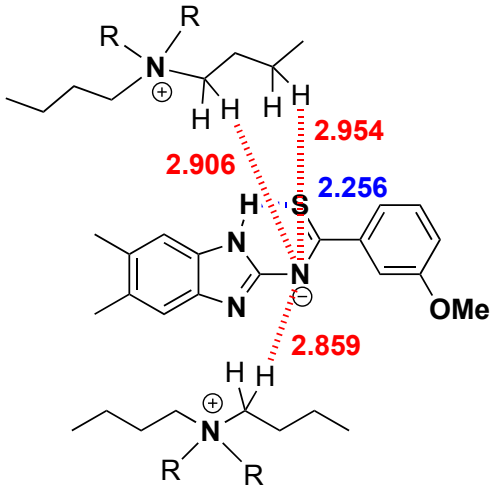
R: *n*-Bu

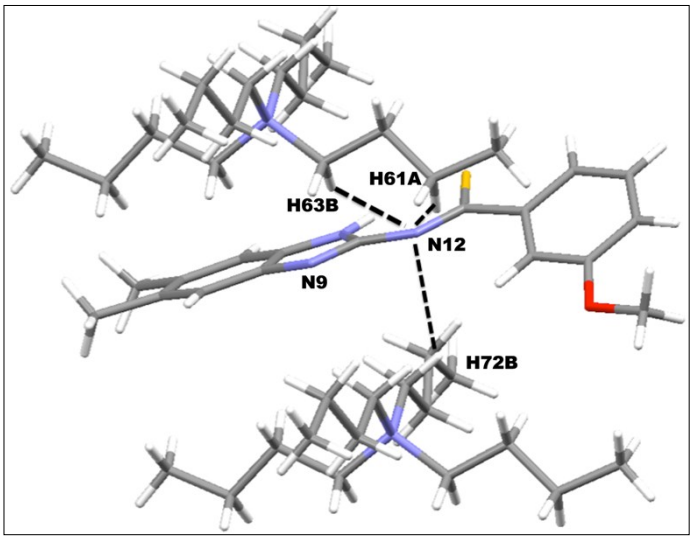
Only one contact was seen between (**1a**–H^+) compounds, through the two OMe groups. The CH_3–O•••H–C distance is 2.745 Å (O7-H8B).

The other close contacts are between one molecule of **(1a–H^+)** and several ***n*Bu_4N^+** cations.

	Intramolecular H-bond NH•••O=C	**Intermolecular N^-•••H-C** (*n*Bu_4N^+)	**Other Short contacts (1a–H^+)•••H-C** (*n*Bu_4N^+)
(1a–H^+).*n*Bu_4N^+	2.080 (<N13H13O10>: 118.99°)	2.795 (N11-H28B, 130.27°), 2.782 (N11-H32B, 155.61°), 2.828 (N11-H29B, 144.41°), 3.016 (N11-H24A, 124.81°),	$N_{benzimidazole}$•••H-C: 2.442 (N16-H24B), 2.658 (N16-H36A), 2.762 (N16-H28A), 2.800 (N16-H32B), 2.906 (N16-H29A) and Multiple contacts between 2.8 and 3.2 Å

Table S8-B. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of **(1b – H^+).*n*Bu_4N^+**, obtained in the presence of ***n*Bu_4N^+.F^-**.





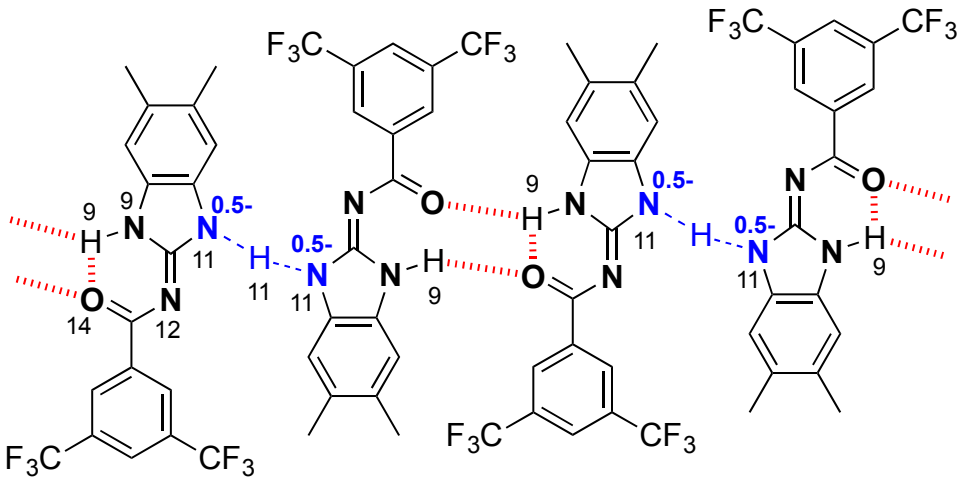
R: *n*-Bu

	Intramolecular distance NH•••S=C	**Intermolecular N⁻•••H-C** (*n*Bu_4N^+)	**Other Short contacts (1a–H^+)•••H-C** (*n*Bu_4N^+)
(1b–H^+).*n*Bu_4N^+	2.256 (<N7-H7-S14>: 135.17°)	2.859 (N12-H72B), 2.906 (N12-H63B), 2.954 (N12-H61A)	$N_{benzimidazole}$•••H-C: 2.477 (N9-H73B), 2.694 (N9-H65B) and Multiple contacts between 2.8 and 3.2 Å.

Only one contact was seen between (**1b**–H^+) compounds, through the two OMe groups. The CH_3–O•••H–C distance is 2.685 Å (O21-H22A).

The other close contacts are between one molecule of **(1b–H^+)** and several ***n*Bu_4N^+** cations.

Table S8-C. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of **(2a – 0.5 H$^+$)$_2$.*n*Bu$_4$N$^+$**, obtained in the presence of ***n*Bu$_4$N$^+$.F$^-$**



ammonium omitted for clarity purpose

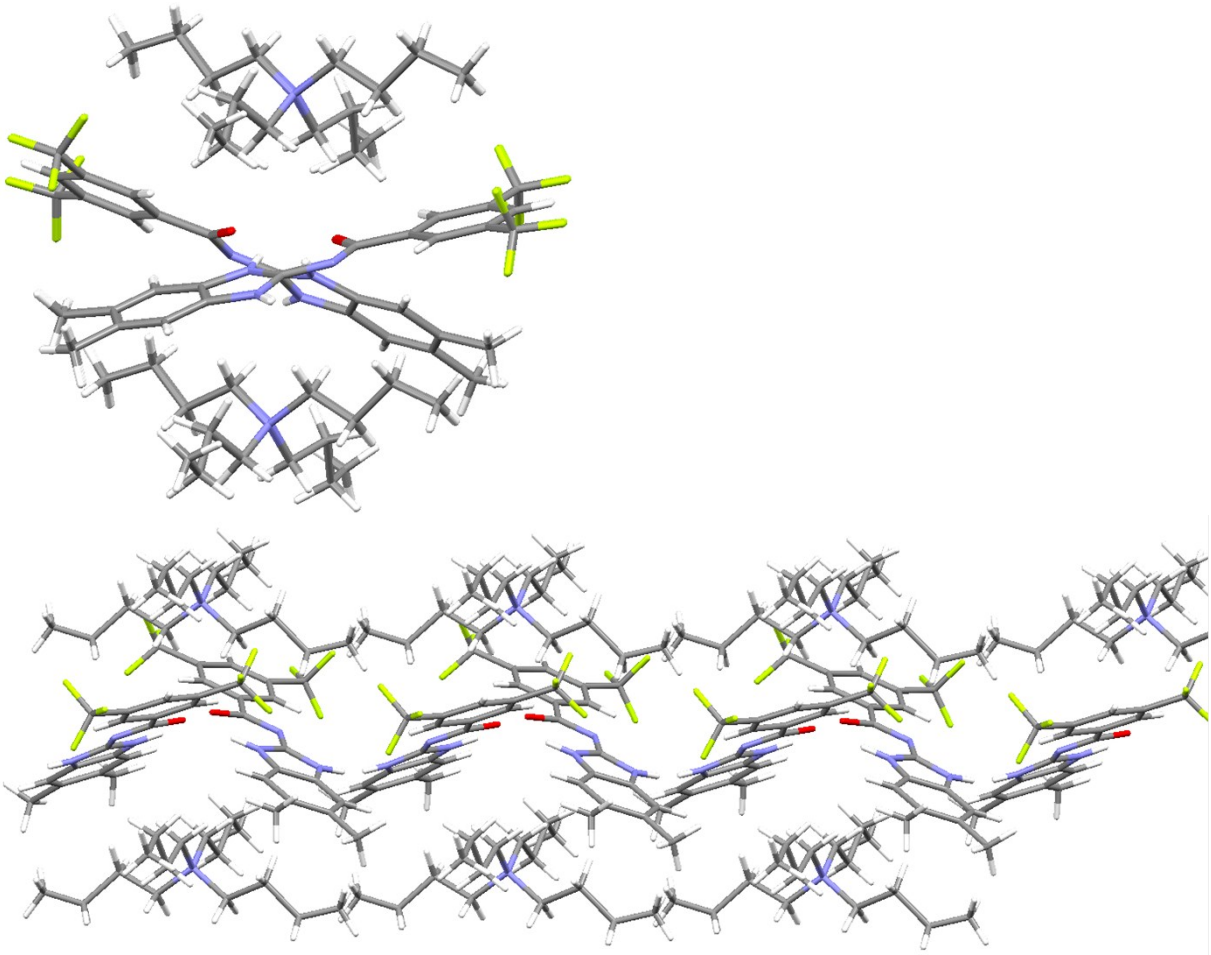
Compound (**2a– 0.5 H$^+$**) is observed as its *N*-(1,3-dihydro-benzimidazol-2-ylidene) tautomer, as already reported.[4] Half-deprotonation was observed on N11 nitrogen. Then, in each dimer arrangement, one residual proton is shared by two N11 provided with a negative charge of –0.5.

	Intramolecular distance NH•••O=C	**Interactions between (2a – 0.5 H$^+$) molecules**	**Other Short contacts (2a–0.5H$^+$)•••H-C** (*n*Bu$_4$N$^+$)
(2a–0.5H$^+$)$_2$.*n*Bu$_4$N$^+$	2.139 (H9•••O14)	H-bonding: 2.109 (H9•••O14) Half-deprotonation: 2.679 (N11$^{0.5-}$···H11···N11$^{0.5-}$)	Multiple contacts between 2.49 and 3.1 Å. 2.486 (O14•••H56B), 2.733 (O14•••H56A), 2.907 (N12•••H54B), 2.917 (N9•••H52B), 2.989 (C10•••H58B)

Each molecule (**2a– 0.5 H$^+$**) is almost flat (angle C13N12C10N9 = -3.2°) and is tilted by 47.2° with the two surrounding ones.

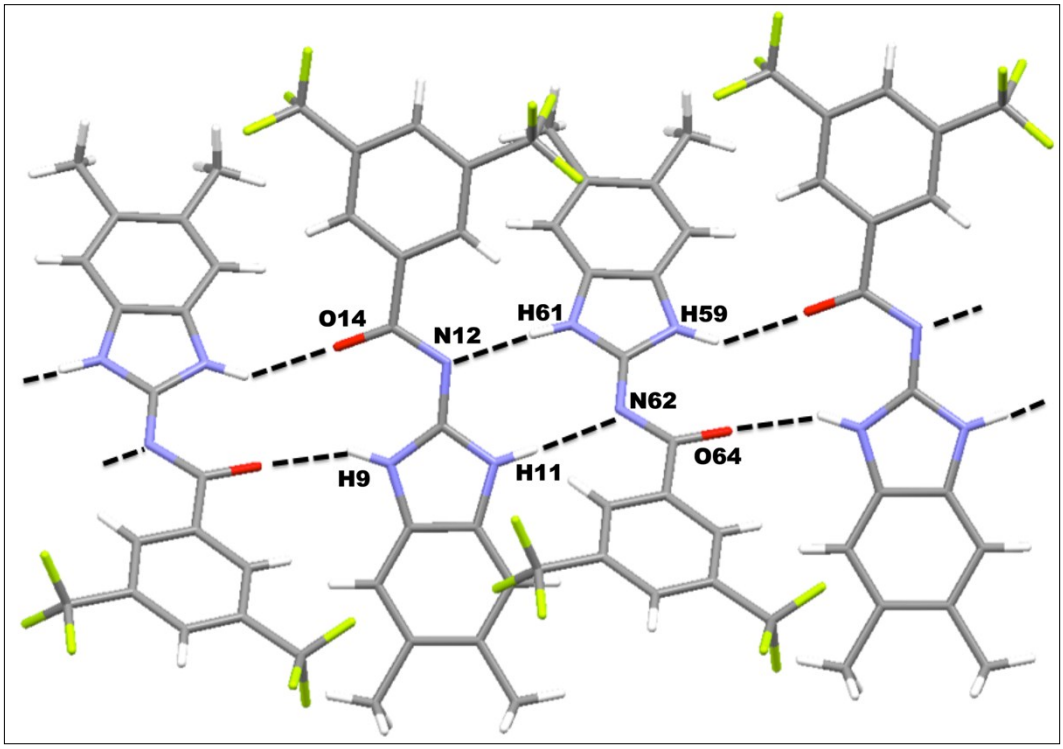
In a zig-zag arrangement, molecules (**2a– 0.5 H$^+$**) are interacting through two short hydrogen bonds with one molecule (d: 2.109 Å) and through a strong interaction N$^{0.5-}$···H···N$^{0.5-}$ (distance between both nitrogen atomes: 2.679 Å) with the second one.

This alignment of amido-benzimidazoles is surrounded by an upper and a lower layer of ***n*Bu$_4$N$^+$** cations in close contact (2.49-3.1 Å, see images below).



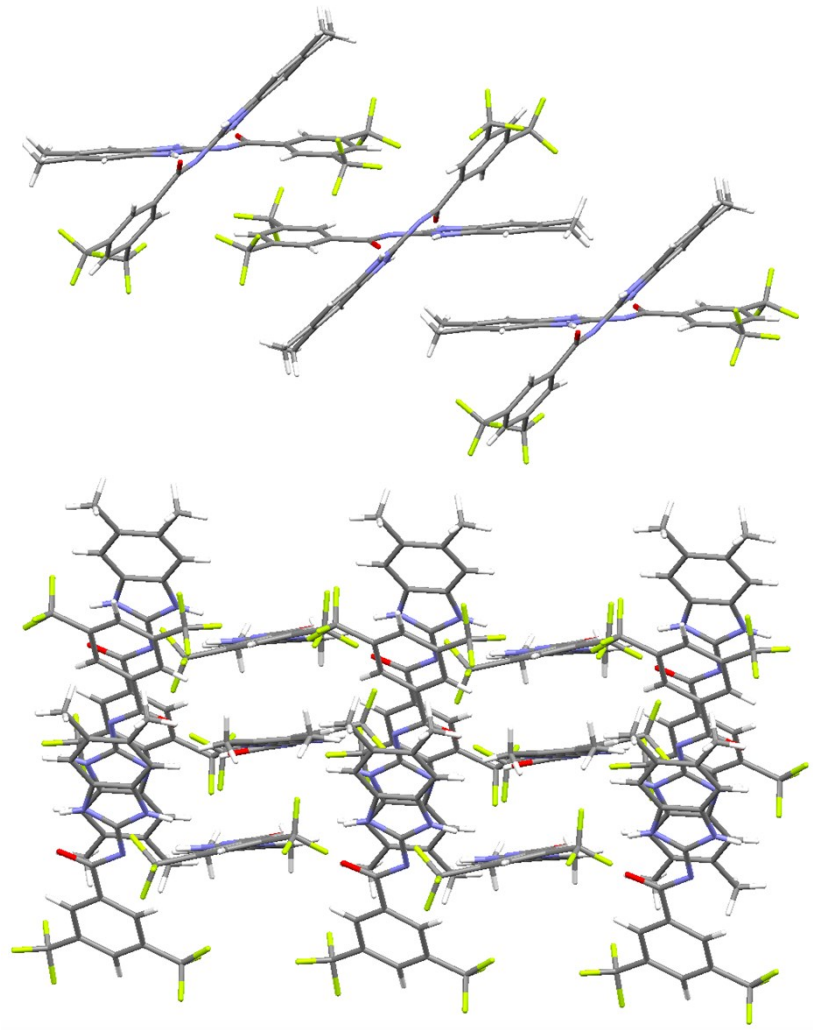
Views in the **(2a – 0.5 H^+)$_2$.*n*Bu_4N^+** crystal. Top: face; down: side view.

