Supporting Information for regulating polystyrene glass transition temperature by varying hydration level of aromatic ring/Li+ interaction

Sze Yuet Chin, [a] Yunpeng Lu,[c] Weishuai Di,[d] Kai Ye, [e] Zihan Li, [g] Chenlu He,[h] Yi Cao,[df] Chun Tang[g], Kai Xue,[ab*]

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[a] Center of High Field NMR Spectroscopy and Imaging, Science Nanyang Technological University, 21 Nanyang Link, Singapore 637371

[b] School of Physical and Mathematical Science, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

[c] School of Chemistry, Chemical Engineering and Biotechnology, Technological University, 21 Nanyang Link, Singapore 637371

[d] Collaborative Innovation Center for Advanced Microstructures, National Laboratory of Solid state microstructure, Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

[e] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639789, Singapore

[f] Institute for Brain Sciences, Nanjing University, Nanjing 210023, People's Republic of China

[g] Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking-Tsinghua Center for life Sciences, Center for Quantitative Biology, Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China

[h] Department of Chemistry, National University of Singapore, Singapore, 117549, Singapore

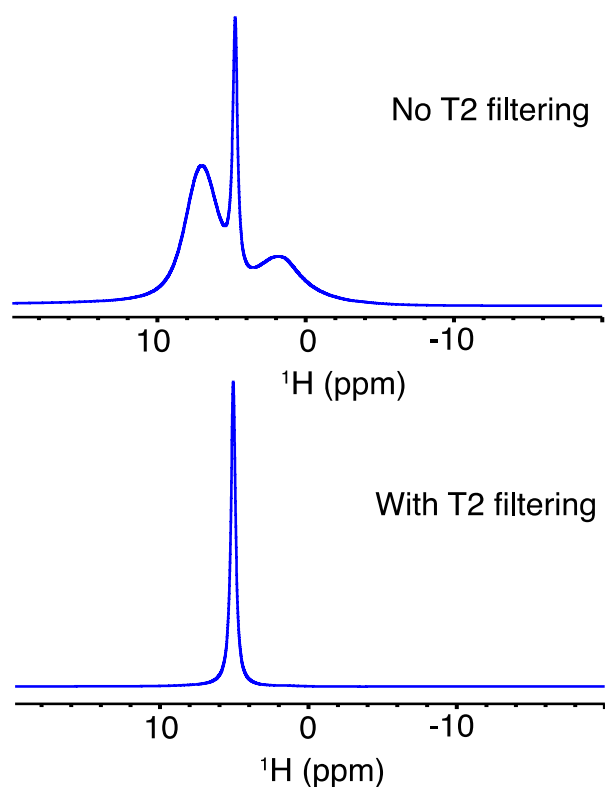To whom correspondence should be addressed:
kai.xue@ntu.edu.sg

Figure S1. Spectra of proton excited experiments with and without T2 filtering. A 200 μs T2 filtering is used in this work.
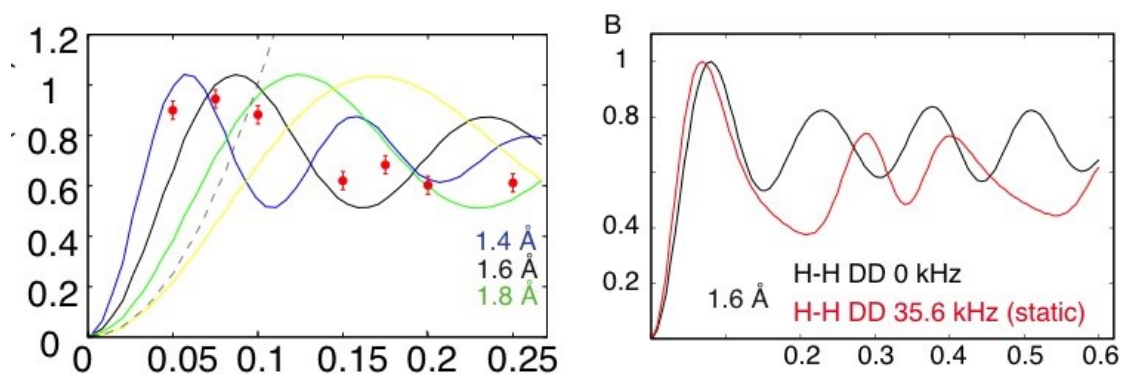

