Supplementary Material (ESI) for New Journal of Chemistry

Viologen based redox switchable anion binding receptors

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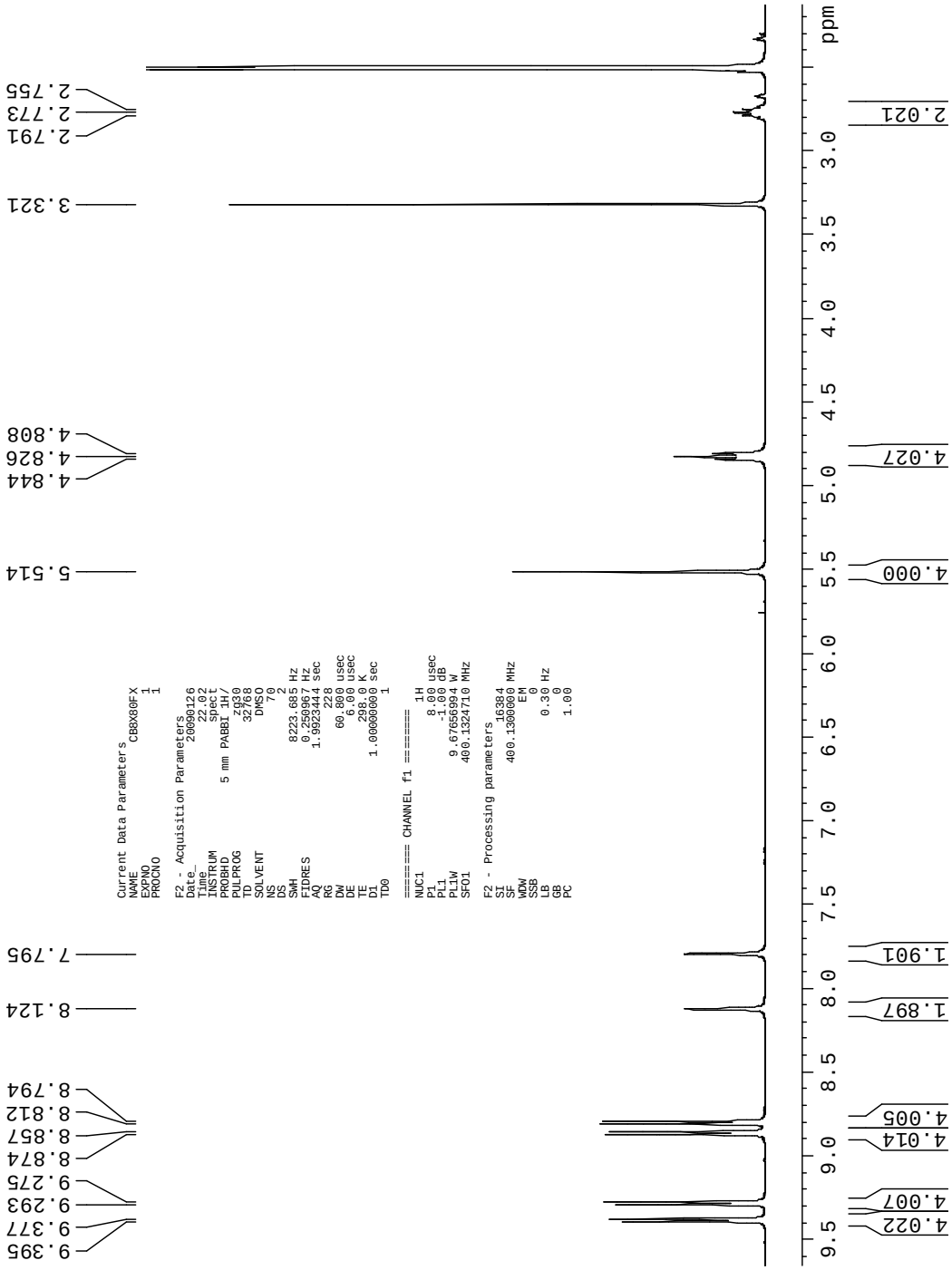
1. RMN ^{1}H spectrum of 2·$(PF_6)_4$ (DMSO d^6)



2. COSY ^{1}H-^{1}H map of 2 (PF_6)$_4$ (DMSO d^6)

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EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
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Time_                   22.06
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PULPROG              cosygpqf
TD                       2048
SOLVENT                  DMSO
NS                          4
DS                          8
SWH                  3472.222 Hz
FIDRES               1.695421 Hz
AQ                   0.2949620 sec
RG                         228
DW                   144.000 usec
DE                     6.00 usec
TE                     298.0 K
D0                   0.00000300 sec
D1                   1.35213399 sec
D13                  0.00000400 sec
D16                  0.00020000 sec
IN0                  0.00028800 sec

======== CHANNEL f1 ========
NUC1                        1H
P0                     8.00 usec
P1                     8.00 usec
PL1                    -1.00 dB
PL1W                 9.67656094 W
SFO1                400.1322935 MHz

===== GRADIENT CHANNEL =====
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GPZ1                   10.00 %
P16                  1000.00 usec

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SW                   8.678 ppm
FnMODE                      QF

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WDW                       SINE
SSB                          0
LB                    0.00 Hz
GB                           0
PC                        1.40