Table S8-D. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of **2a**



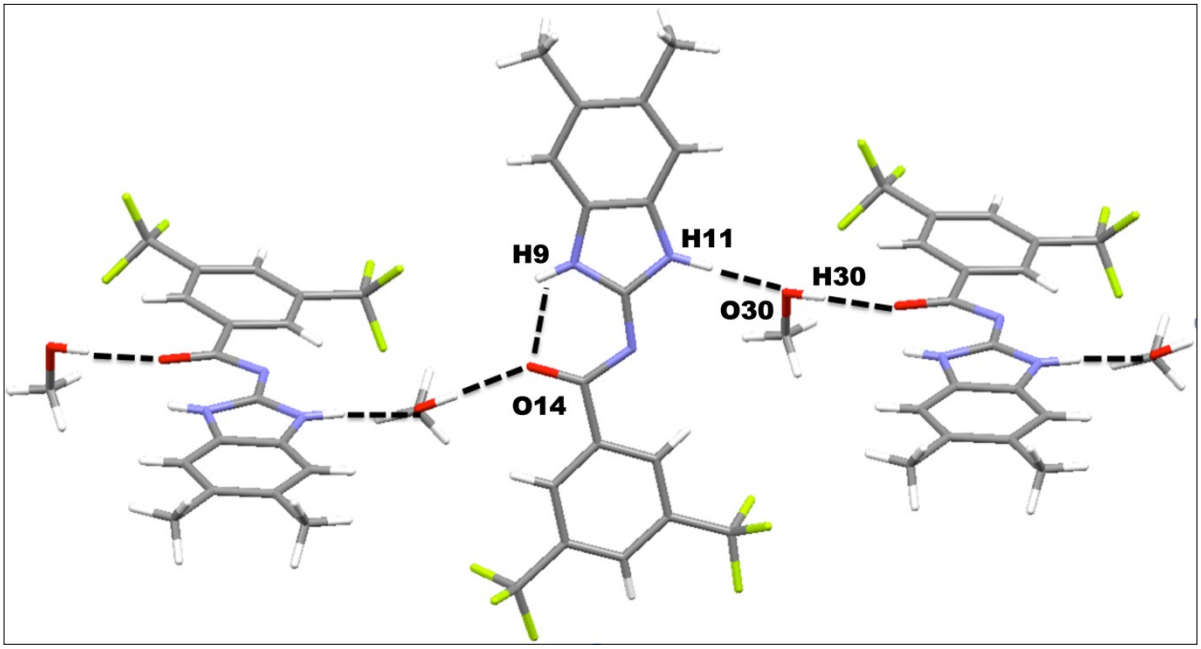
	Intramolecular distance N<u>H</u>•••<u>O</u>=C	**Intermolecular H-bond**	**Short contacts**
2a (2 independent molecules **A** and **B**)	**A**: 2.195 <N11-H11-O14>: 115.48° B: 2.203 <N59-H59-O64>: 114.89°	2.023 (N–H•••N, N11-H11/N62, 170.25°), 2.032 (N–H•••N, N61H61/N12, 173.33°) 2.087 (N–H•••O, N59-H59/O14, 145.55°), 2.121 (N–H•••O, N9-H9/O64, 145.18°).	**C–<u>F</u>•••<u>F</u>-C**: 2.863 (F26-F73), 3.216 (F72-F77), 3.457 (F72-F78), 3.502 (F23-F26) and **Pi-Pi stacking** between between two fluorinated aromatics (inter-centroïd distance: 3.993 Å) and between two 2,3-trimethyl-benzene (inter-centroïd distance: 3.898 Å.

Each **2a** molecule (**A** or **B**) is almost planar and these two planes are tilted by ca. 47.77°. This X-shape arrangement is propagating along the same axis and interacts with the other ones through Pi-stacking between 3,5-$(CF_3)_2$-C_6H_3 moieties or 2,3-trimethyl-benzene from benzimidazoles.



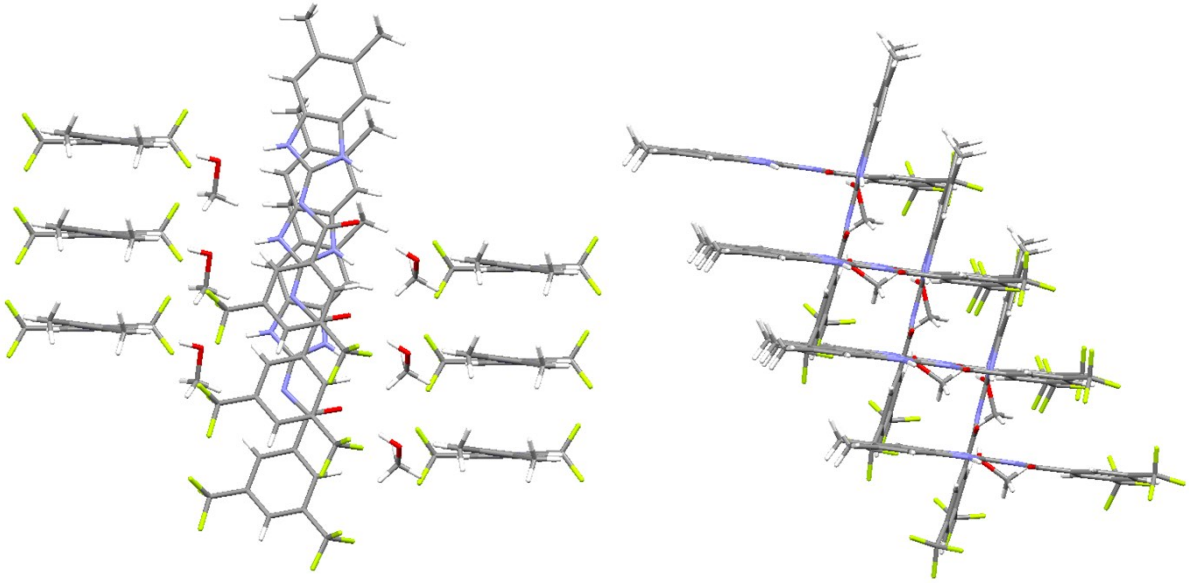
Views in the **2a** crystal. Top: face; down: side view.

Table S8-E. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of **(2a.CH_3OH)**



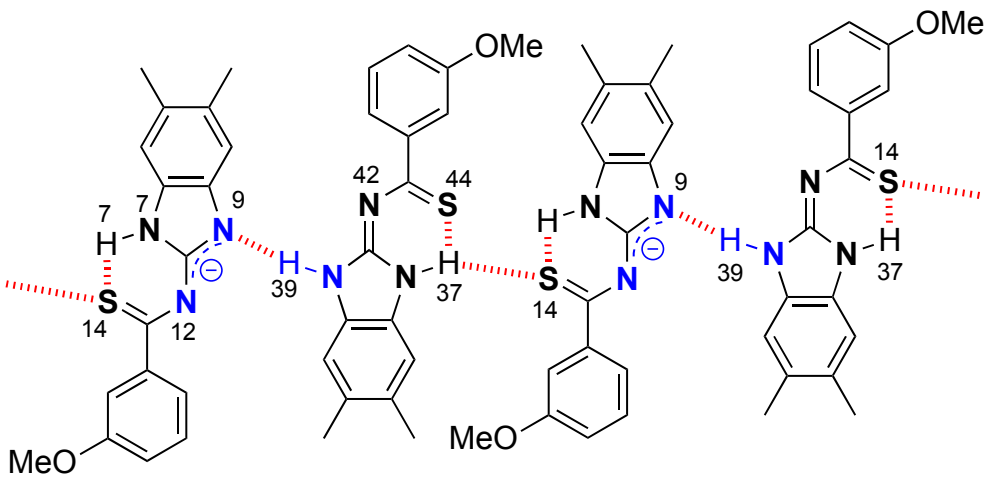
	Intramolecular distance N<u>H</u>•••<u>O</u>=C	**Intermolecular H-bond** between **2a** and **CH_3OH**	**Short contacts**
2a.CH_3OH	2.085 <N9-H9-O14>: 121.10°	1.887 (O–H•••O_{amide}, O30H30/O14, 179.33°), 1.893 (N–H•••O–H, N11H11/O30, 173.26°)	**C–<u>F</u>•••<u>F</u>-C**: 2.993 (F23-F24) and Multiple contacts due to Pi-Pi stacking between between **2a** molecules.

The flat **2a** molecules stacked in a slightly off-set arrangement (centroid distance between benzimidazole units: 4.828 Å). Each aromatic stack is surrounded by two methanol "channels", and is tilted by ca. 82.4° from the next aromatic stack..



Views in the **2a.CH_3OH** crystal. Left: face; right: side view.

Table S8-F. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of **(1b).(1b – H$^+$).*n*Bu$_4$N$^+$** obtained in the presence of *n*Bu$_4$N$^+$.PhCO$_2^-$



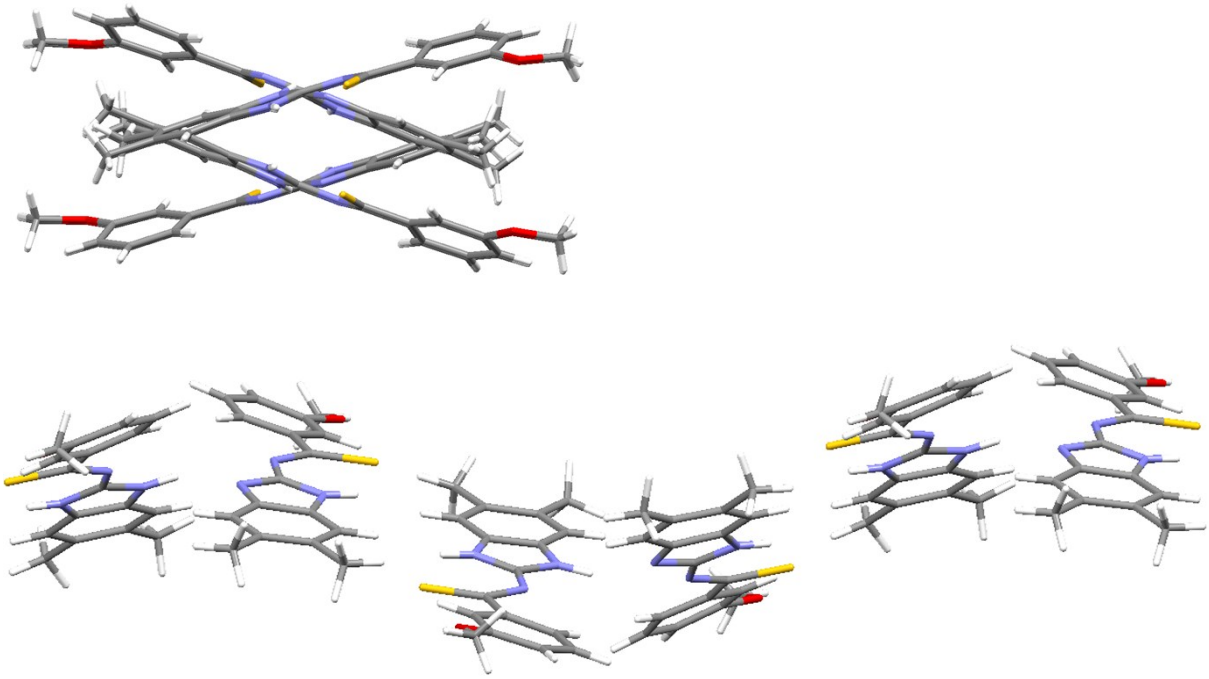
Ammonium omitted for clarity purpose

Compound	**Intramolecular contact (1b)**	**Intermolecular contacts between 1b molecules**	**Other Short Contacts**
(1b).(1b – H$^+$).*n*Bu$_4$N$^+$	N-H•••S=C: 2.304 (H37-S44), 2.462 (H7-S14)	N-H•••S=C: 2.930 (H37-S14) N-H•••N$^{0.5-}$: 1.722 (H39-N9) C$_{Ar}$-H•••N: 2.763 (H31-N12), 2.783 (H1-N42)	Multiple contacts between **(1b)** or **(1b – H$^+$)** and the surrounding ammoniums (CH bond) with distances between 2.7 and 3.2 Å: 2.737 (N9-H73B), 2.802 (N39-H65B), 2.748 (N9-H63A)

Each **1b** and **(1b – H$^+$)** molecule is almost planar (C46C45C43N42 angle = 14.63° for **1b** and C16C15C13N12 angle = 11.43° for **(1b – H$^+$)** . In **(1b – H$^+$)** molecule, the negative charge is delocalized between N9 and N12.

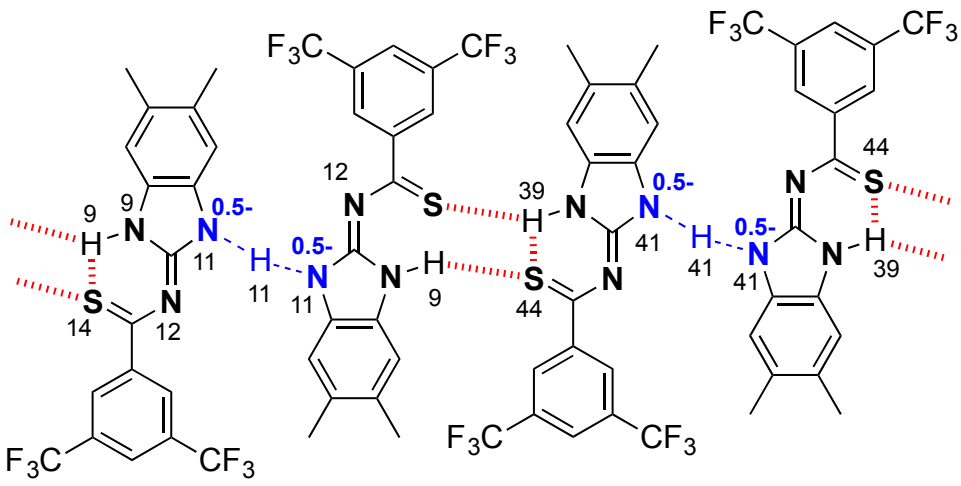
Species **1b** and **(1b – H$^+$)** form a dimer strongly tied by a N-H•••N$^-$ interaction (d = 1.722 Å)with a delocalized negative charge over the benzimidazole nitrogen atoms. This dimer has an X-shape arrangement (angle of 43.54° between **1b** and **(1b – H$^+$)** planes). Each **1b.(1b – H$^+$)** dimer is in close contact with two other dimers through a N-H•••S=C contact (d = 2.930 Å) and C$_{Ar}$-H•••N contacts (d = 2.76-2.78 Å)

The zig-zag arrangement of these **1b.(1b – H$^+$)** dimers is surrounding by an upper and lower layer of *n*Bu$_4$N$^+$ in short contacts (d = 2.7-3.2Å).



Views in the (**1b**).(**1b** – **H**$^{+}$).*n*$\mathbf{Bu_4N^+}$ crystal (ammoniums omitted for clarity). Left: face; right: side view.