Figure S2. Fitting of Li to water distances. A) dipolar couplings are varied for 1.4-2.0 angstrom. B) Two protons are considered in a symmetric geometry, in black we assumed H-H dipolar couplings are completely averaged out by motion while in red is the case of complete static and no average of H-H dipolar couplings.
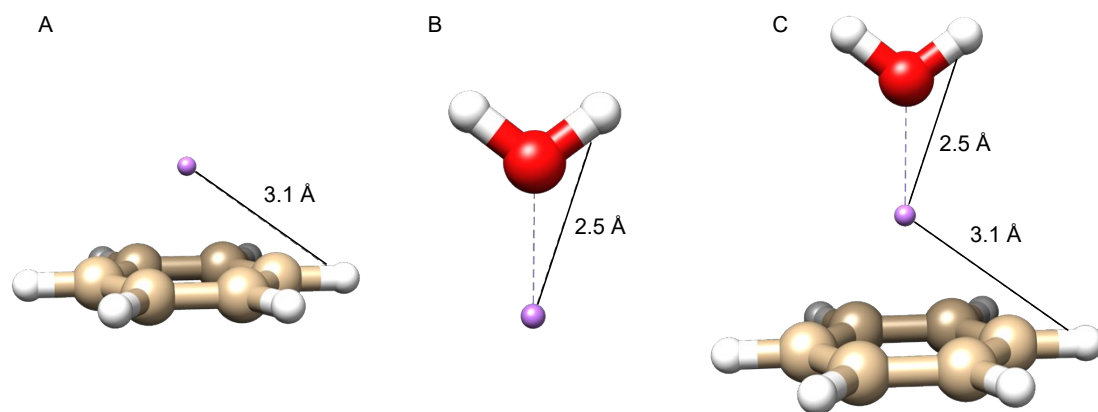
Figure S3. DFT simulated model considering lithium mediate in between aromatic ring and water molecule. A) only lithium (purple) and benzene are considered, B) lithium and one water molecule are considered, C) three component system consists of a benzene, water and lithium. Since in the sample preparation water was absorbed to LiCl from the humidity in the air not an aqueous solution, we believe the simulation with 1:1 ratio can already be representative enough for the binding scheme. The second and third water molecule form a second hydration shell by interacting with protons from the first water molecule. Details on simulation is in computational method section.