F1 - Processing parameters
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LB                    0.00 Hz
GB                           0
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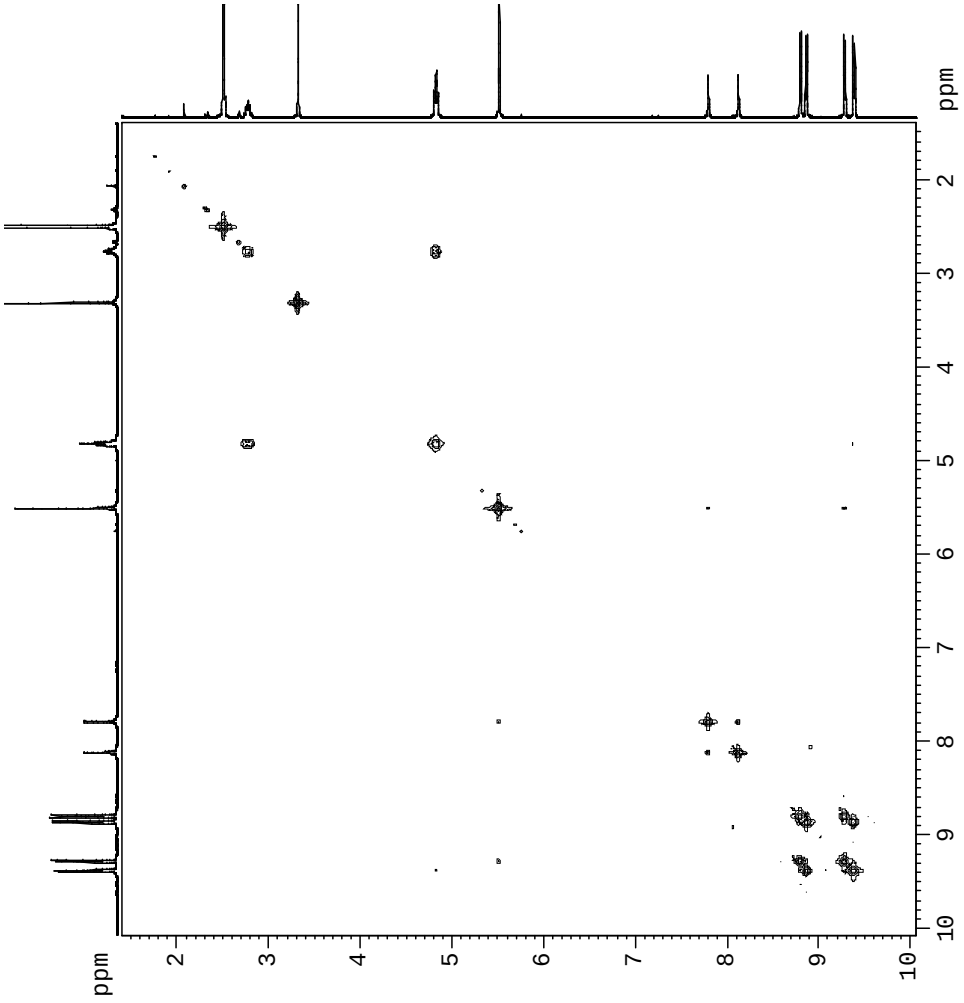
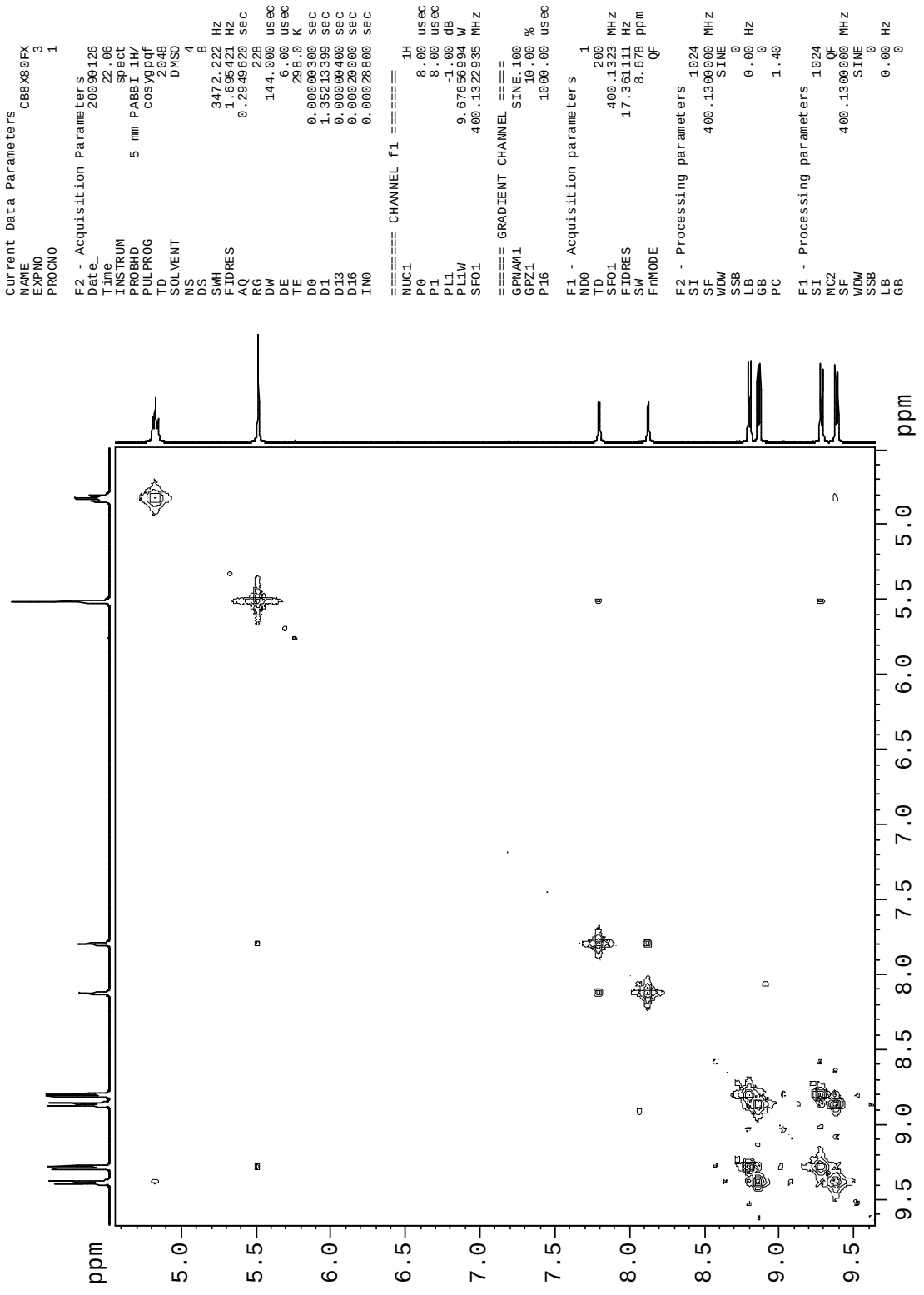
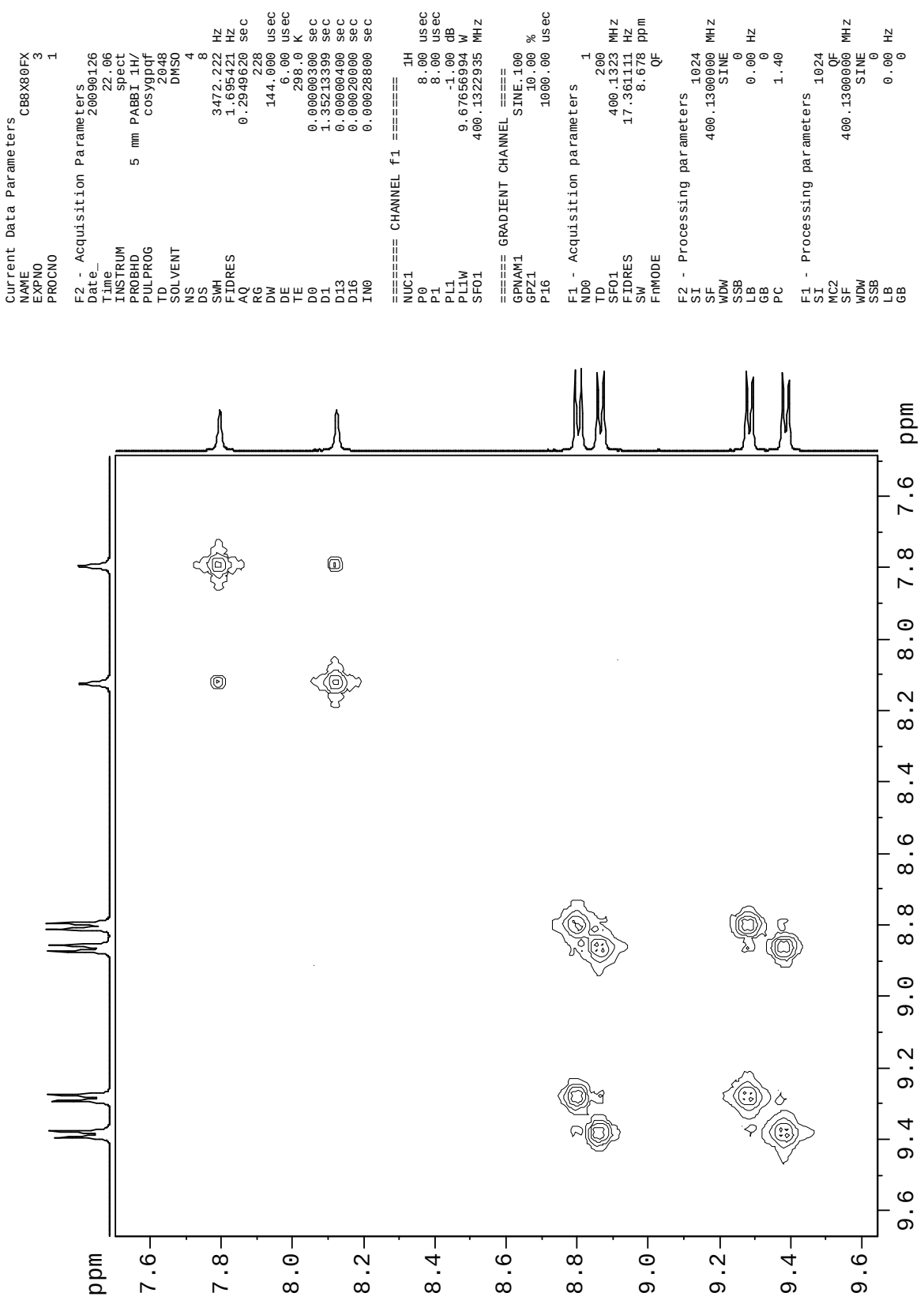