Table S8-G. Selected Hydrogen Bond length (Å) and angles (°) in monocrystal of (**2b – 0.5 H⁺**).(**2b – 0.5 H⁺**).***n*Bu$_4$N$^+$ obtained in the presence of *n*Bu$_4$N$^+$.PhCO$_2^-$

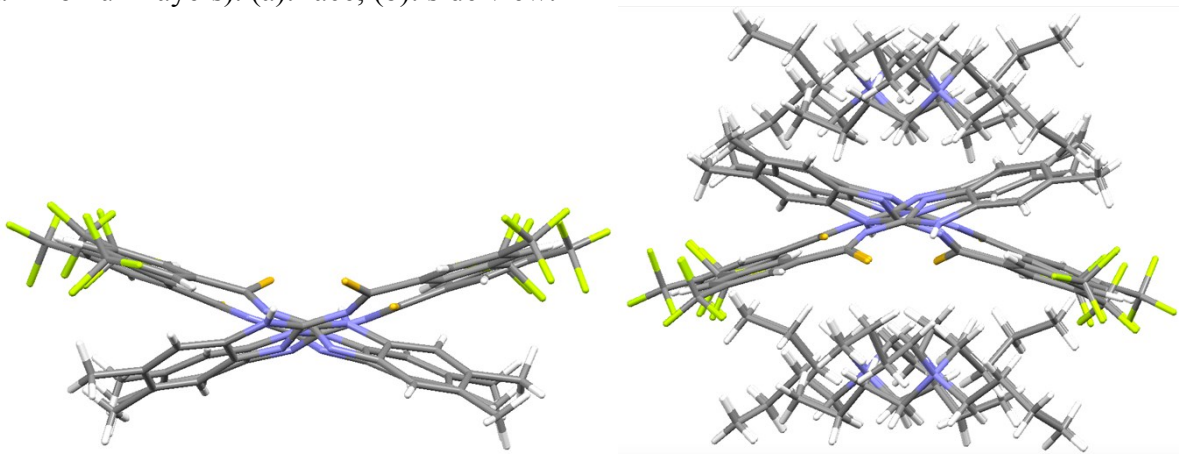


ammonium omitted for clarity purpose

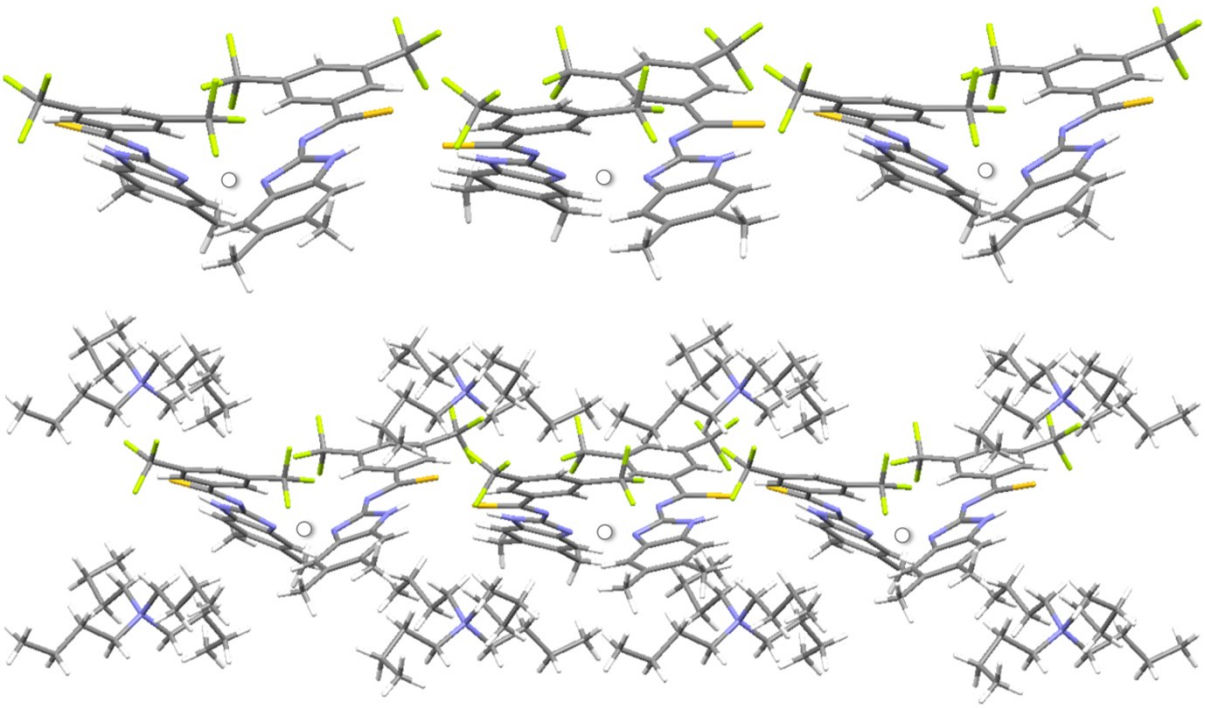
Compound	**Intramolecular contact** (**2b** – 0.5 H⁺)	**Intermolecular contacts** between (**2b** – 0.5 H⁺) molecules	**Other Short Contacts**
(**2b** – 0.5 H⁺).(**2b** – 0.5 H⁺).*n*Bu$_4$N$^+$ (2 independent molecules)	N-H•••S=C: 2.319 (H9-S14), 2.380 (H39-S44)	N-H•••S=C: 2.631 (H39-S14), 3.008 (H9-S44) Half-deprotonation ($\underline{N}^{0.5-}$···H···$\underline{N}^{0.5-}$): 2.702 (N11 H11 N11), 2.604 (N41 H41 N41) C_{Ar}-H•••N: 3.122 (H31-N42), 3.501 (H1-N12)	Multiple contacts between (**2b – 0.5 H⁺**) molecules and the surrounding ammoniums (CH bond) with distances between 2.7 and 3.2Å: 2.690 (H75B-S14), 2.921 (H83B-S14), 2.860 (H83A-S44), 3.020 (H75A-S44).

In the crystal, the two independent (**2b** – 0.5 H⁺) molecules are observed. each conjugated structure is slightly tilted: -11.3° (angle C20C15C13N12) and 5.3° (C50C45C43N42).
Each (**2b** – 0.5 H⁺) compound is involved in a dimer association with an identical molecule, which is tied by a strong $N^{0.5-}$···H···$N^{0.5-}$ interaction (distances between nitrogen atoms = 2.60-2.70 Å). This dimer has an X-shape arrangement (angles of 48.00° and 39.58° within both different dimers). Each 2.(**2b** – 0.5 H⁺) dimer is in close contact with two other dimers through N-H•••S=C contacts (d = 2.63-3.01 Å).
The zig-zag arrangement of these dimers is surrounding by an upper and lower layer of *n*Bu$_4$N$^+$ in short contacts (d = 2.7-3.2Å).

Views in the (**2b** – 0.5 H^+).(**2b** – 0.5 H^+).$n$$Bu_4N^+$ crystal (without and with surrounding ammonium layers). (a): face; (b): side view.



a)



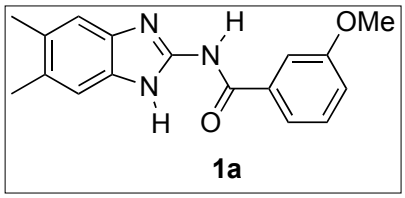
b)

UV-Visible Titrations between Compounds 1–2 and salts in acetonitrile

Acetonitrile was dried over calcium hydride and freshly distilled. Commercially available *n*-tetrabutylammonium salts (X^-: F^-, Br^-, CN^-, $H_2PO_4^-$, $CH_3CO_2^-$, $PhCO_2^-$) were dried under vacuum at 60°C overnight and used.

UV-Visible Titrations: all solutions were freshly prepared. Equilibrium constants (K_{eq}) between hosts **1**–**2** and guests (*n*-Bu_4NX) were determined using titrations monitored by UV-Visible (host signals) in acetonitrile. A solution (2.5 mL) of host (2.5×10^{-5} M) was introduced in a quartz cuvette at 20°C. Increasing aliquots (20 μL) of guest stock solution (5×10^{-3}–10^{-2} M in CH_3CN) were successively added until the final total volume reached 2.8 ml at maximum. At each addition, the same aliquot was added to the reference tank (acetonitrile, 2.5 mL) The titration data (Δε *versus* guest concentration) were fitted using the nonlinear curve-fitting procedure with a (1:1) or (1:2) binding equation using Letagrop program.[5]

1) Amido- Benzimidazole 1a:

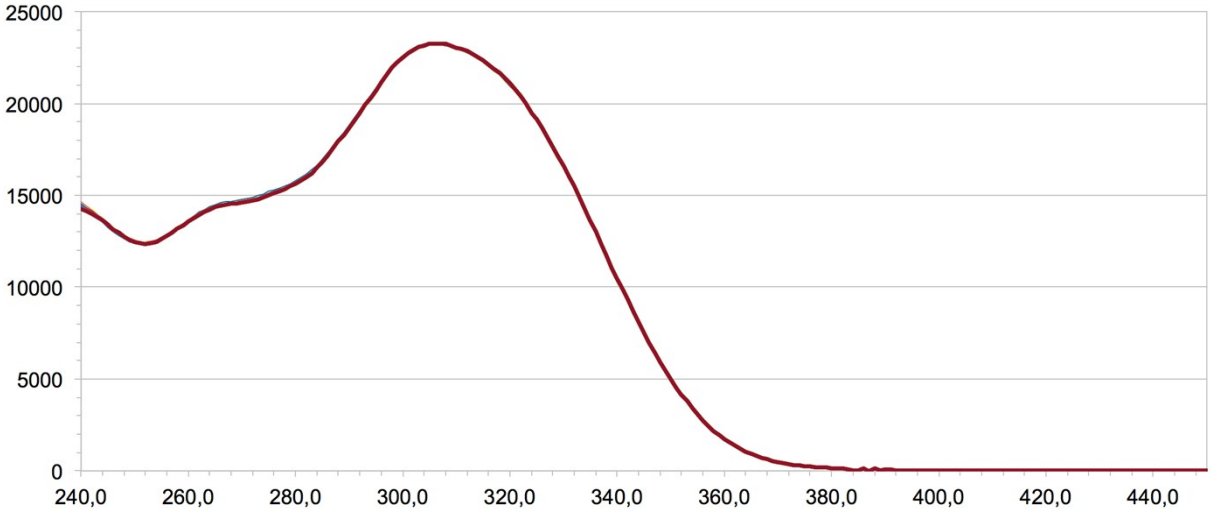


1a

1a) UV-Vis. Titration between 1a and *n*-Bu_4N^+. Br^-

Host: 1 eq.; Guest: 0–38 equivalents

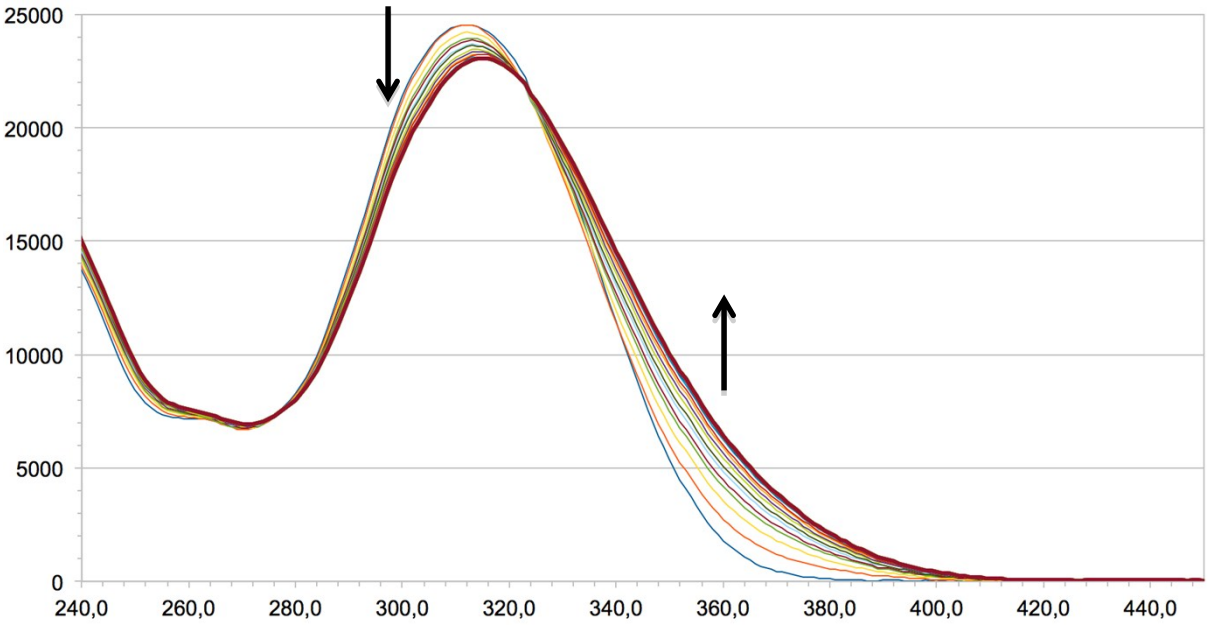
ε = f(λ)



1b) UV-Vis. Titration between 1a and *n*-Bu_4N^+. $H_2PO_4^-$

Host: 1 eq.; Guest: 0–57 equivalents; **log K_{eq} (1:1)= 3.3099 ± 0.0005**

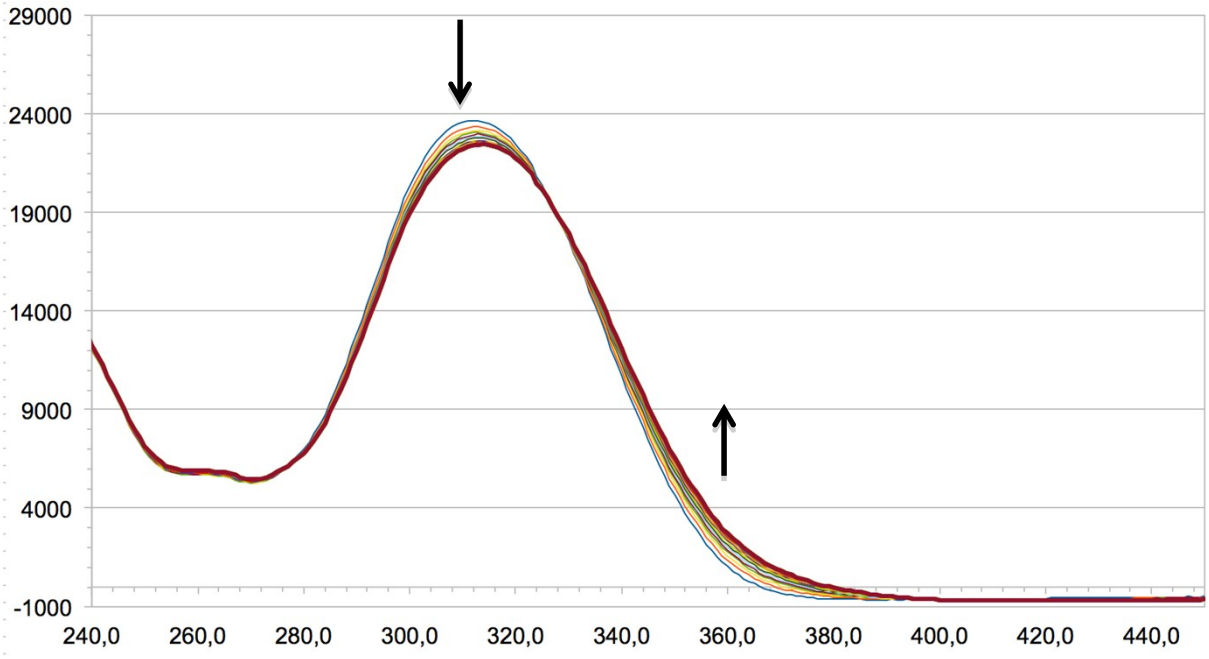
ε = f(λ)



