Lariat ethers with fluoroaryl side-arms: a study of CF…metal cation interaction in the complexes of *N*-(*o*-fluoroaryl)azacrown ethers

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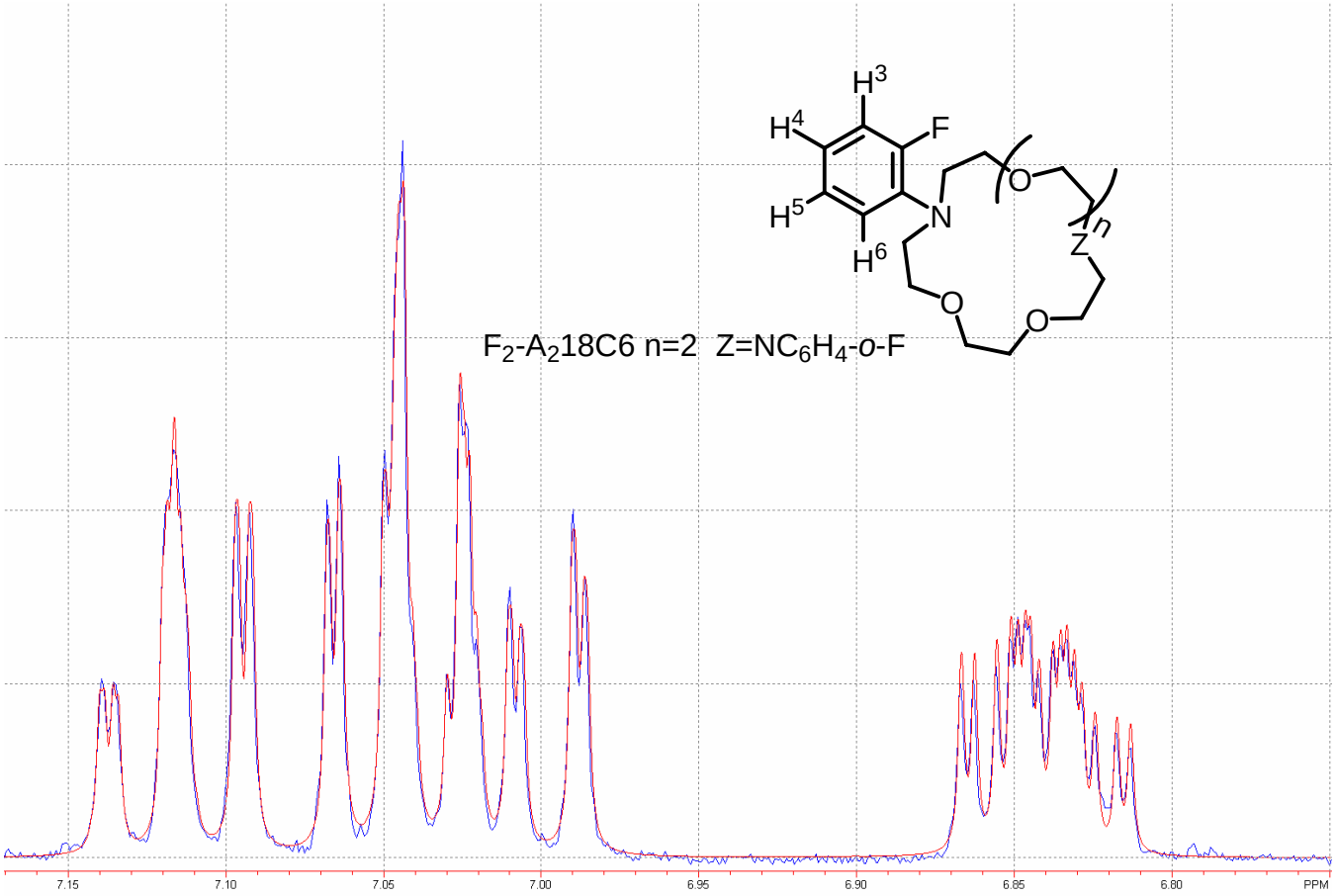
Electronic supplementary information