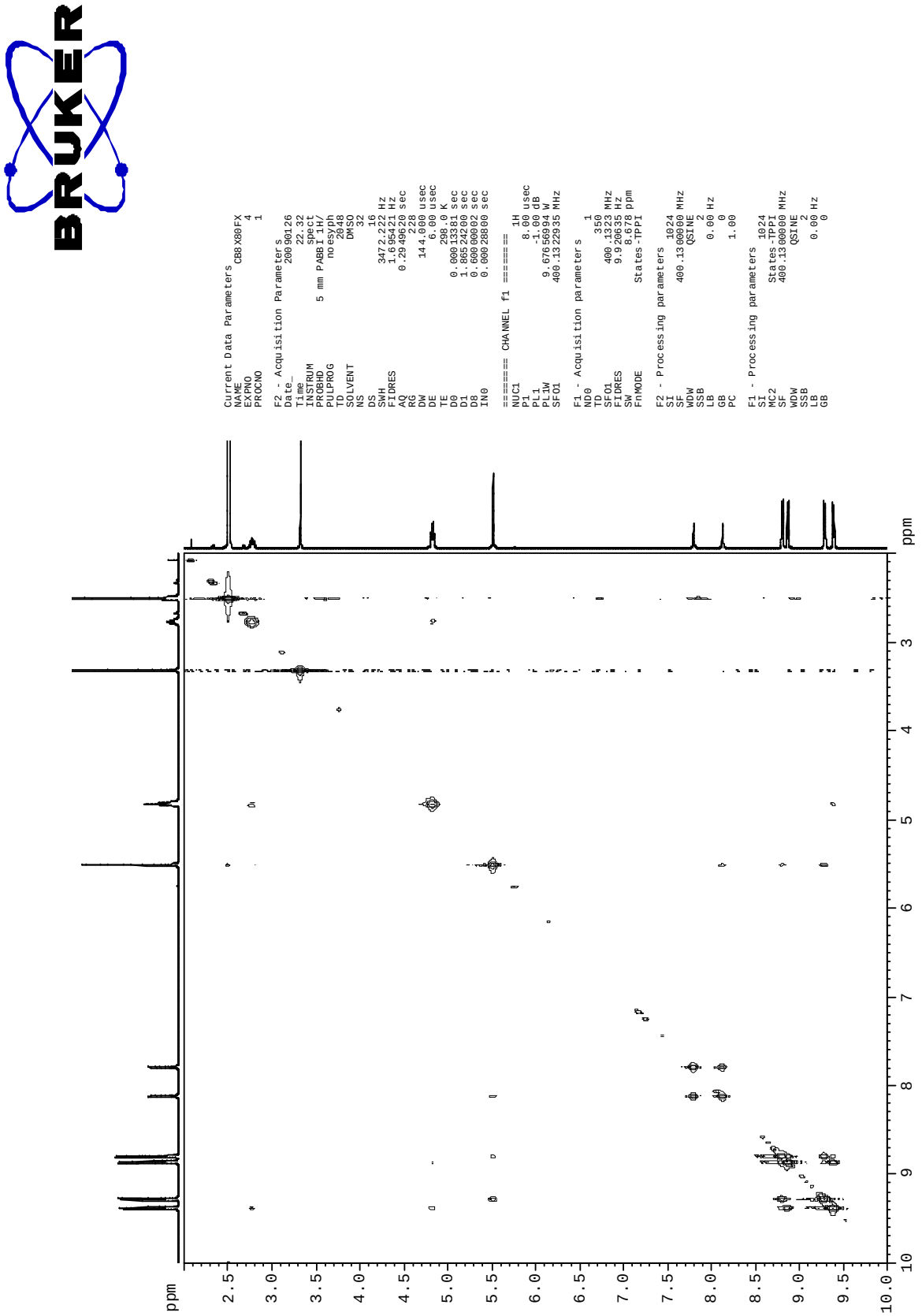
3. COSY ^{1}H-^{1}H map of 2 (PF_6) (DMSO d^6)



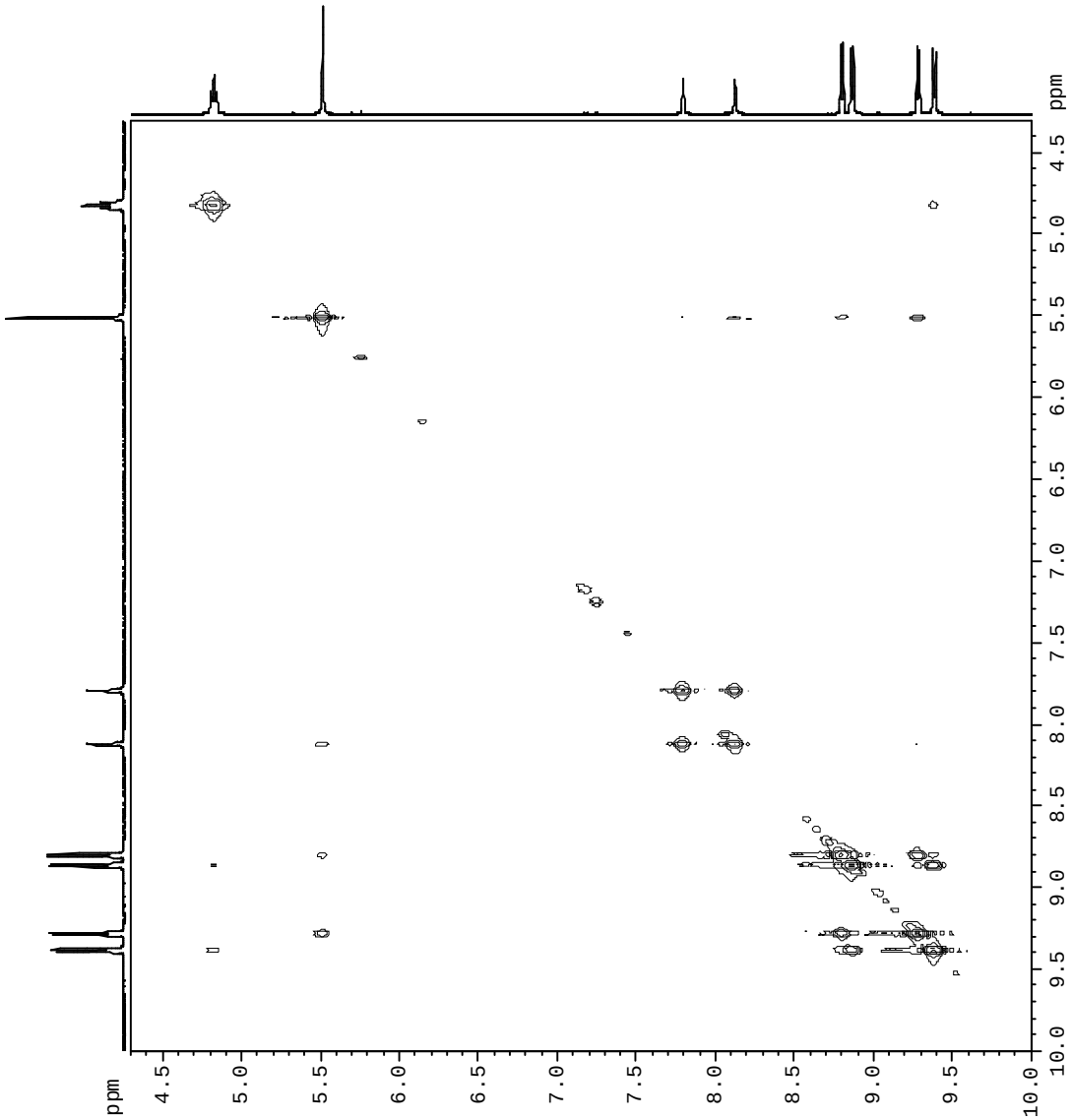
4. COSY ^{1}H-^{1}H map of $2\cdot(PF_6)_4$ (DMSO d^6)



5. NOESY ^{1}H-^{1}H map of 2·$(PF_6)_4$ (DMSO d^6)



6. NOESY ^{1}H-^{1}H map of 2·$(PF_6)_4$ (DMSO d^6)



7. NMR titration of of 1·$(PF_6)_2$ with TBA.Cl

(8 mM, 300 mHz, DMSO d^6, 2% D_2O)

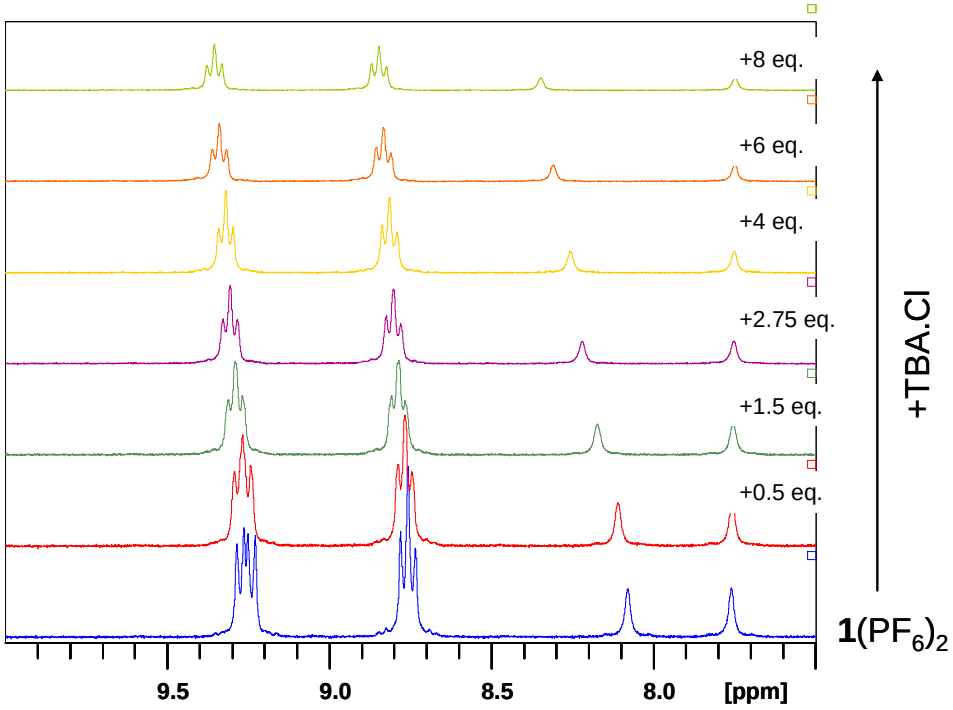
1-determination of the binding constant from Δδ(NHa) = f ($C_{Chloride}$)