1c) <u>UV-Vis. Titration between 1a and *n*-Bu_4N^+. $PhCO_2^-$</u>

Host: 1 eq.; Guest: 0–38 equivalents; **log K_{eq} (1:1)= 3.4634 ± 0.0339**

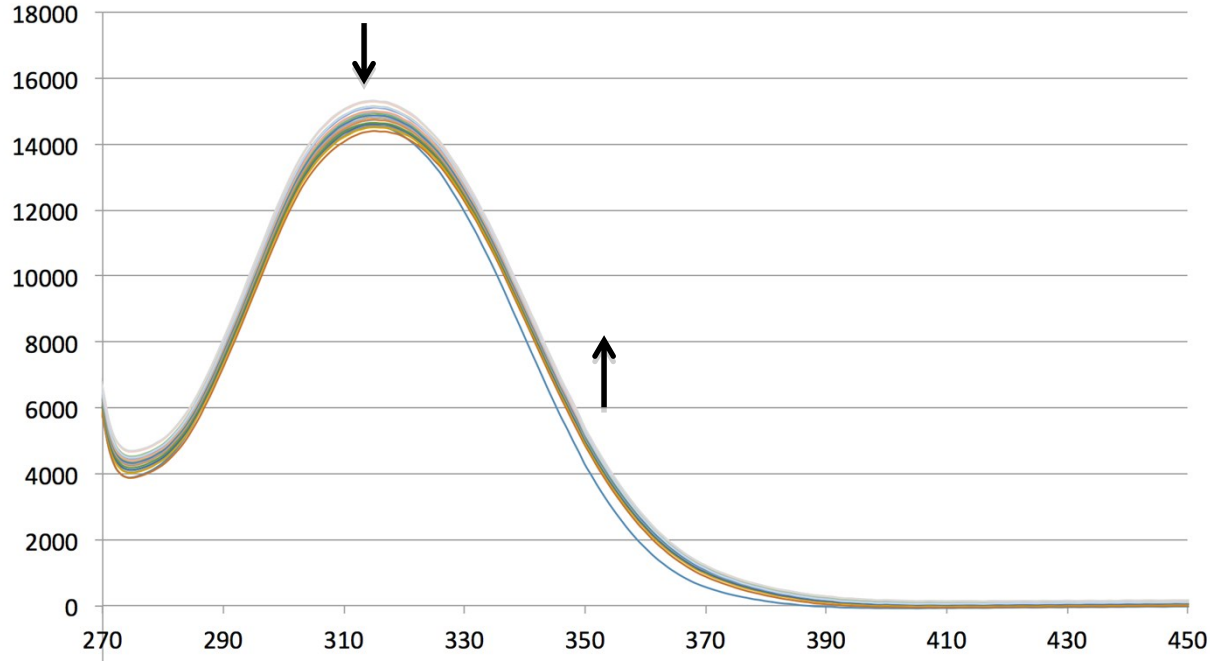
ε = f(λ)



1d) <u>UV-Vis. Titration between 1a and *n*-Bu_4N^+. $CH_3CO_2^-$</u>

Host: 1 eq.; Guest: 0–40 equivalents; **log K_{eq} (1:1)= 3.4300 ± 0.0003**

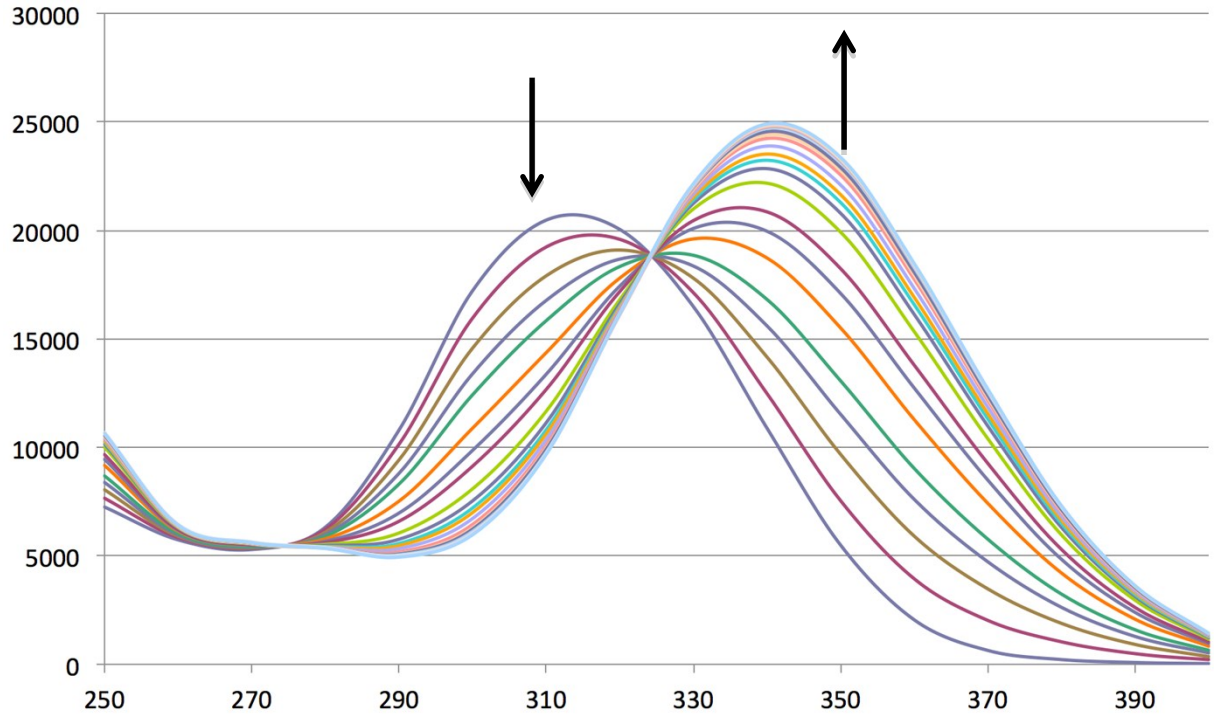
ε = f(λ)



1e) UV-Vis. Titration between 1a and *n*-Bu_4N^+. CN^-

Host: 1 eq.; Guest: 0–40 equivalents; **log K_{eq} (1:1)= 4.7704 ± 0.0252**

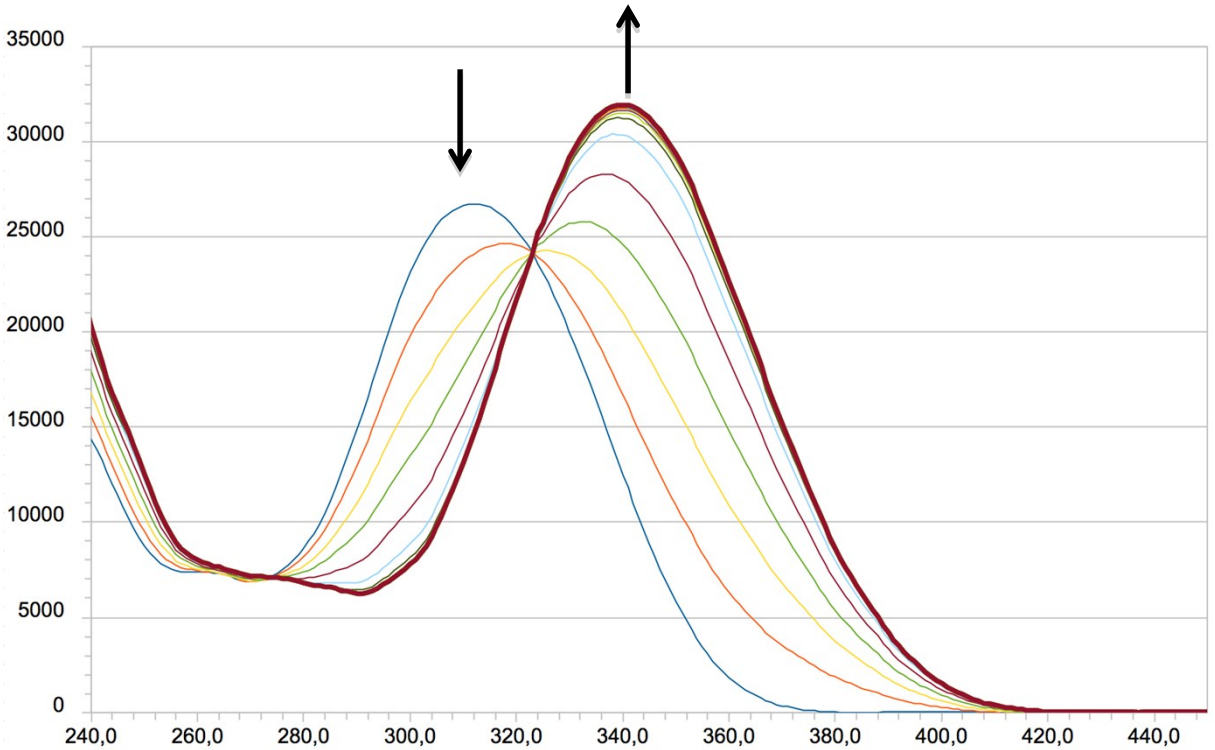
ε = f(λ)



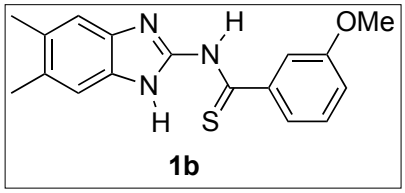
1f) UV-Vis. Titration between 1a and *n*-Bu_4N^+. F^-

Host: 1 eq.; Guest: 0–16 equivalents; **log K_1 = 4.6742 ± 0.0003** and **log β= 9.8219 ± 0.0454**

ε = f(λ)



2) Thioamide-Benzimidazole 1b:

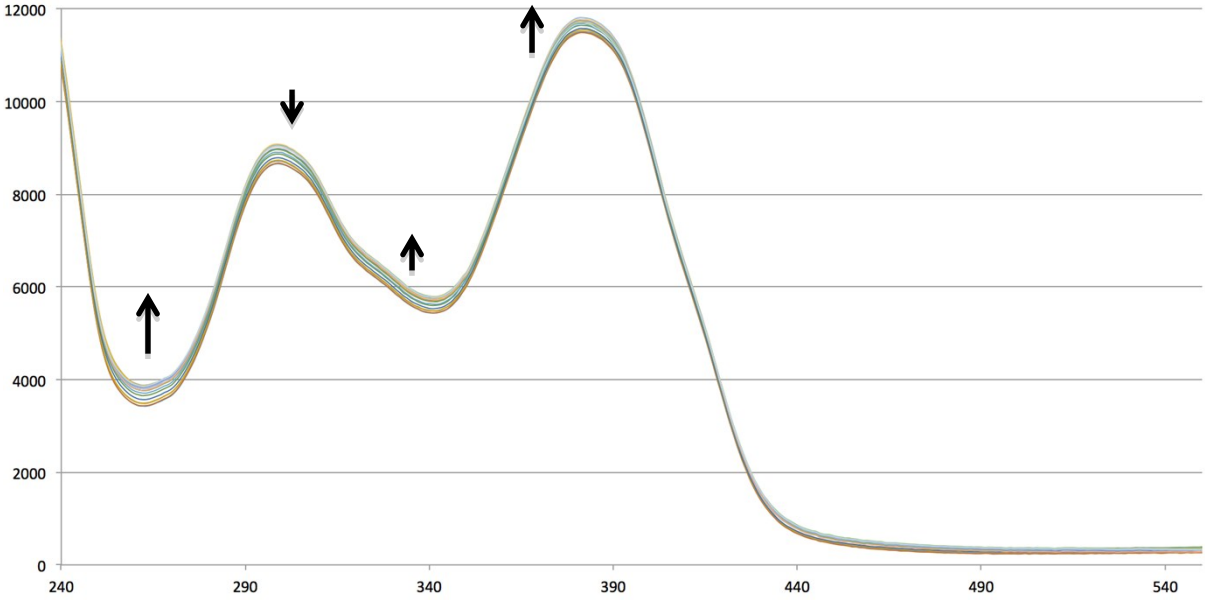


1b

2a) Titration between 1b and *n*-$Bu_4N^+.Br^-$

Host: 1 eq.; Guest: 0–20 equivalents

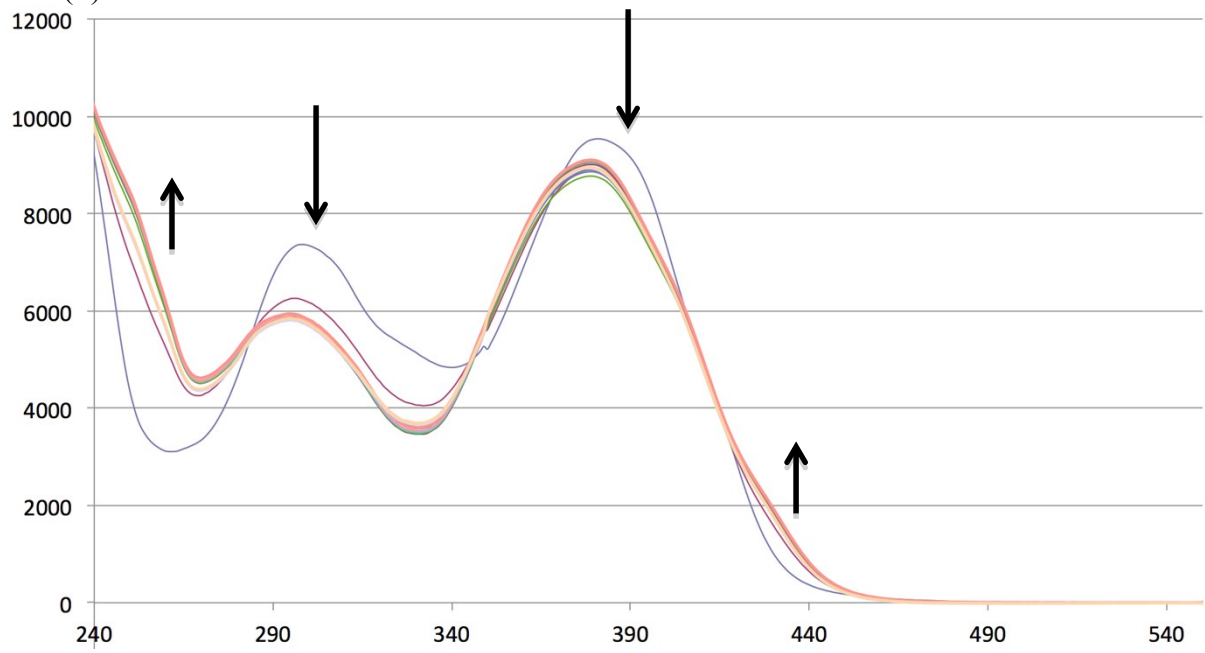
ε = f(λ)