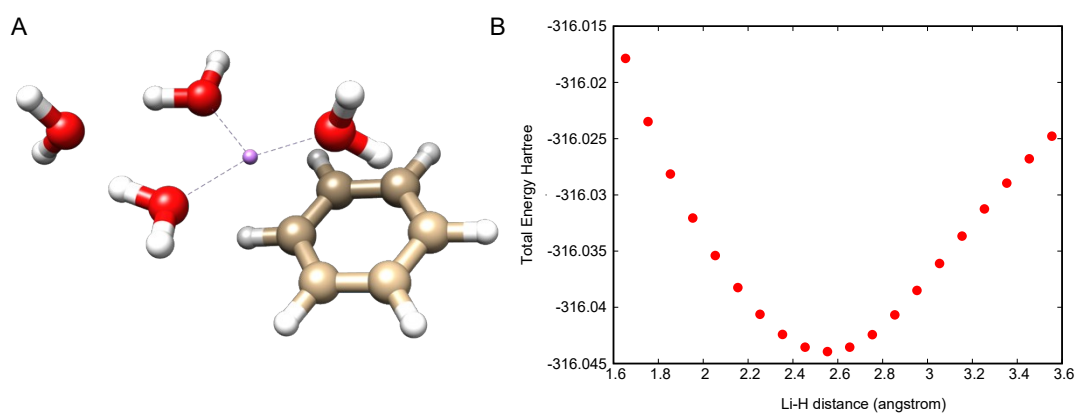**Figure S4.** A) DFT simulated geometry 4 water hydrated LiCl + aromatic system. Cation-π interation is weakened and lithium is driven away from the centroid position of aromatic ring. B) Surface energy map from simulation. Simulations are performed with a fixed lithium to proton distance and minimize the total energy of the system. Details for simulation please see to computational methods section.
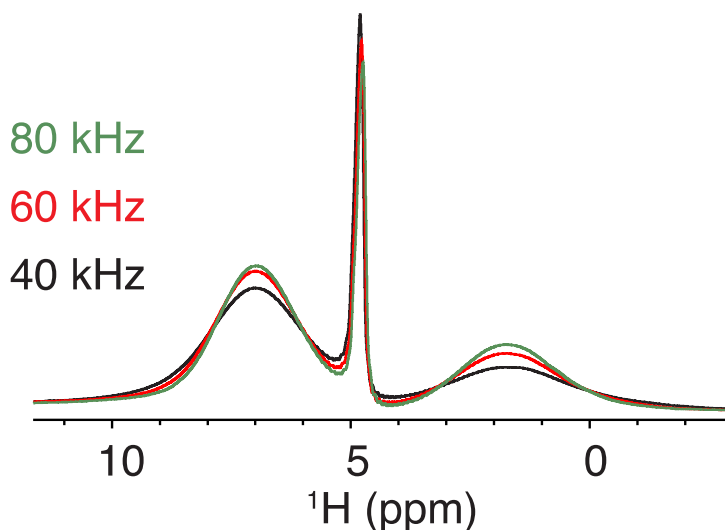
Figure S5. MAS dependent proton excitation on PS+LiCL sample after exposing in the air.
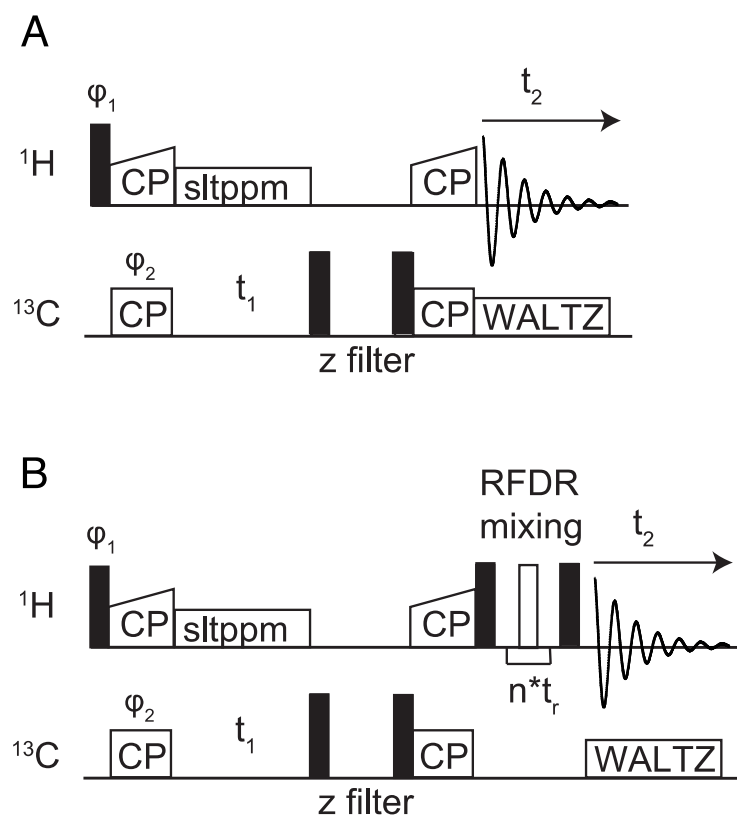
Figure S6. HCH and HCHH-RFDR pulse sequences. In CP settings, 700 ms were set in the first H-C cp step and 500 ms were set in the second CP to assure the polarization transfer is limited to one bond. 0-80% ramp were used on 1H CP power. 10 kHz waltz were used on ^{13}C for decoupling on direct dimension and 20 kHz sltppm were used for ^{1}H decoupling during t1. In RFDR mixing, a gullion phase cycling XY4 were used and hard pulse power of 278 kHz were used during recoupling.