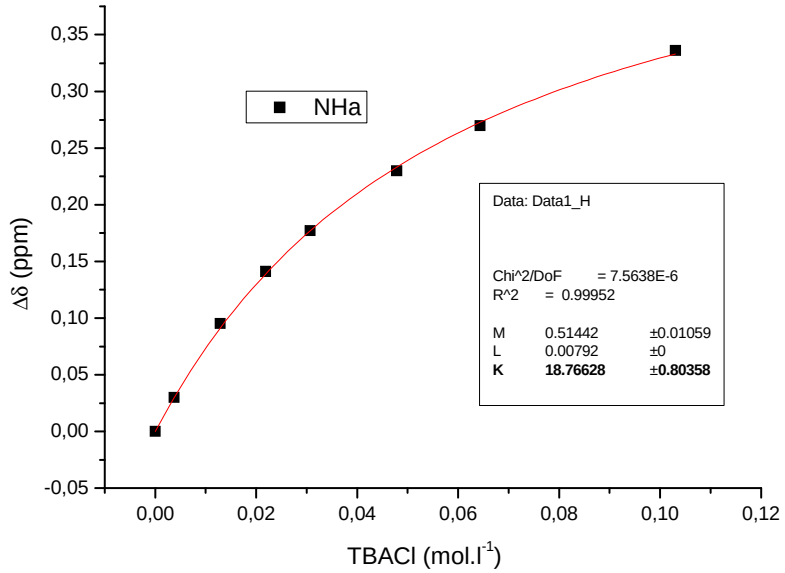
According to the equilibrium

L + S = LS

$\Delta\delta=(\Delta\delta_{max} /(2*L))*((L+S+(1/K))-(sqrt(((L+S+(1/K))^2)-4*L*S)))$

With L : total concentration in L
S : total concentration in S
K : binding constant
$\Delta\delta = \delta_{obs}-\delta_0$





8. NMR titration of of $1\cdot(PF_6)_2$ with TBA.Br

(8 mM, 300 mHz, DMSO d^6, 2% D_2O)

determination of the binding constant from $\Delta\delta(NHa) = f(C_{Chloride})$

According to the equilibrium

L + S = LS

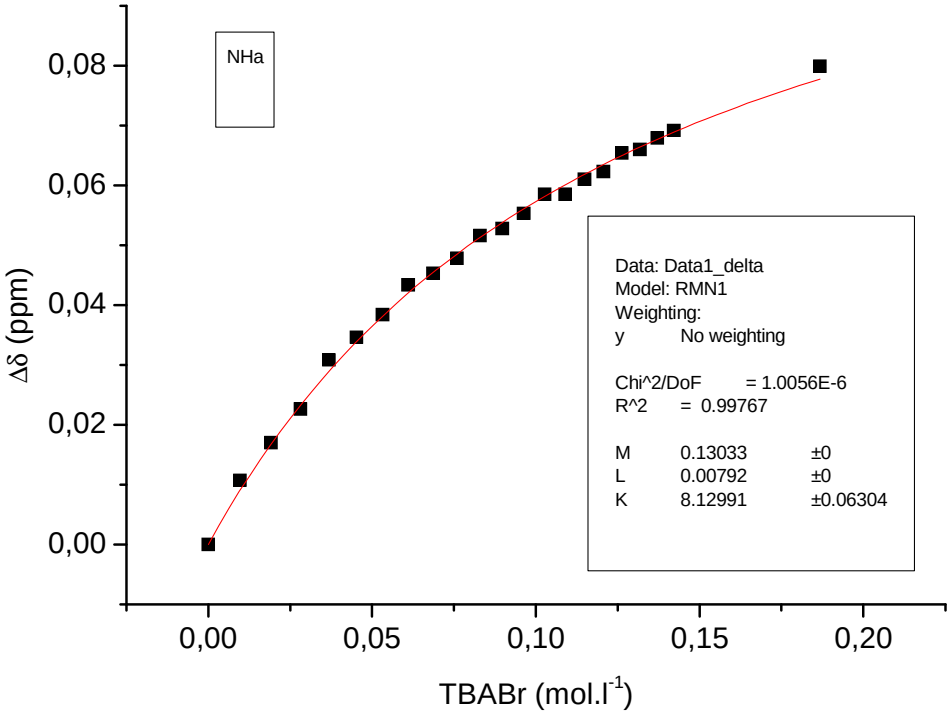
$\Delta\delta=(\Delta\delta_{max} /(2*L))*((L+S+(1/K))-(sqrt(((L+S+(1/K))^2)-4*L*S)))$