2b) Titration between 1b and *n*-$Bu_4N^+.\ H_2PO_4^-$

Host: 1 eq.; Guest: 0–20 equivalents; **log K_{eq} (1:1)= 4.4053 ± 0.0493**

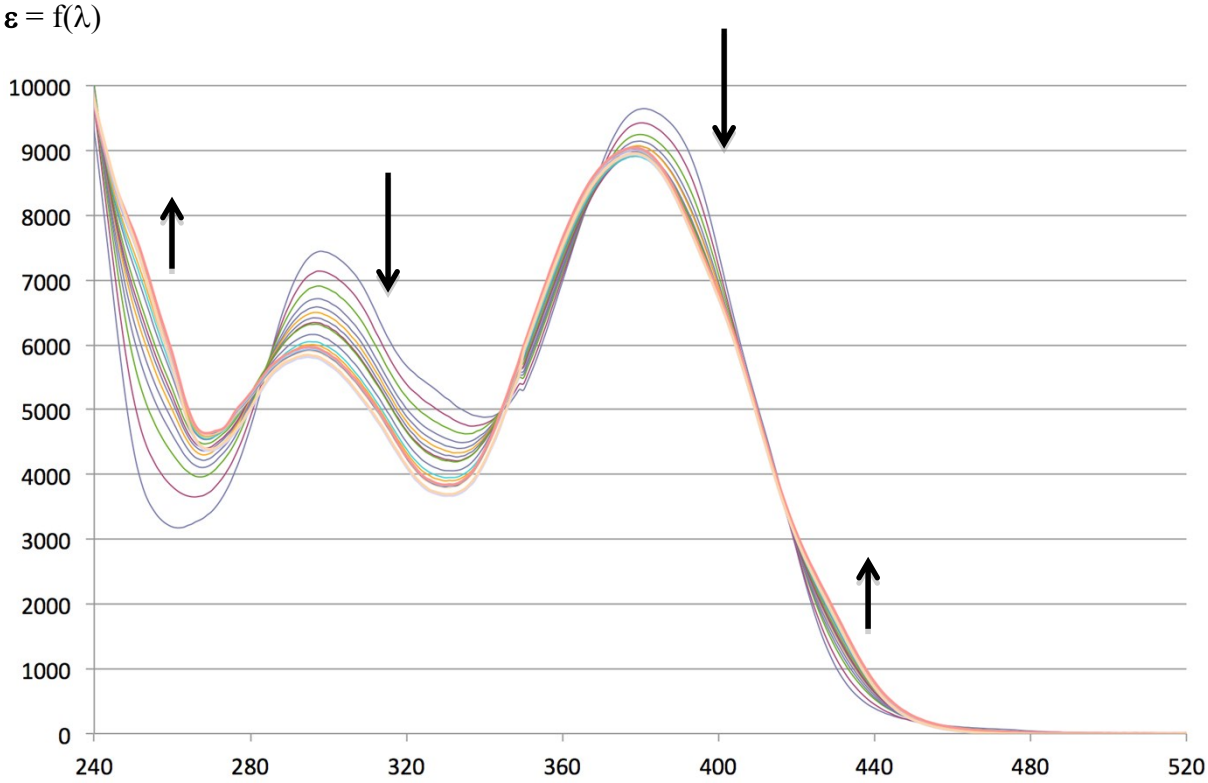
ε = f(λ)



2c) <u>UV-Vis. Titration between 1b and *n*-Bu_4N^+. $PhCO_2^-$</u>

Host: 1 eq.; Guest: 0–32 equivalents; **log K_{eq} (1:1)= 4.1751 ± 0.0243**

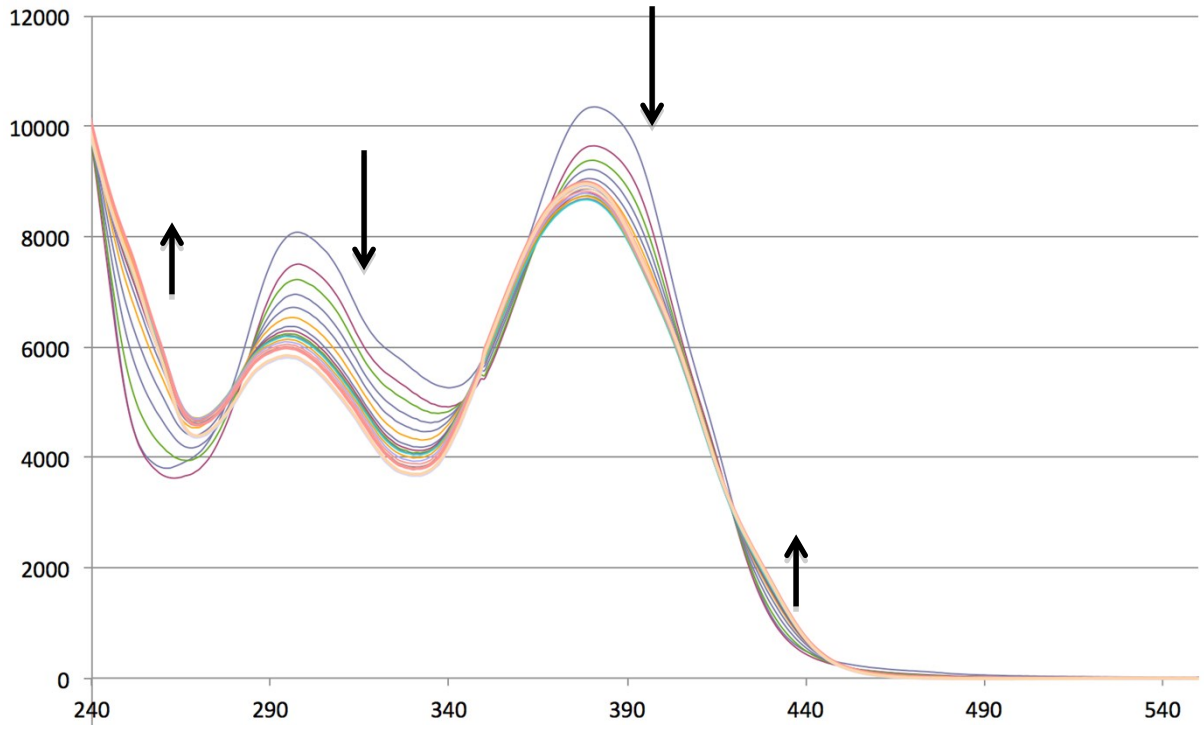
ε = f(λ)



2d) <u>UV-Vis. Titration between 1b and *n*-Bu_4N^+. $CH_3CO_2^-$</u>

Host: 1 eq.; Guest: 0–20 equivalents; **log K_{eq} (1:1)= 5.1912 ± 0.0904**

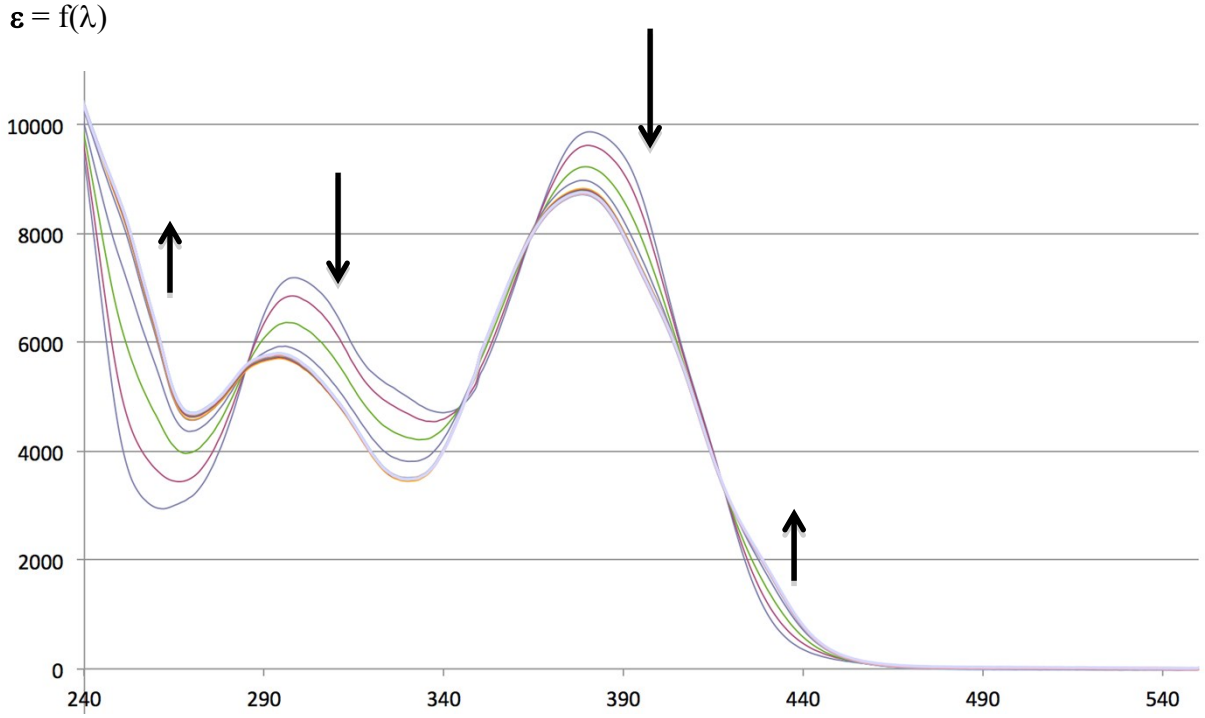
ε = f(λ)



2e) <u>UV-Vis. Titration between 1b and *n*-Bu_4N^+. CN^-</u>

Host: 1 eq.; Guest: 0–40 equivalents; **log K_{eq} (1:1)= 5.0941 ± 0.1699**

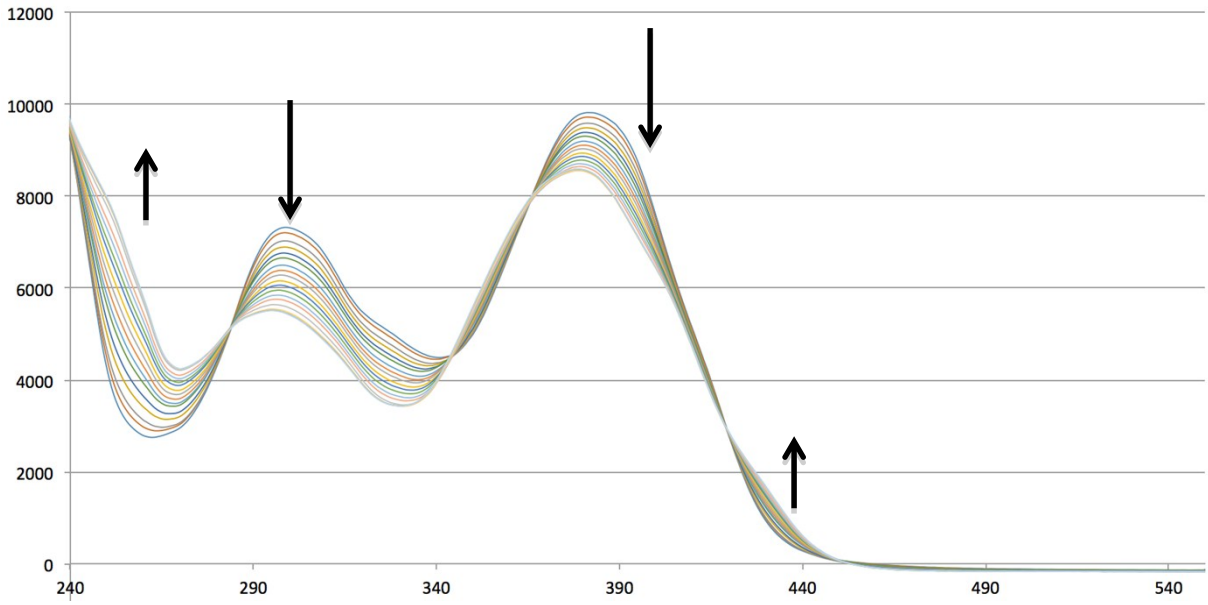
ε = f(λ)



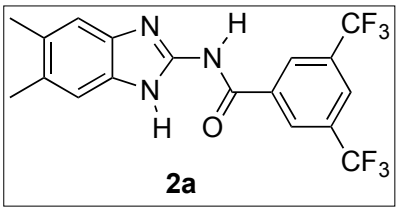
2f) <u>UV-Vis. Titration between 1b and *n*-Bu_4N^+. F^-</u>

Host: 1 eq.; Guest: 0–40 equivalents; **log K_1 (1:1)= 3.4506 ± 0.0231** and **log β= 8.4103 ± 0.0296**

ε = f(λ)



3) Amido-benzimidazole 2a:

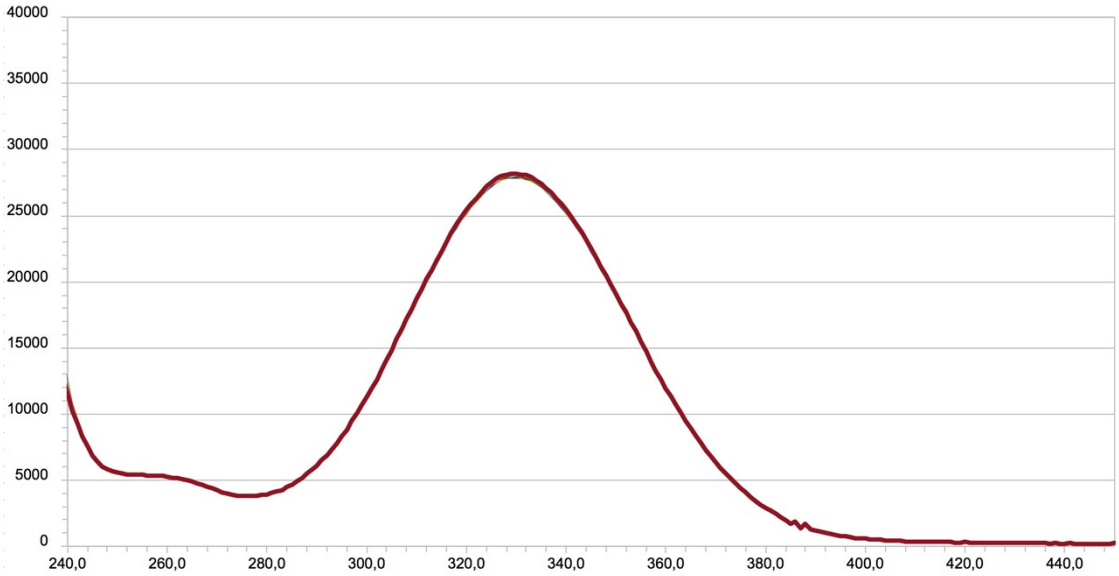


2a

3a) UV-Vis. Titration between 2a and *n*-Bu_4N^+. Br^-

Host: 1 eq.; Guest: 0–80 equivalents

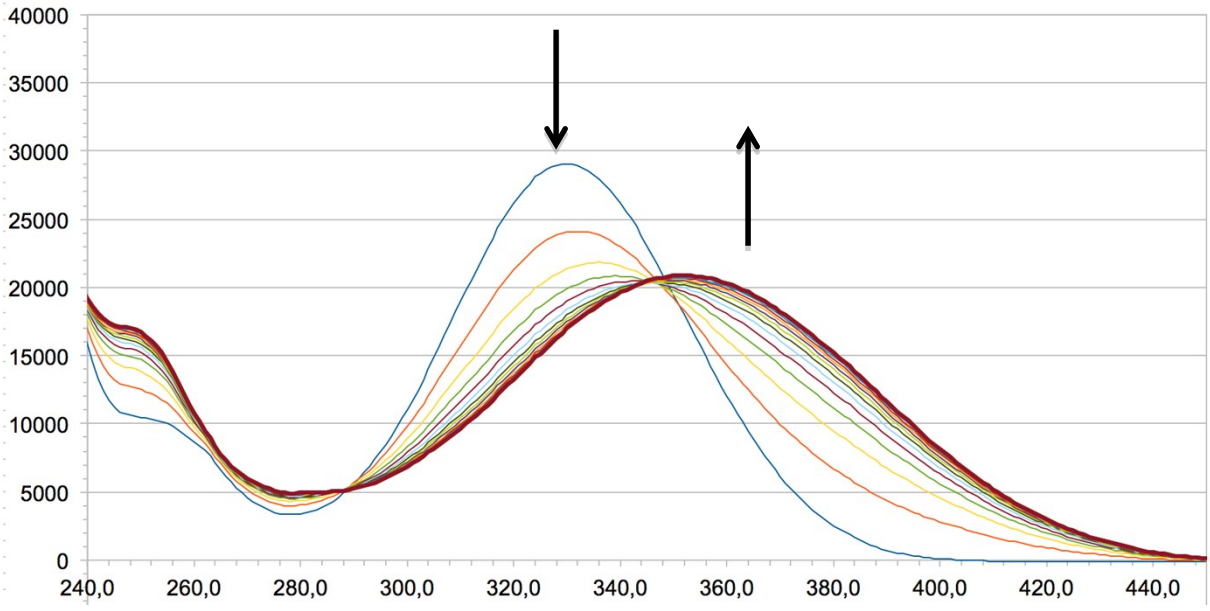
ε = f(λ)