δ: H^6 (7.115) H^5 (7.048) H^3 (7.015) H^4 (6.841)
$J(H^3,H^4)$=8.1 Hz; $J(H^4,H^5)$=7.3 Hz; $J(H^5,H^6)$=8.1 Hz; $J(H^3,H^5)$=1.5 Hz; $J(H^4,H^6)$=1.6 Hz; $J(H^3,H^6)$=0.4 Hz; $J(H^3,F)$=13.7 Hz; $J(H^4,F)$=4.5 Hz; J(H5,F)=-0.7 Hz ; J(H6,F)=9.2 Hz

Figure S1. Experimental (blue, in acetone-d_6) and simulated (red, with parameters given above) ^{1}H NMR spectra of aromatic protons of F_2-$A_2$18C6. Simulation performed with WinNuts program.

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Solvent	Acetone	***Sweep Width (Hz)***	(4000.00, 4000.00)		

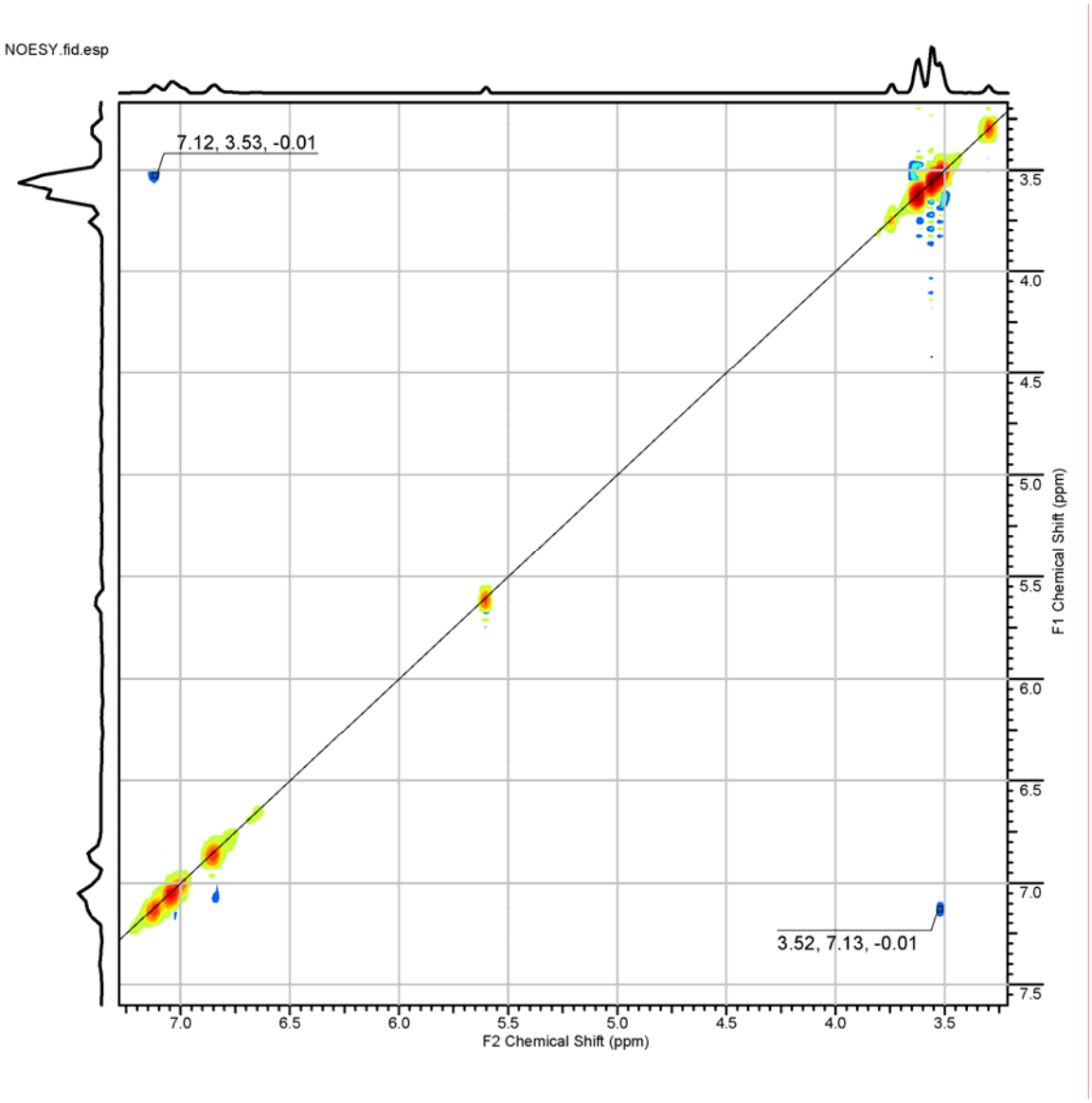

Figure S2. 2D NOESY spectrum of F_2-$A_2$18C6 (acetone d_6). Cross-peaks observed between a triplet at 7.12 ppm and a triplet at 3.52 ppm allow to assign these signals to protons H^6 and NCH_2, respectively.

Acquisition Time (sec)	(0.1280, 0.0320)	***Comment***	F3A3 NOESY	***Date***	23 Sep 2008 10:55:00
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Solvent	Acetone	***Sweep Width (Hz)***	(4000.00, 4000.00)		