With L : total concentration in L

S : total concentration in S

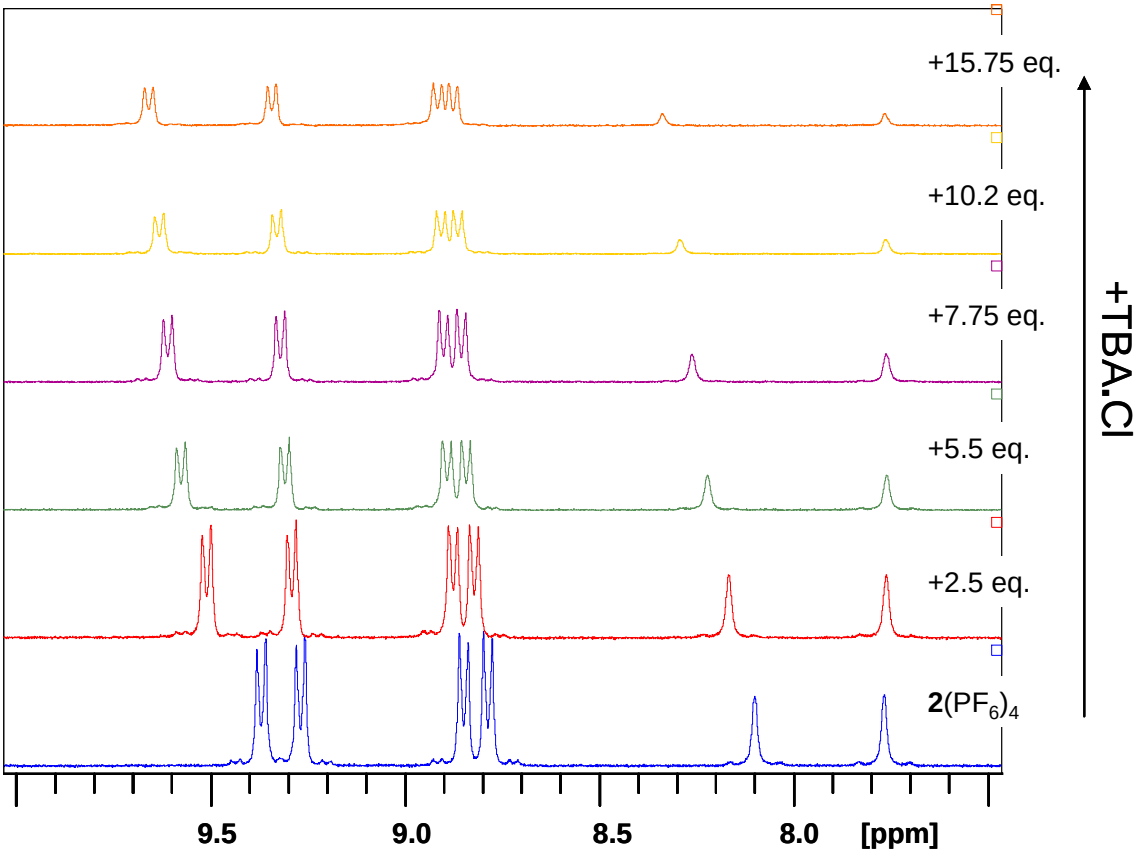
K : binding constant

$\Delta\delta = \delta_{obs}-\delta_0$



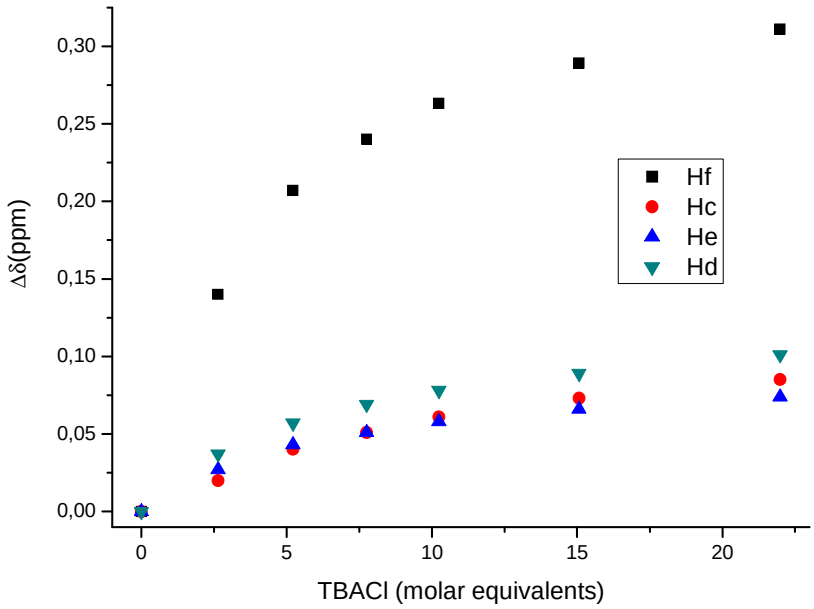
9. NMR titration of of 2·$(PF_6)_4$ with TBA.Cl

(3.9 mM, 300 mHz, DMSO d6, 2% D_2O)



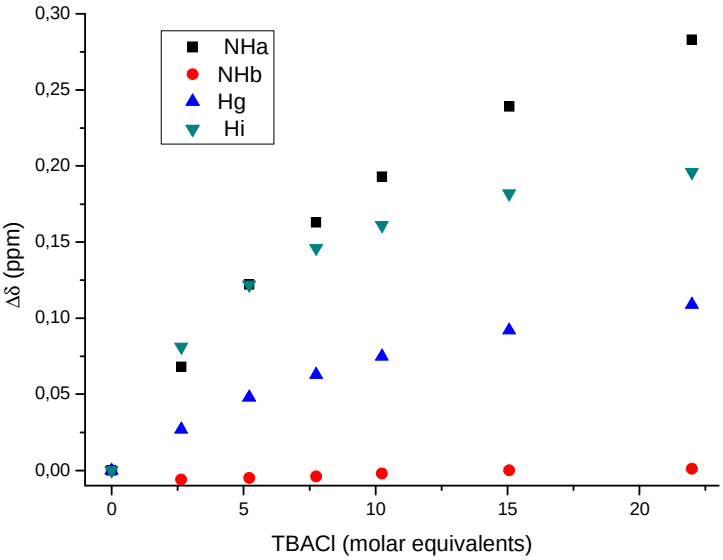
10. NMR titration of of 2·$(PF_6)_4$ with TBA.Cl _Shift of Hf, Hc, He, Hd

(3.9 mM, 300 mHz, DMSO d^6, 2% D_2O)



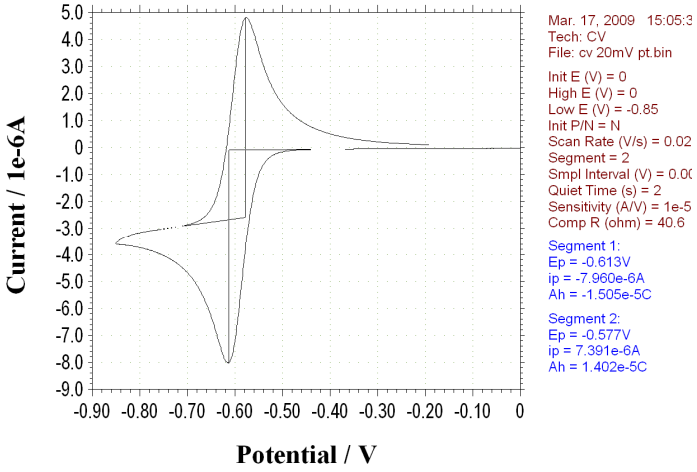
11. NMR titration of of 2-(PF$_6$)4 with TBACl – Shift of Hi, Hg, Ha, Hb

(3.9 mM, 300 mHz, DMSO d^6, 2% D_2O)

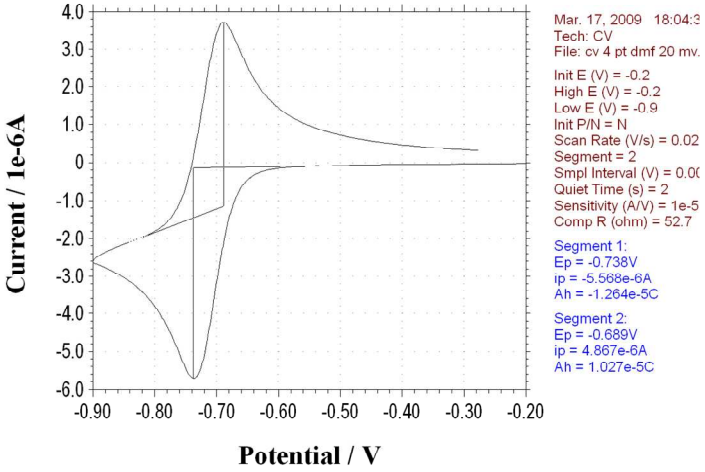


12. Cyclic voltammograms of $2.(PF_6)_4$

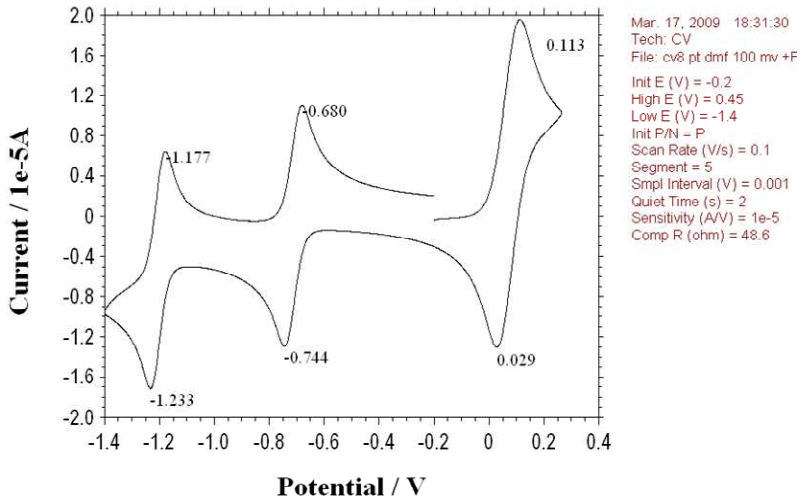
10A→ (10^{-3} M, **20mV/s,** Pt Ø=2 mm, CD_3CN 0.1 $MTBAPF_6$)



10B→ **(10^{-3} M, 20mV/s, Pt Ø=2 mm, DMF 0.1 $MTBAPF_6$)**

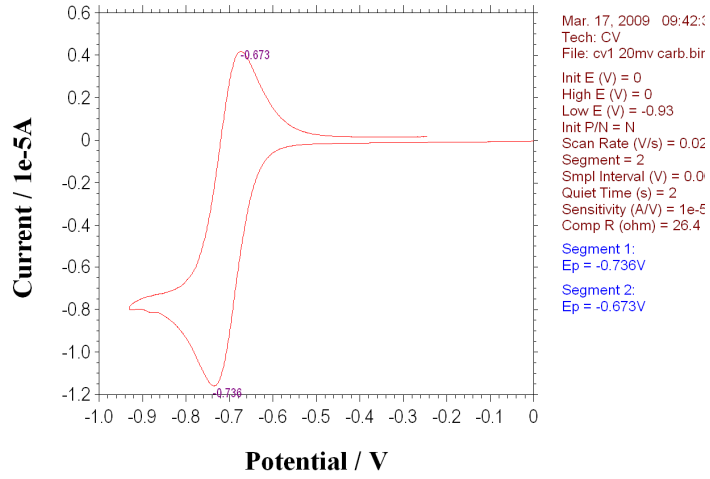


10C→ **(10^{-3}M + Ferrocene as int. ref., 100mV/s, Pt Ø=2 mm, DMF 0.1 $MTBAPF_6$)**