3b) UV-Vis. Titration between 2a and *n*-Bu_4N^+. $H_2PO_4^-$

Host: 1 eq.; Guest: 0–60 equivalents; **log K_{eq} (1:1)= 3.7567 ± 0.0086**

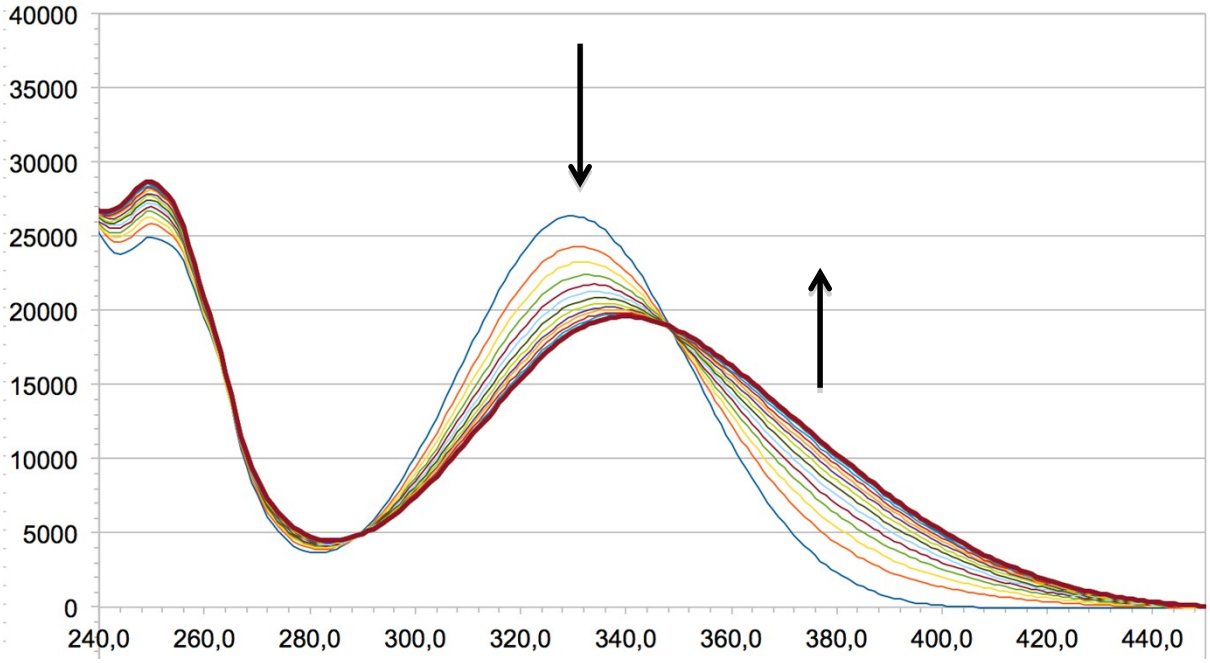
ε = f(λ)



3c) <u>UV-Vis. Titration between 2a and *n*-Bu_4N^+. $PhCO_2^-$</u>

Host: 1 eq.; Guest: 0–50 equivalents; **log K_{eq} (1:1)= 3.5984 ± 0.0224**

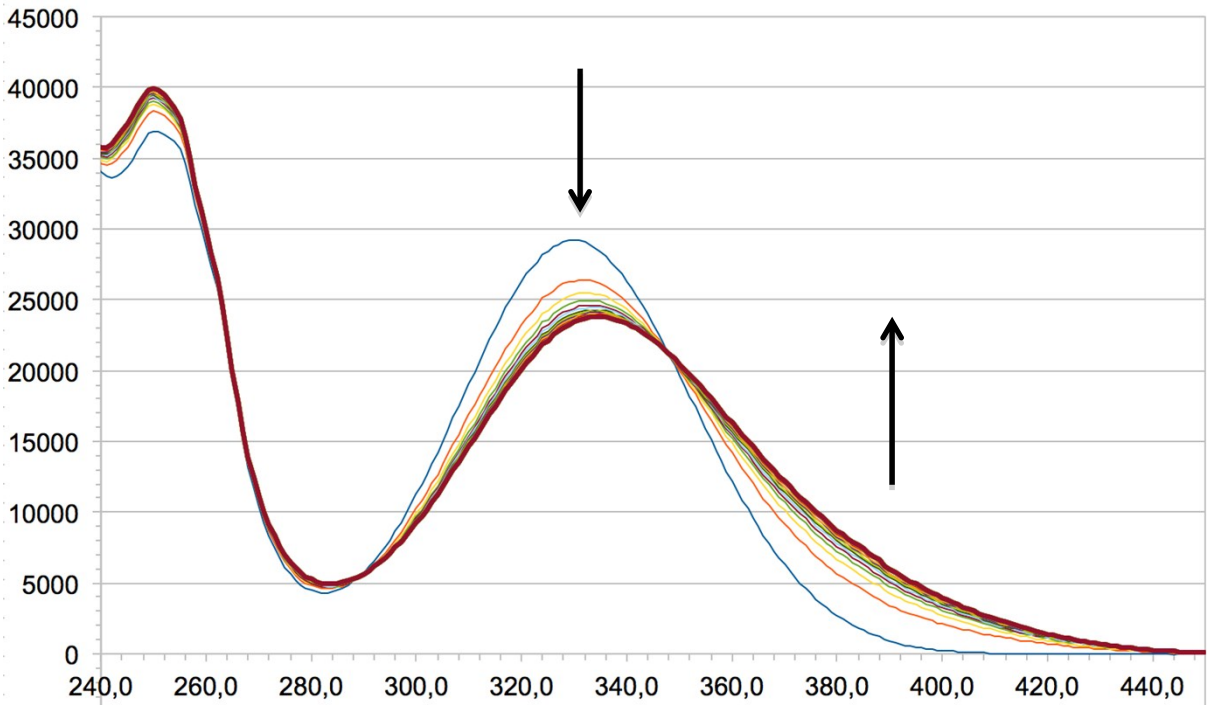
ε = f(λ)



3d) <u>UV-Vis. Titration between 2a and *n*-Bu_4N^+. $CH_3CO_2^-$</u>

Host: 1 eq.; Guest: 0–16 equivalents; **log K_{eq} (1:1)= 4.9007 ± 0.0100**

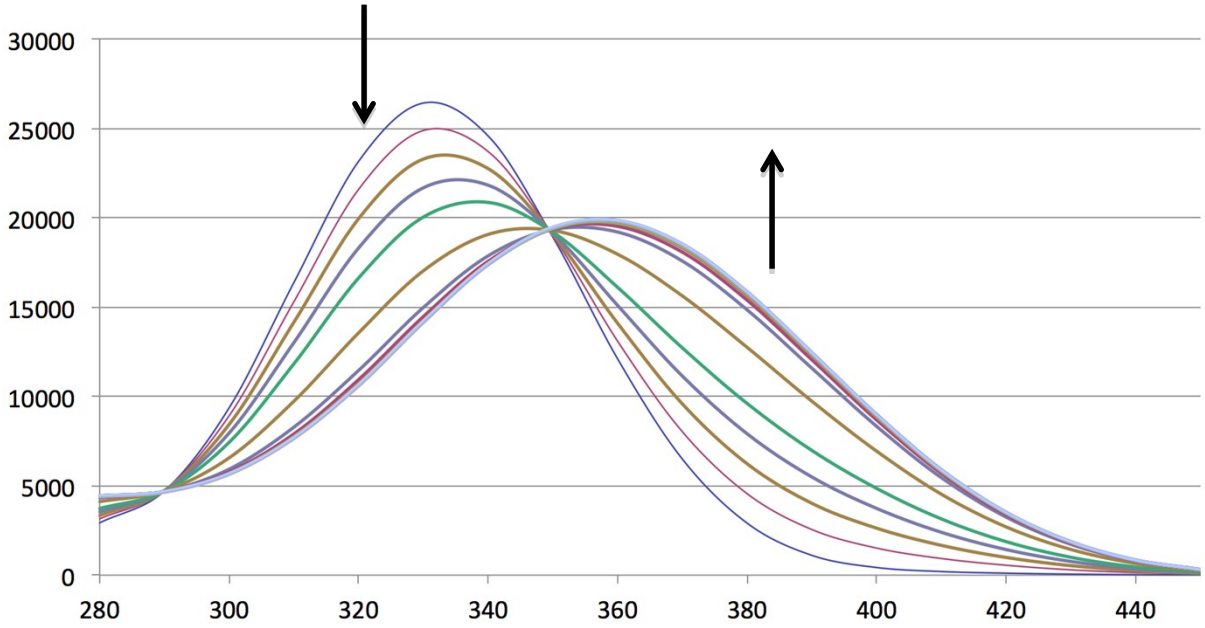
ε = f(λ)



3e) UV-Vis. Titration between 2a and *n*-Bu_4N^+. CN^-

Host: 1 eq.; Guest: 0–40 equivalents; **log K_{eq} (1:1)= 5.4639 ± 0.0290**

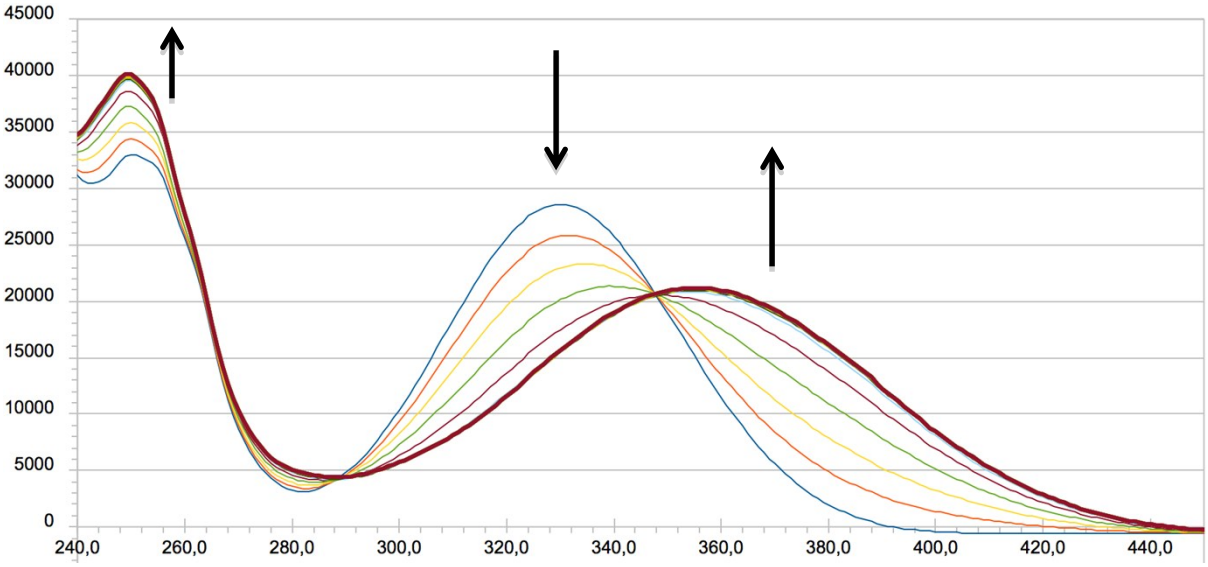
ε = f(λ)



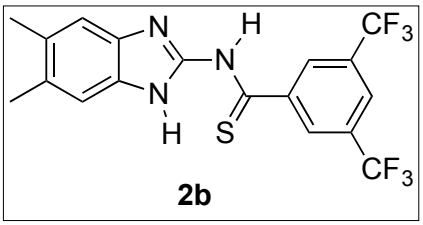
3f) UV-Vis. Titration between 2a and *n*-Bu_4N^+. F^-

Host: 1 eq.; Guest: 0–16 equivalents; **log K_1 = 4.2071 ± 0.0108 and log β= 9.0959 ± 0.0804**

ε = f(λ)



4) Thioamido-Benzimidazole 2b:

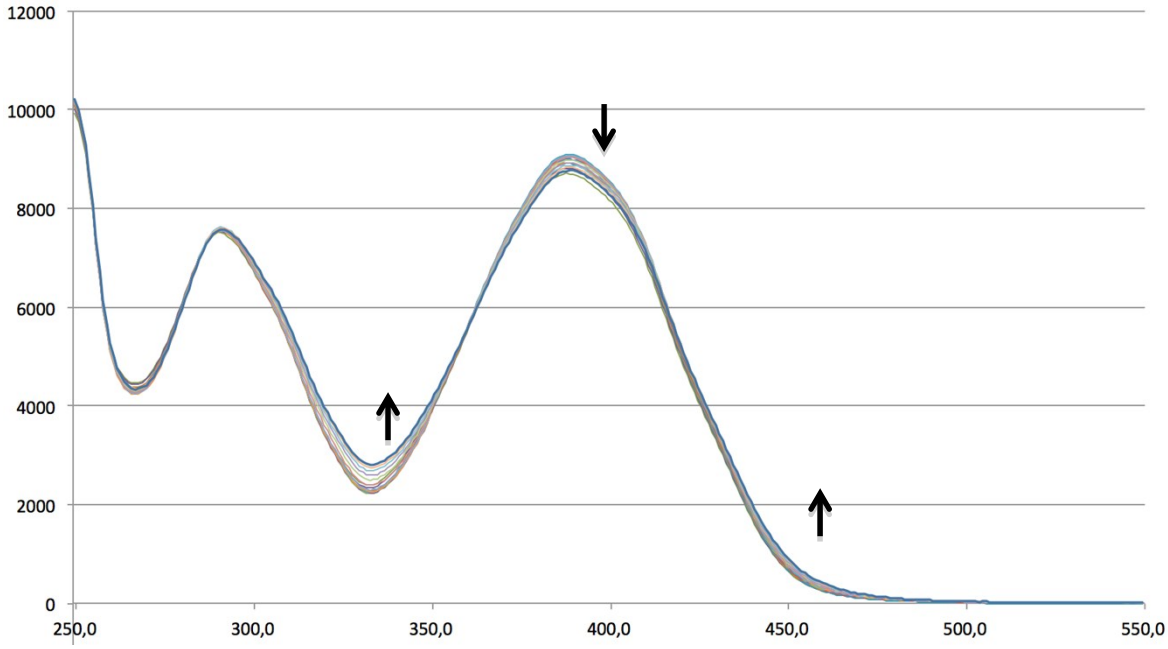


2b

4a) UV-Vis. Titration between 2b and *n*-Bu_4N^+. Br^-

Host: 1 eq.; Guest: 0–40 equivalents

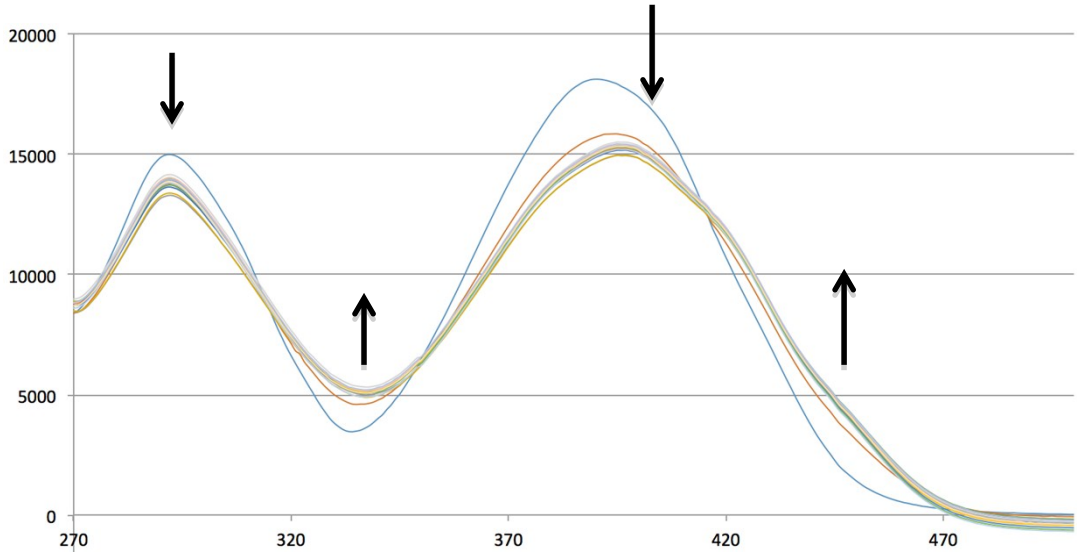
ε = f(λ)