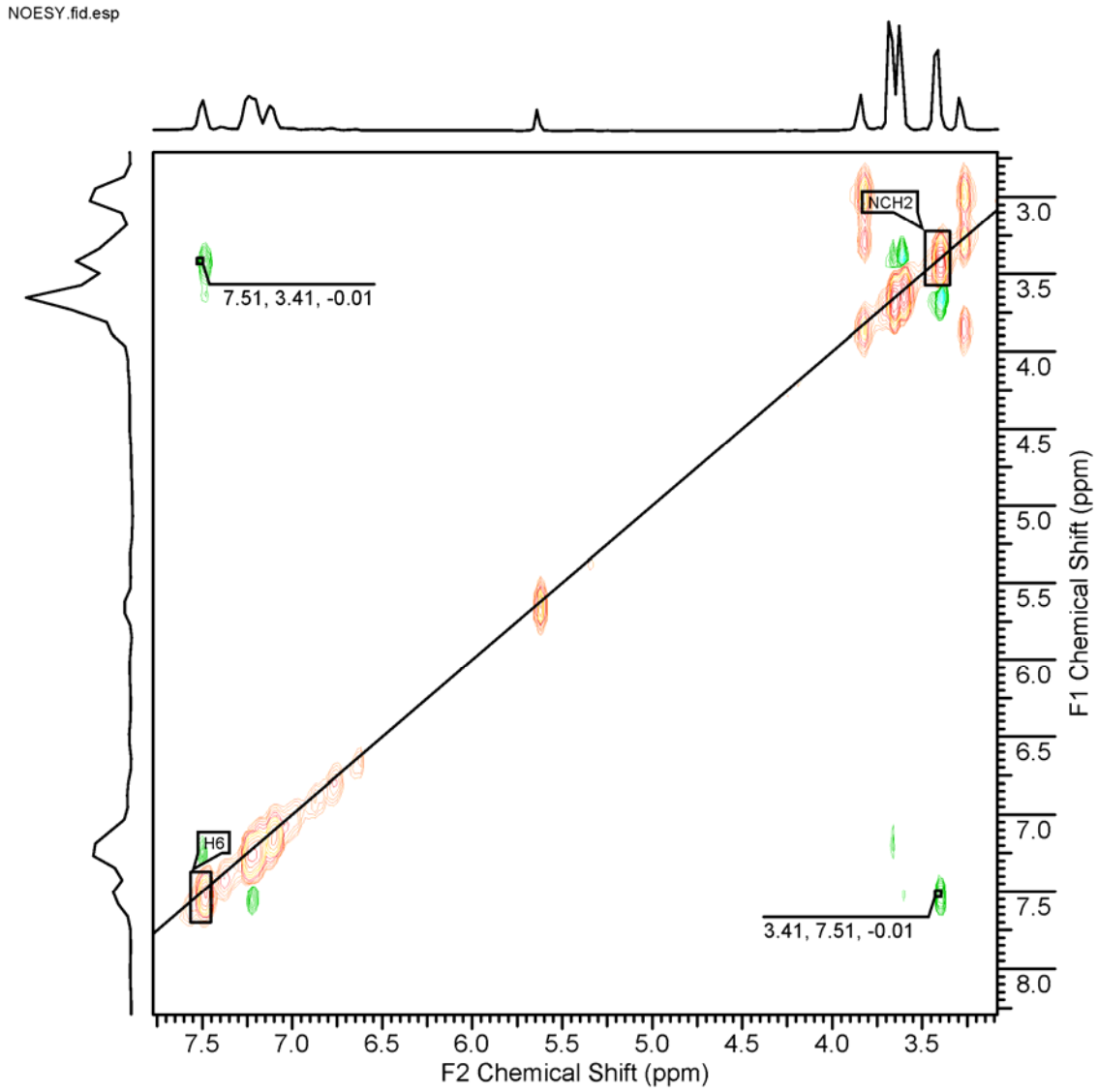

Figure S3. 2D NOESY spectrum of the Na^+ complex of F_2-$A_2$18C6 (acetone d_6, 3 equiv. NaI). Cross-peaks observed between a triplet at 7.51 ppm and a triplet at 3.41 ppm allow to assign these signals to protons H^6 and NCH_2, respectively.