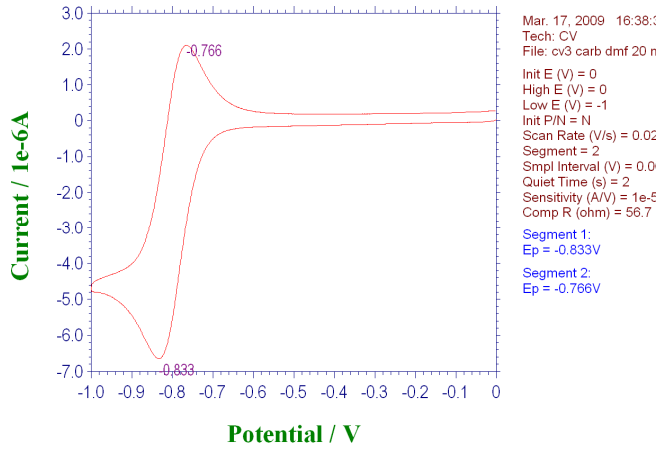


13. Cyclic voltammograms of 1.$(PF_6)_2$

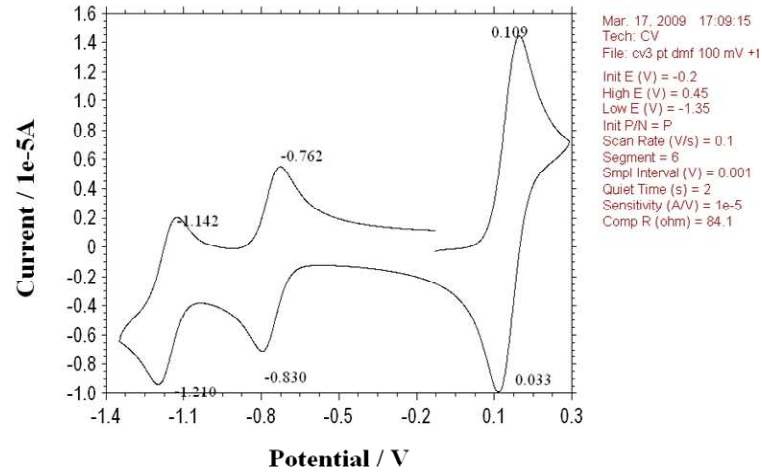
11A→ (10^{-3} M, Pt Ø=2 mm, 20mV/s, CD_3CN 0.1 MTBAPF_6)



11B→ (10^{-3} M, CV Pt Ø=2 mm, 20mV/s, DMF 0.1 MTBAPF_6)

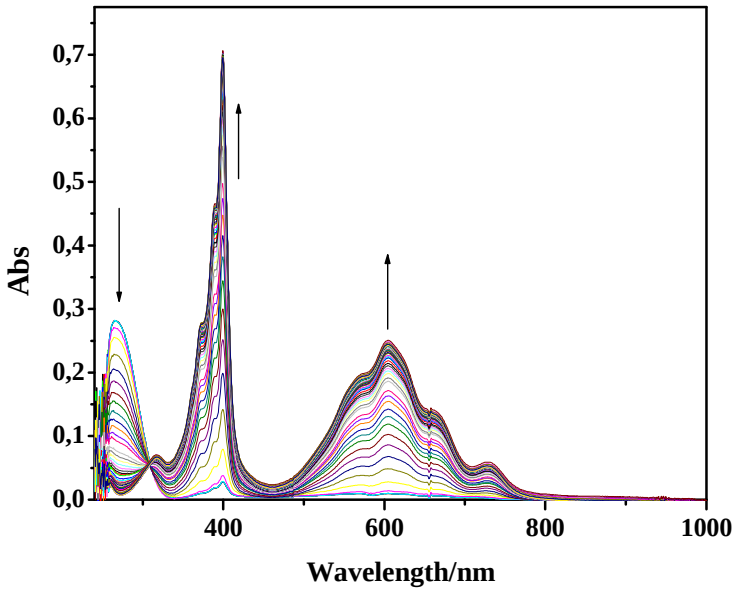


11C→ (10^{-3}M + Ferrocene as int. ref., 100mV/s, Pt Ø=2 mm, DMF 0.1 MTBAPF_6)



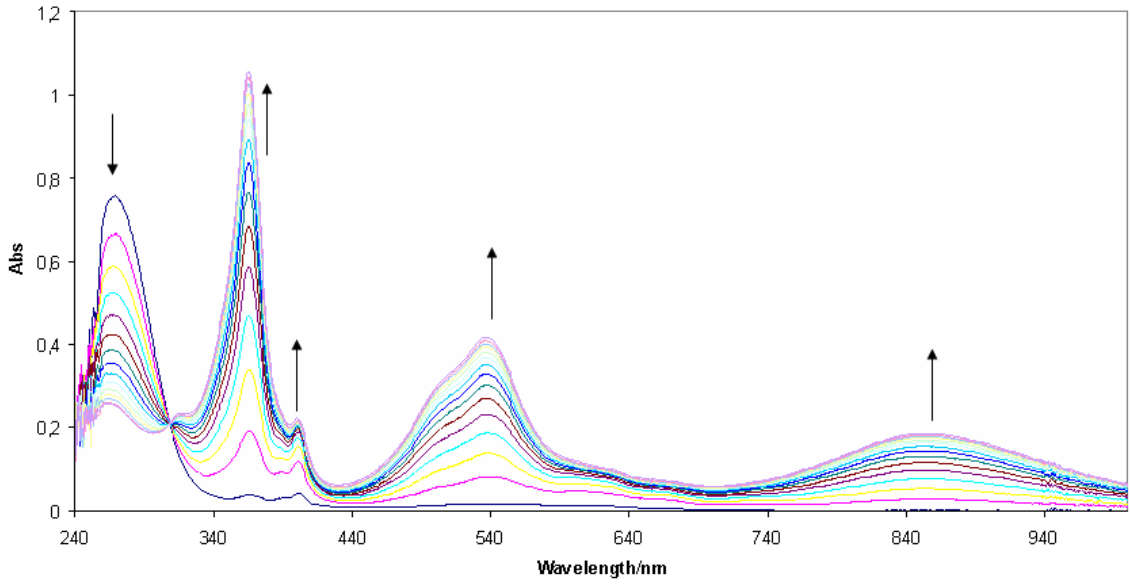
14. Spectroelectrochemistry experiment carried out with 1.$(PF_6)_2$

Evolution of the UV-vis abs. spectum during the 1e⁻ reduction of 1.$(PF_6)_2$ at – 1.0 V (*E* vs Ag/Ag^+, 2.5×10^{-4} M, V= 25 mL DMF 0.1 M TBAP**)**. Spectra were recorded at ca. 10 s intervals . Arrows indicate the directions of absorbance change



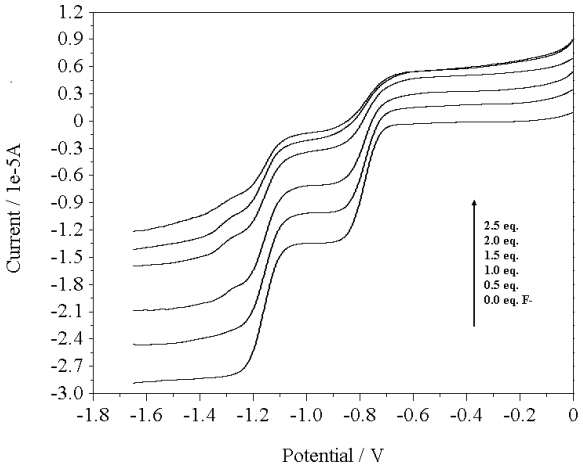
15. Spectroelectrochemistry experiment carried out with 2.$(PF_6)_4$

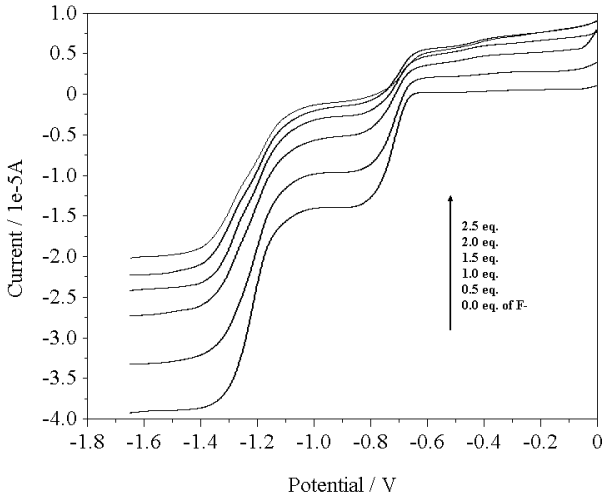
Evolution of the UV-vis abs. spectum during the 2e⁻ reduction of 2.$(PF_6)_4$ at – 1.0 V (*E* vs Ag/Ag^+, 2.5×10^{-4} M, V= 25 mL DMF 0.1 M TBAP**)**.
Spectra were recorded at ca. 10-s intervals .