4b) UV-Vis. Titration between 2b and *n*-Bu_4N^+. $H_2PO_4^-$

Host: 1 eq.; Guest: 0–40 equivalents; **log K_{eq} (1:1)= 5.0967 ± 0.0966**

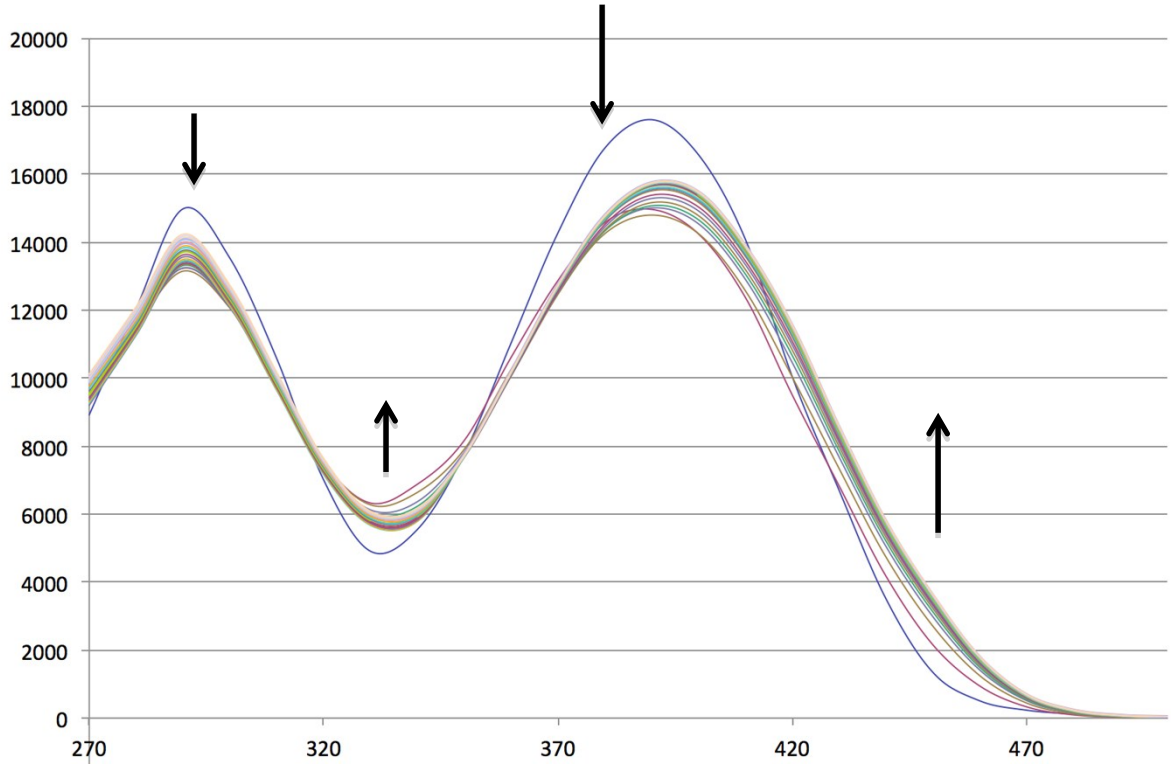
ε = f(λ)



4c) <u>UV-Vis. Titration between 2b and *n*-Bu_4N^+. $PhCO_2^-$</u>

Host: 1 eq.; Guest: 0–40 equivalents; **log K_{eq} (1:1)= 5.0567 ± 0.0918**

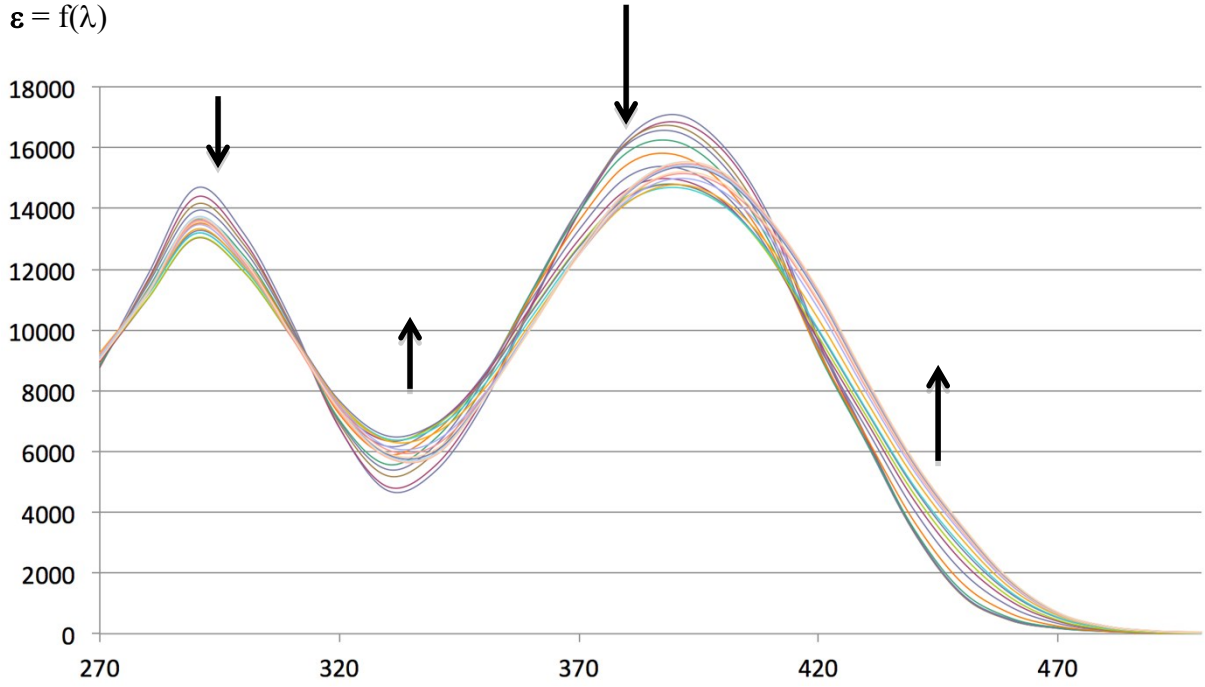
ε = f(λ)



4d) <u>UV-Vis. Titration between 2b and *n*-Bu_4N^+. $CH_3CO_2^-$</u>

Host: 1 eq.; Guest: 0–16 equivalents; **log K_{eq} (1:1)= 4.8024 ± 0.1827**

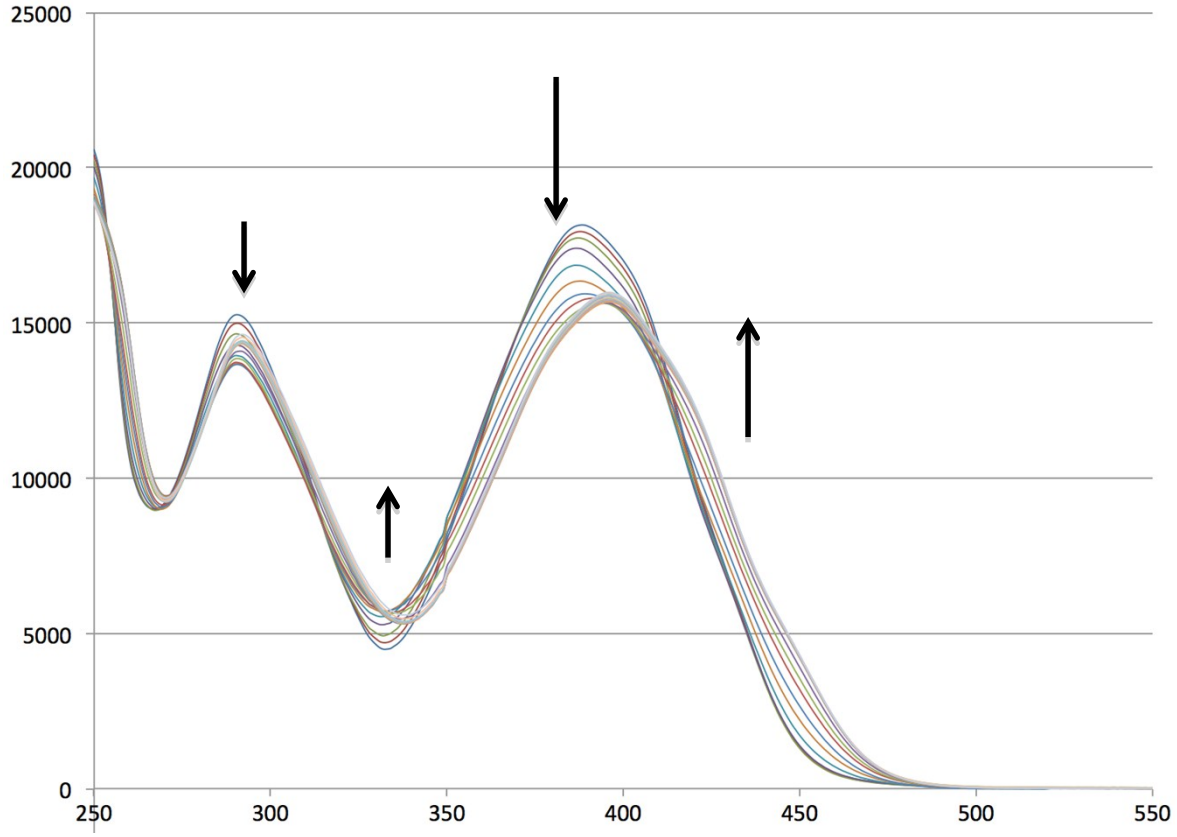
ε = f(λ)



4e) <u>UV-Vis. Titration between 2b and *n*-Bu_4N^+. CN^-</u>

Host: 1 eq.; Guest: 0–17 equivalents; **log K_{eq} (1:1)= 4.6607 ± 0.1015**

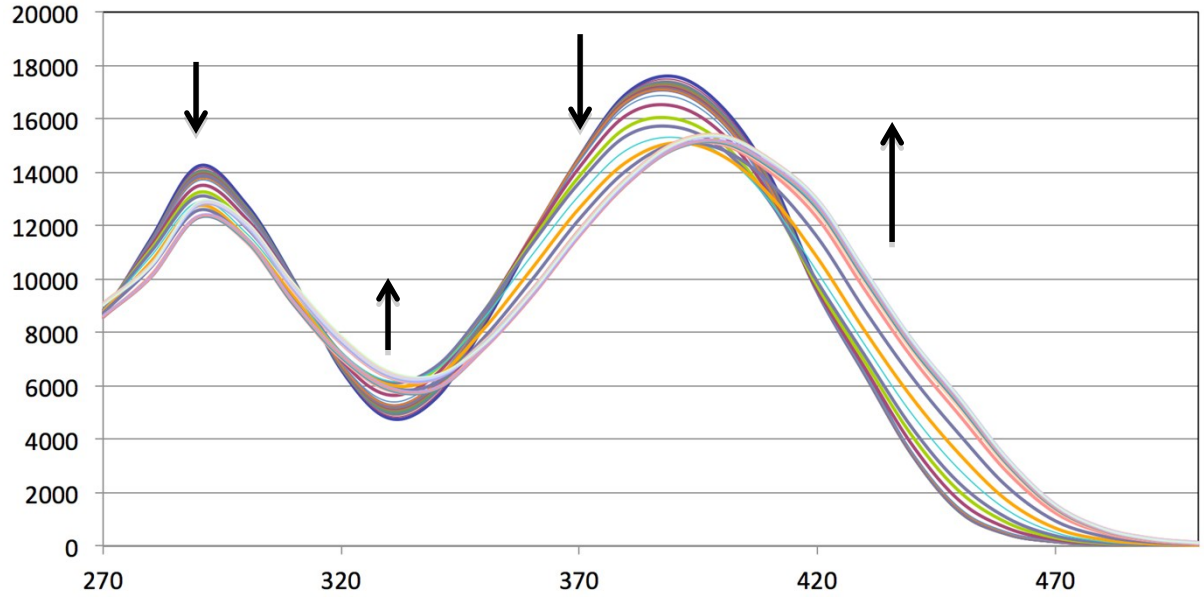
ε = f(λ)



4f) <u>UV-Vis. Titration between 2b and *n*-Bu_4N^+. F^-</u>

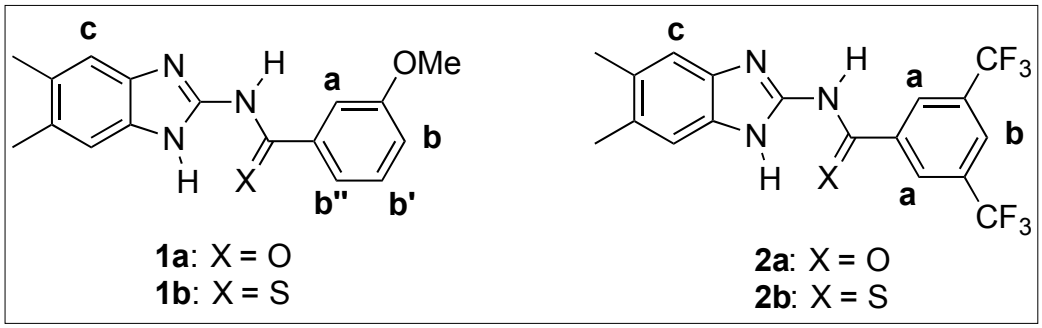
Host: 1 eq.; Guest: 0–40 equivalents; **log K_1= 3.4406 ± 0.0611 and log β= 8.5425 ± 0.0379**

ε = f(λ)



^{1}H NMR monitoring of compounds 1–2 in the presence of fluoride

Procedure: Deuterated solutions were freshly prepared. Acid-base reactions between (thio)amido-benzimidazoles **1–2** and *n*-tetrabutylammonium fluoride were monitored by ^{1}H NMR in CD_3CN. A solution (100 µL) of host (~25 mM, CD_3CN) was introduced in each NMR tube (5 experiments). Increasing aliquots of fluoride stock solution (~ 50 mM, CD_3CN) were added and the total volume (500 µL) was adjusted with CD_3CN.