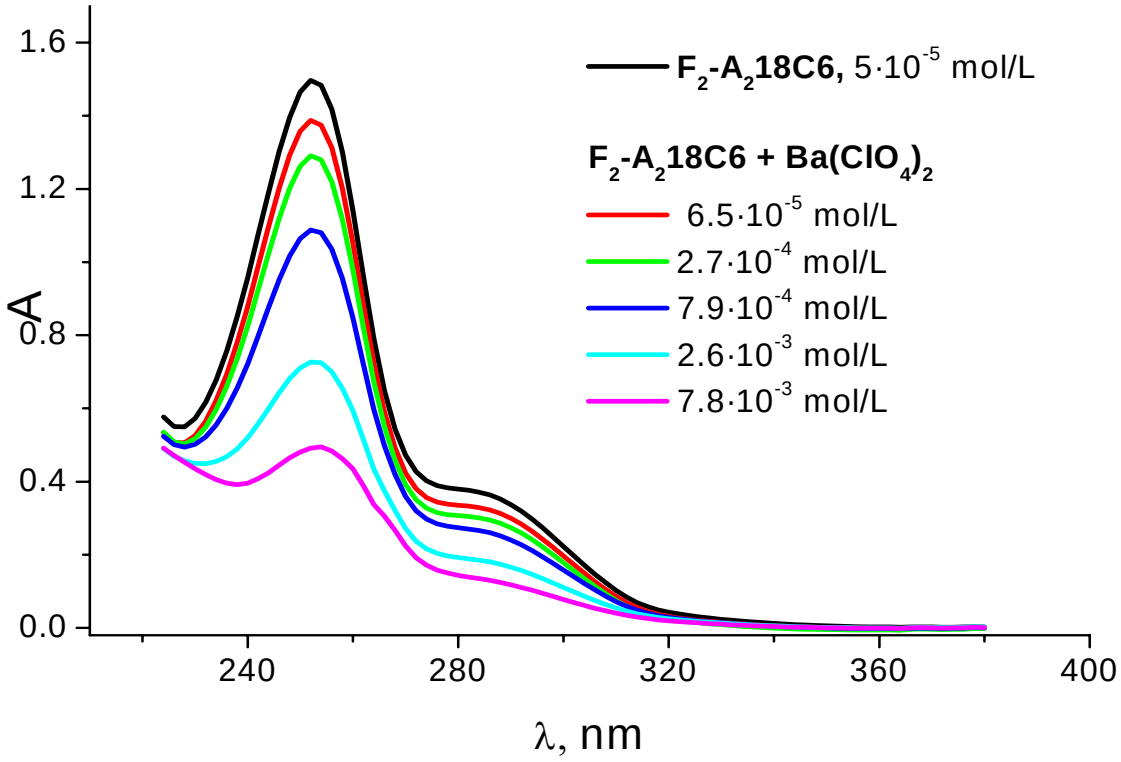

Figure S4. UV-spectra of F_2-$A_2$18C6 ($5\cdot10^{-5}$ mol/L , methanol, 22°C) as a function of $Ba(ClO_4)_2$ concentration.

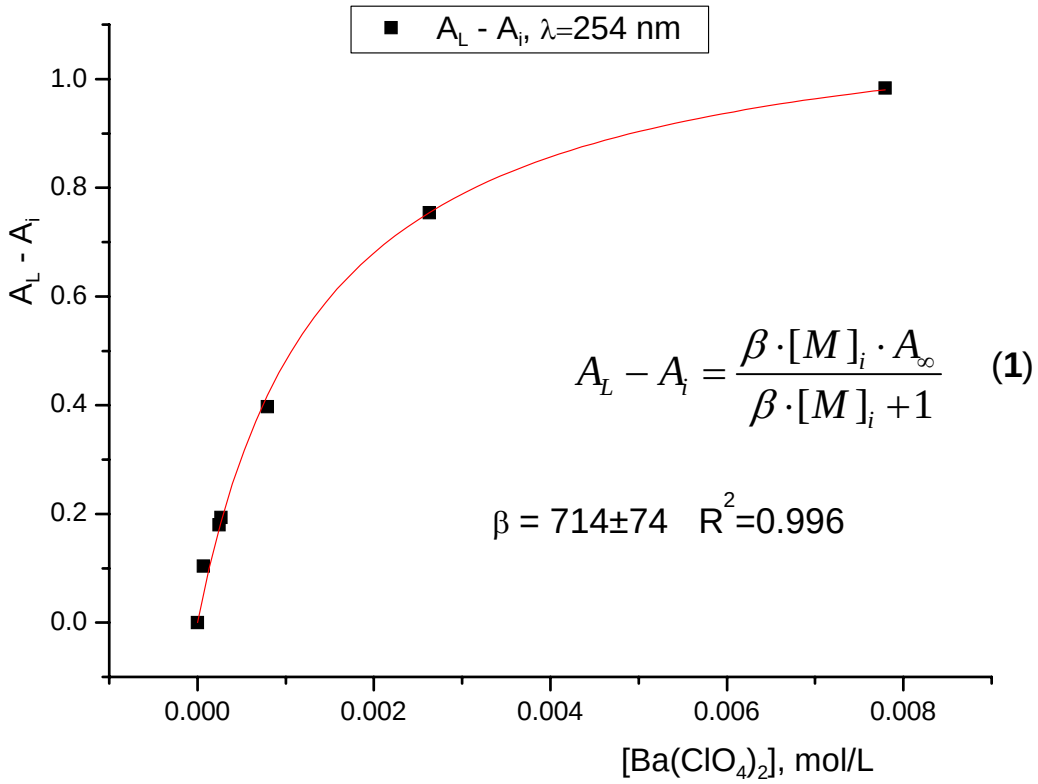

Figure S5. The dependence of the absorbance of F_2-$A_2$18C6 (at 254 nm) on the concentration of $Ba(ClO_4)_2$ (methanol, 22°C) and its fitting to equation (**1**).
A_L is the absorbance of the starting ligand solution, $[M]_i$ is the molar concentration of the metal salt, metal binding constant (β) and the absorbance of the complex (A_∞) are the objective variables.