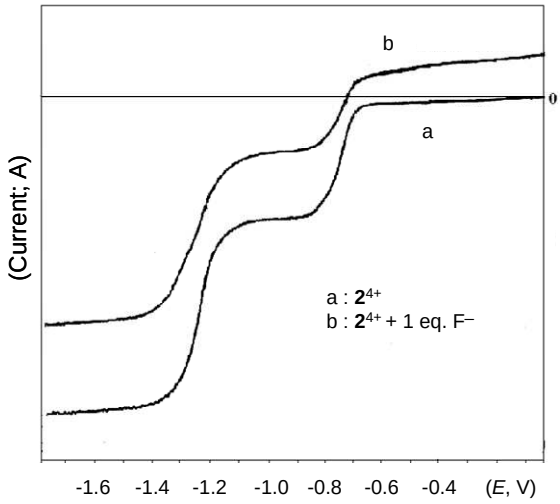


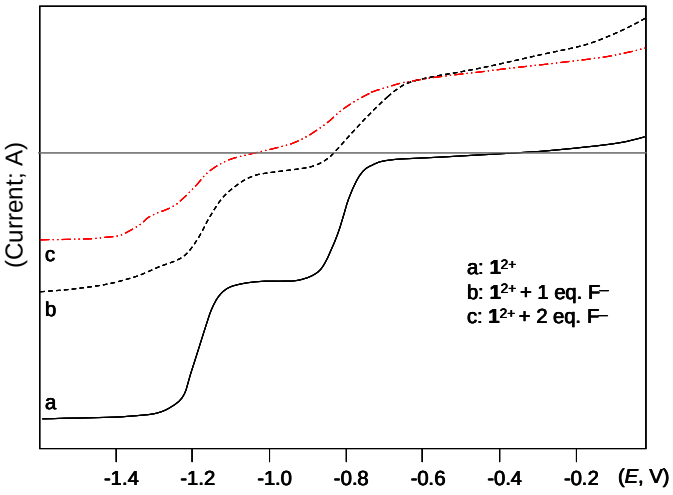
16. RDE experiments carried out with $2.(PF_6)_4$ and $1.(PF_6)_4$ in presence of Fluoride

Rotating disc measurements conducted in glove box on (left) $1.(PF_6)_4$ and (right) $2.(PF_6)_4$ in DMF at 1×10^{-3} M in presence of increasing amounts of fluoride (TBAF).





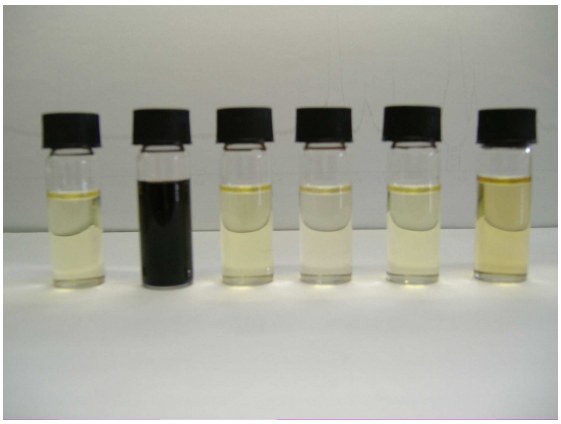


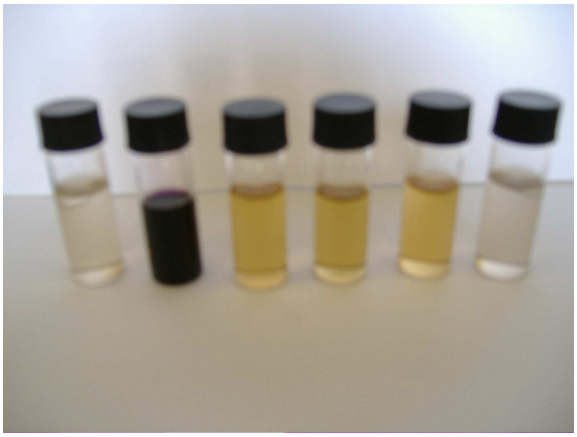


17. UV-Visible changes observed with 2.$(PF_6)_4$ and 1.$(PF_6)_4$ in presence of Fluoride

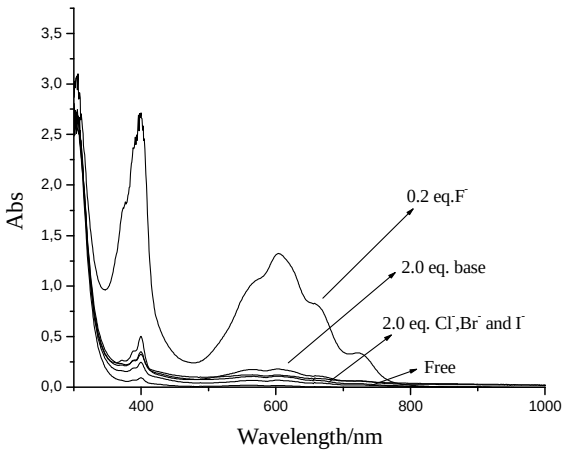
15A→ Color changes observed before and after addition of 0.2 equiv. of F^- or 2 equiv. of representative anions or base in DMF solutions of the receptors (R) and 1.$(PF_6)_4$ or 2.$(PF_6)_4$ (1mM, Argon atm) (from the left to the right: R, R+F^-, R+Cl^-, R+Br^-, R+I^-, R+Di-isopropylamine)

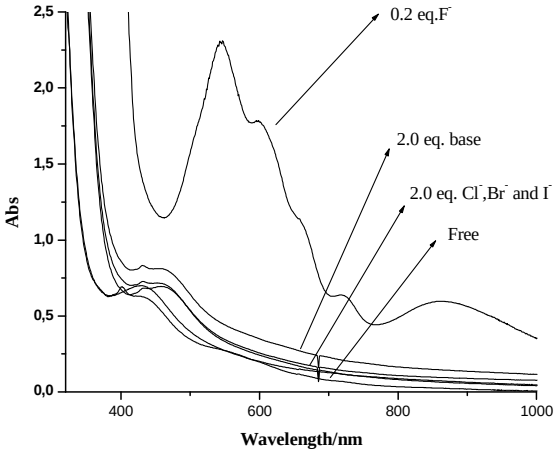
1.$(PF_6)_4$ **2.$(PF_6)_4$**





15B→ **Changes in the** Absorption spectrum of 2.$(PF_6)_4$ and 1.$(PF_6)_4$ (1mM) in DMF under argon atmosphere upon addition of various amounts of tetra-n-butylammonium salts of F^- (0.2 equiv.) or Cl^-, Br^-, I^- and Di-isopropylamine (2 equiv.).





18. Computational Details

The quantum chemistry calculations were carried out with both the CP2KQuickStep program and the Gaussian03[1] program. With this latter code, we used the BLYP, B3LYP[2], B3LYP-CP[3] (Corrected Potential) and MP2[4] functional with the 6-31+G(d,p)[5] basis sets.

Solvent effects have been evaluated using the polarizable continuum model (PCM)[6] in which the cavity is created via a series of overlapping spheres.

The *ab initio* Born-Oppenheimer dynamics calculations were performed using the CP2K- QuickStep program[7] at the DFT level with the BLYP[8] + D[9] functional. QuickStep is an implementation of the Gaussian Plane Waves (GPW) method based on the Kohn- Sham formulation of the density functional theory (DFT). It is a hybrid method using a linear combination of Gaussian-type orbitals to describe the Kohn-Sham orbitals, whereas an auxiliary plane waves basis set is employed to expand the electronic charge density.

The basis set used was a double-ζ valence set of Gaussian orbitals[10] in conjunction with the Goedecker-Teter-Hutter[11] pseudopotentials. The auxiliary PW basis set was defined by a cubic box of 25 $Å^3$ and by a density cutoff of 360 Ry.

Metadynamics[12] has been used to overcome the problem of observing rare events in conventional molecular dynamics and determining the energy barrier of our system. The method consist in a series

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1 M. J. Frisch et all ; Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, **2004**.