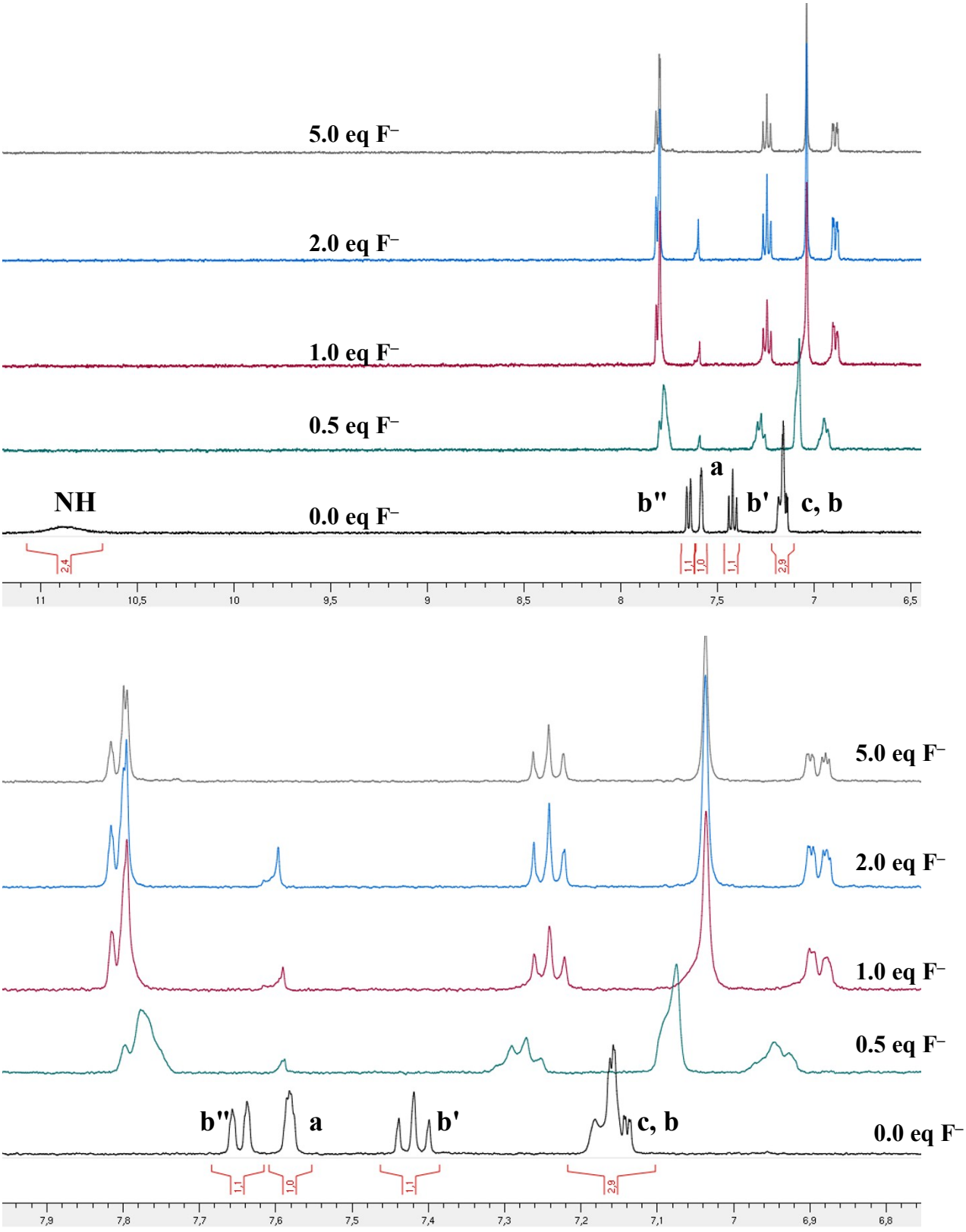


Figure S1: ^{1}H NMR (400 MHz, CD_3CN, 298K) monitoring of reaction between **1a** (5 mM) and increasing amount of *n*-$Bu_4N^+.F^-$ (0, 0.5, 1, 2 and 5 equivalents). Top: spectra in the 11-7 ppm region showing the disappearance of the NH protons. Bottom: spectra in the aromatic region (8-6.5 ppm).

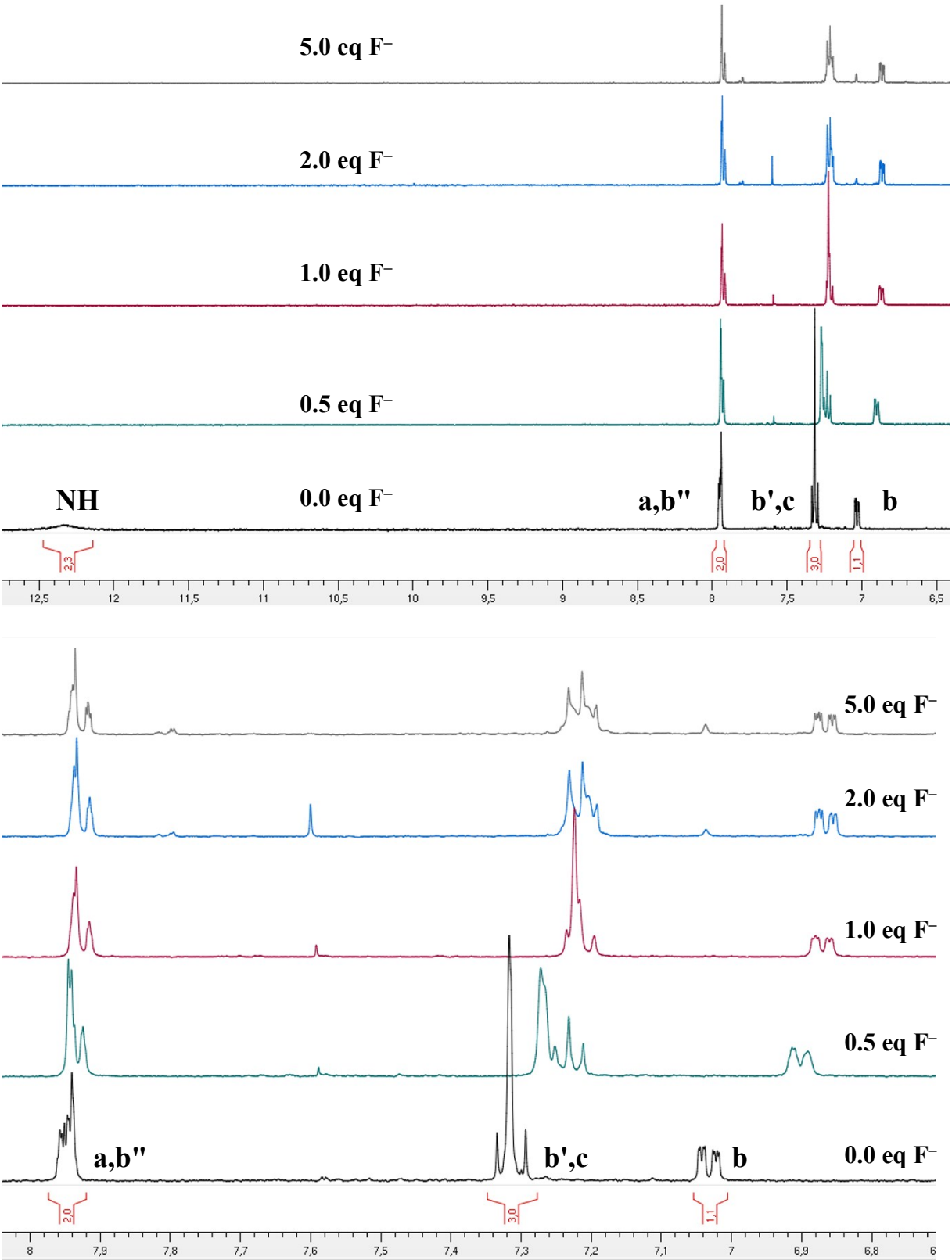


Figure S2: ^{1}H NMR (400 MHz, CD_3CN, 298K) monitoring of reaction between **1b** (5 mM) and increasing amount of *n*-$Bu_4N^+.F^-$ (0, 0.5, 1, 2 and 5 equivalents). Top: spectra in the 13-6 ppm region showing the disappearance of the NH protons. Bottom: spectra in the aromatic region (8-6.5 ppm).

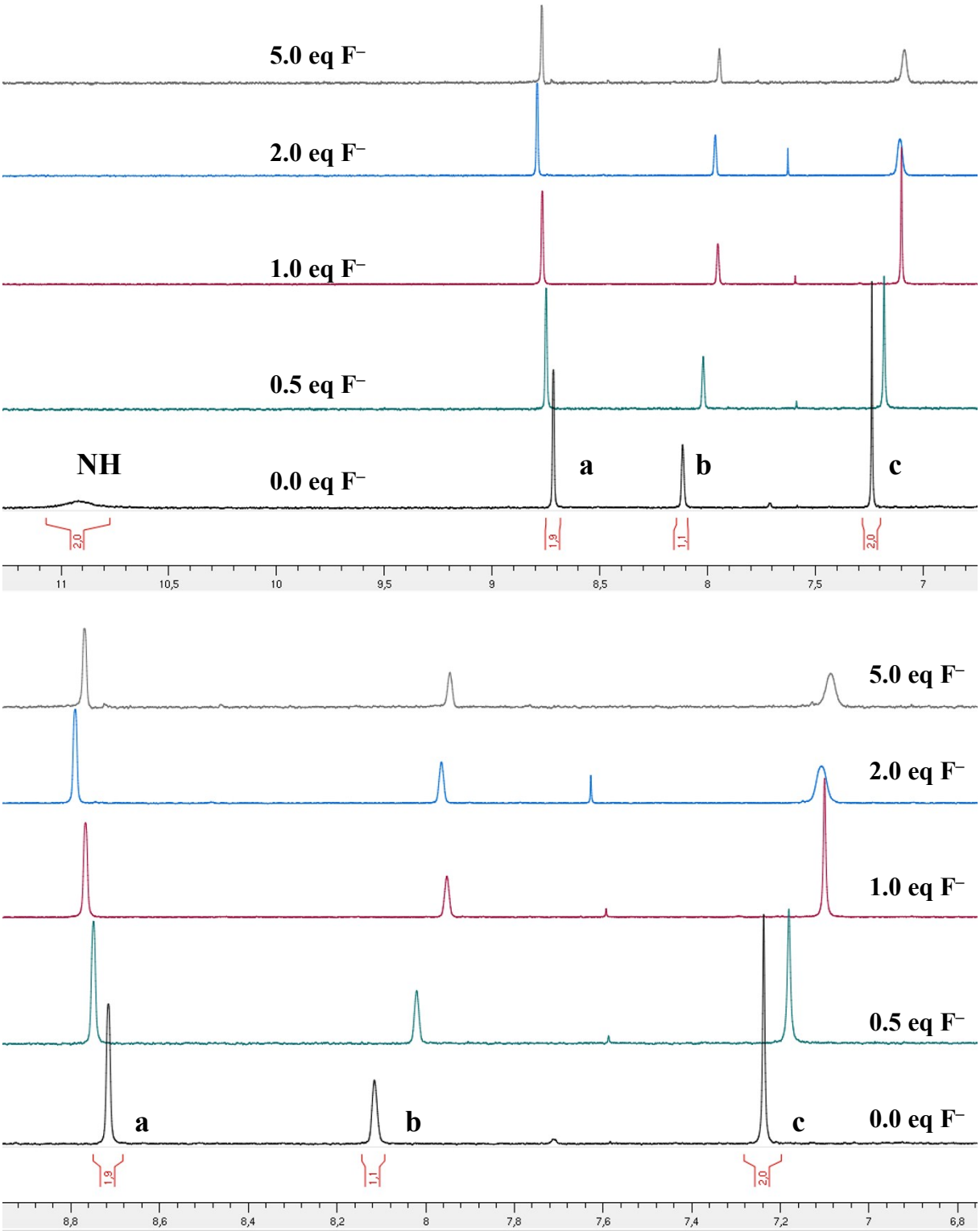


Figure S3: ^{1}H NMR (400 MHz, CD_3CN, 298K) monitoring of reaction between **2a** (5 mM) and increasing amount of *n*-$Bu_4N^+.F^-$ (0, 0.5, 1, 2 and 5 equivalents). Top: spectra in the 11-7 ppm region showing the disappearance of the NH protons. Bottom: spectra in the aromatic region (9-7 ppm).

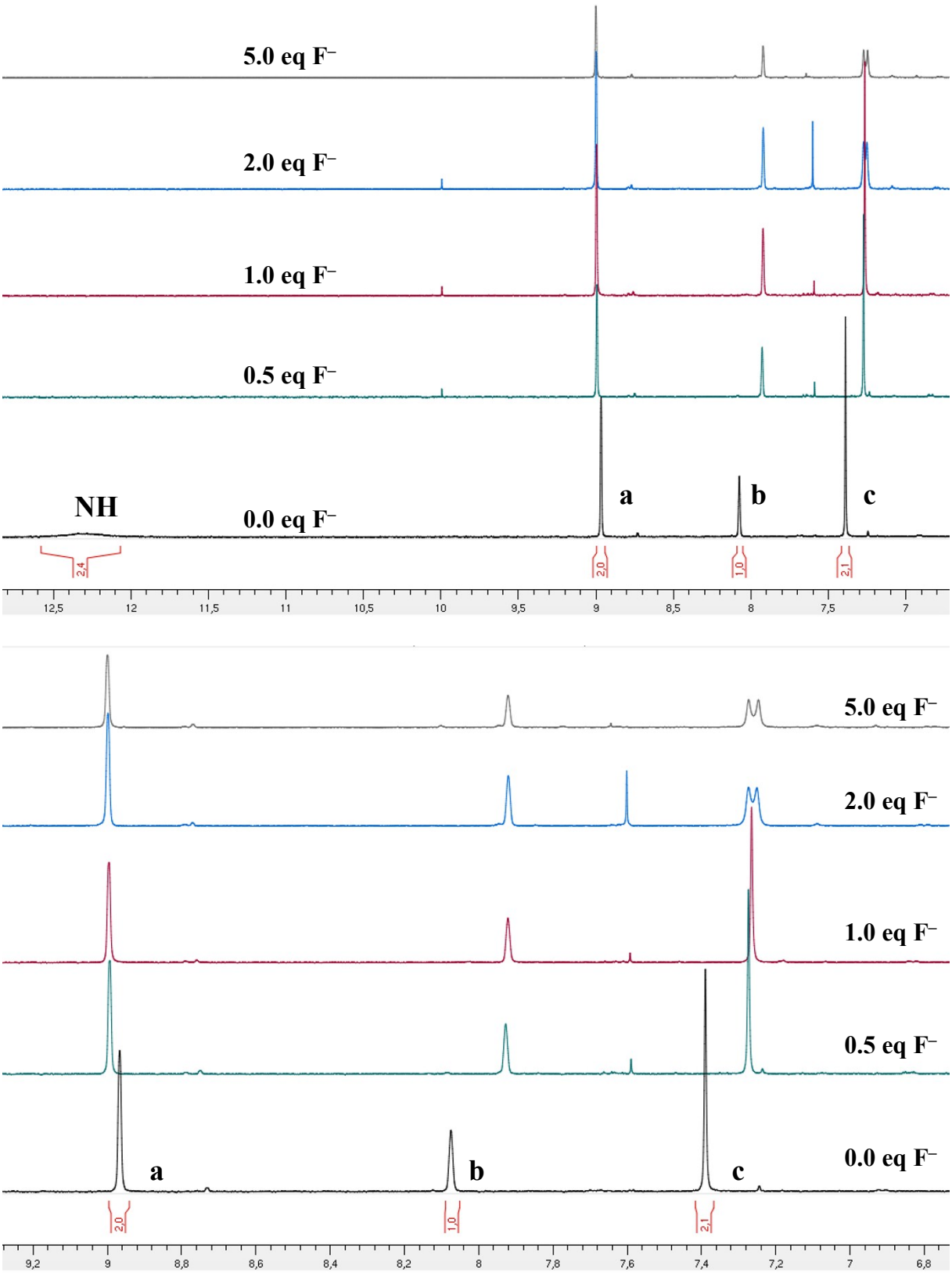


Figure S4: ^{1}H NMR (400 MHz, CD_3CN, 298K) monitoring of reaction between **2b** (5 mM) and increasing amount of *n*-$Bu_4N^+.F^-$ (0, 0.5, 1, 2 and 5 equivalents): (Top) spectra in the 13-7 ppm region, (bottom) spectra in the aromatic region (9-7 ppm).

References

1. CrystalClear-SM Expert 2.1 (Rigaku, Jun 7th **2013**) Software, Version 5.6.2.0, Tokyo, Japan.
2. G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122.
3. L. J. Farrugia, *J. Appl. Cryst*. **1999**, *32*, 837-838
4. S. Koeller, J. Kadota, F. Peruch, A. Deffieux, N. Pinaud, I. Pianet, S. Massip, J.-M. Léger, J.-P. Desvergne, B. Bibal, *Chem. Eur. J.* **2010**, *16*, 4196-4205.
5. a) L. G. Sillen and B. Warnquist, *Ark. Kemi*. **1968**, *31*, 315-339; b) L. G. Sillen and B. Warnquist, *Ark. Kemi*. **1968**, *31*, 377-390; c) J. Havel, Haltafalspefo program, Mazaryle University, Brno, Maravia, Czech Republic.