2 Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648

3 Gino A. DiLabio; *Chem. Phys. Lett.* , **2008**,455, 348-353

4 C. Moller and M. S. Plesset, *Phys. Rev*. **1934**, 46, 618

5 (a) M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* , **1984**, 80, 3265 ; (b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comp. Chem.* , **1983**, 4, 294

6 (a)M. T. Cancès, B. Mennucci, and J. Tomasi, *J. Chem. Phys.* **1997**,107, 3032; (b) M. Cossi, V. Barone, B. Mennucci, and J. Tomasi, *Chem. Phys. Lett.* **1998**,286, 253; (c) B. Mennucci and J.Tomasi, *J. Chem. Phys.* **1997**, 106, 5151; (d) M. Cossi, G. Scalmani, N. Rega, and V. Barone*, J. Chem. Phys.* **2002**, 117, 43

7 (a) CP2K, http://cp2k.berlios.de, 2000-2009. (b) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing T.; Hutter, J. *Comput. Phys. Commun.* **2005**, *167*, 103.

8 (a) Becke, A. D. *Phys Rev. A* **1988**, *38*, 3098. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

9 S. Grimme; *J. Comput. Chem.* , **2006**, 27, 1787-1799

10 VandeVondele, J.; Hutter, J. *J. Chem. Phys.* ,**2007**, 127, 114105

11 (a)Goedecker, S.; Teter, M.; Hutter, *J. Phys. Rev. B* **1996**, *54*, 1703. (b) Hartwigsen et all., *J. Phys. Rev. B* **1998**, 58, 3641 (c) Krack, M. THEORETICAL CHEMISTRY ACCOUNTS, **2005**, 114 (1-3), 145-152

12 A. Laio and M. Parrinello *Proc. Natl Acad. Sci. USA*, **2002**, 99, 12562–6 (b) A. Laio and F. L. Gervasio *Rep. Prog. Phys*. **2008**, 71, 126601 (c) C. Michel, A. Laio, F. Mahomed, M. Krack, M. Parrinello and A. Milet, *Organometallics* **2007,** *26*, 1241-1249

of small repulsive Gaussian potentials, centered on the values of some collective variables, added during the dynamics, preventing the system from revisiting the same points in configurational space and creating a historydependent multidimensional biasing potential. A time step of 1 fs is used for the dynamics, and the deposition rate of the hills is every τ_G=20 fs. The height (w) and with (δs) of the Gaussians-shaped potential hills added are 0.6 kcal/mol and 1 Bohr respectively.

In the present study, we considered distances R1 and R2 as collective variables. The definition of R1 and R2 can be seen in the figure 1. Velocity rescaling algorithm was used to enforce the system to a given temperature T, of 300 Kelvin. The Hydrogen atoms are changed to Deuterium in conjunction with integration step of 1 fs. The duration of our simulation is approximately 5 ps of Metadynamics and after 3 ps the system starts to opening. This is clearly emphasized by the variation of the collective variable R1 showed in the figure 2.

The free energy surface F(**S(R)**) is then reconstructed on a 100 × 100 grid in the (1.052Å < R1 < 6.843Å) × (1.362Å < R2<16.560Å) region with an integration step of 0.111Å and 0.290Å respectively see figure 3.

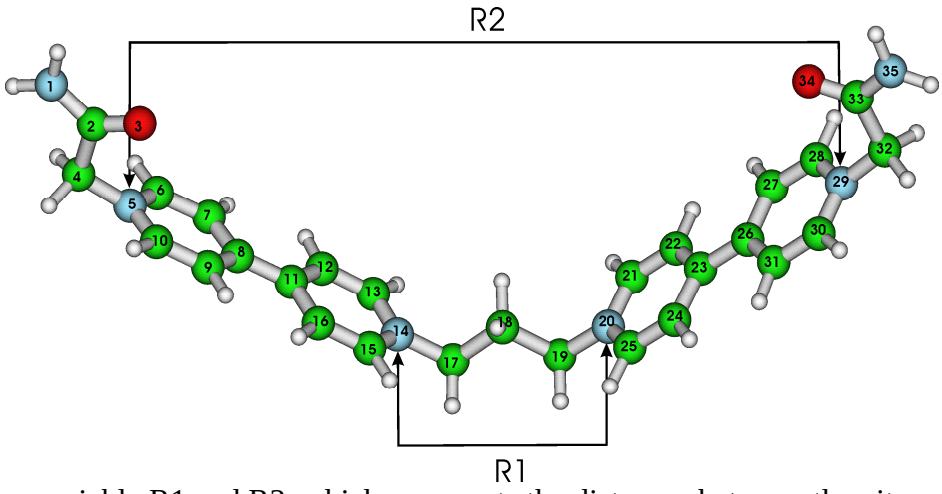

Fig.1 Collective variable R1 and R2, which represents the distances between the nitrogen atoms.

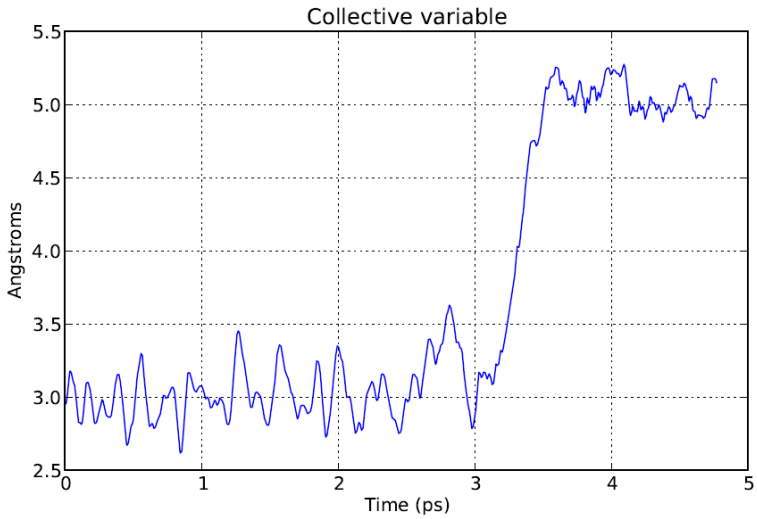

Fig.2 Time evolution of collective variable R1

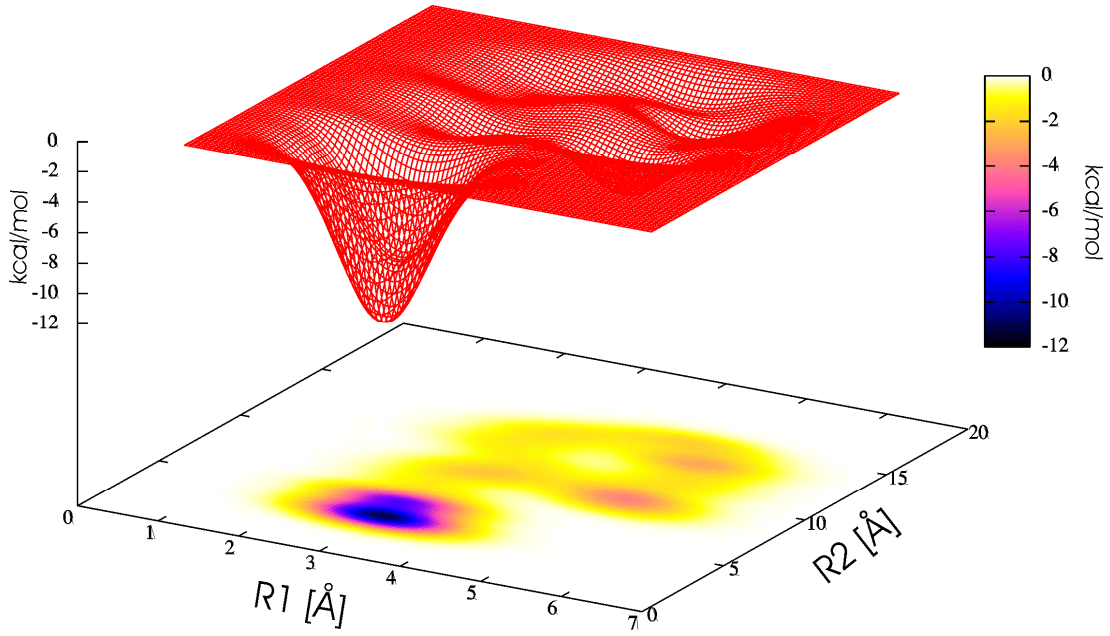

Fig. 3 Free energy surface reconstructions from Metadynamics run at T=300K with the bottom representations of the Free Energy Surface depth.