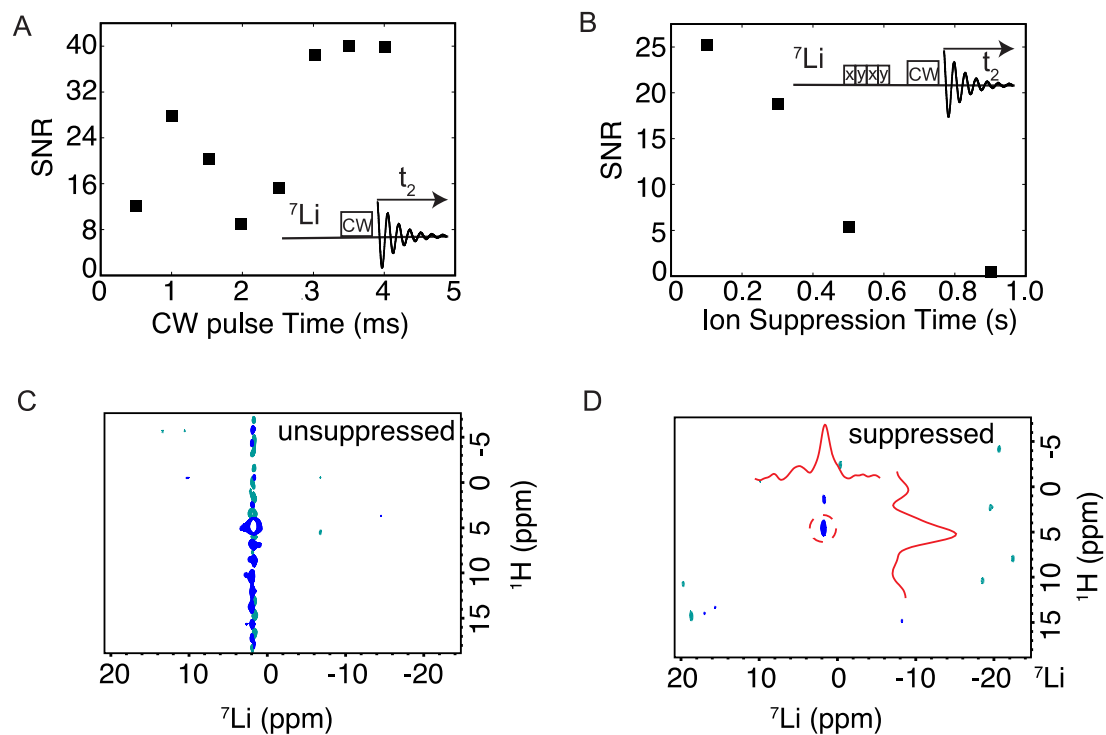
Figure S7. A) Excess lithium signals were observed when 60 kHz radio frequencies (rf) was put in the channel. Phase cycling is designed to averaged out this signal with each 4 scans, however the signal was still significant. Signal builds up to a higher intensity with 3-4 ms of pulsing. B) Signal of lithium after different ion suppression times. We saw signal intensities through this pathway drops down. 0.8-0.9 s of presaturation was needed in ion suppression. This is longer than the previously reported 0.1-0.3 s for solvent suppression[1]. C) and D) a comparison of ion suppressed and unsuppressed HETCORE spectrum are shown.

Figure S8. Illustrations for molecular structure of A) chain transfer agent (CTA) and B) Polystyrene (PS) with ending groups.

Materials

The PS was synthesized by the RAFT method [1-2] but adapted from previous literature [3-4]. The RAFT chain transfer agent (CTA) is shown 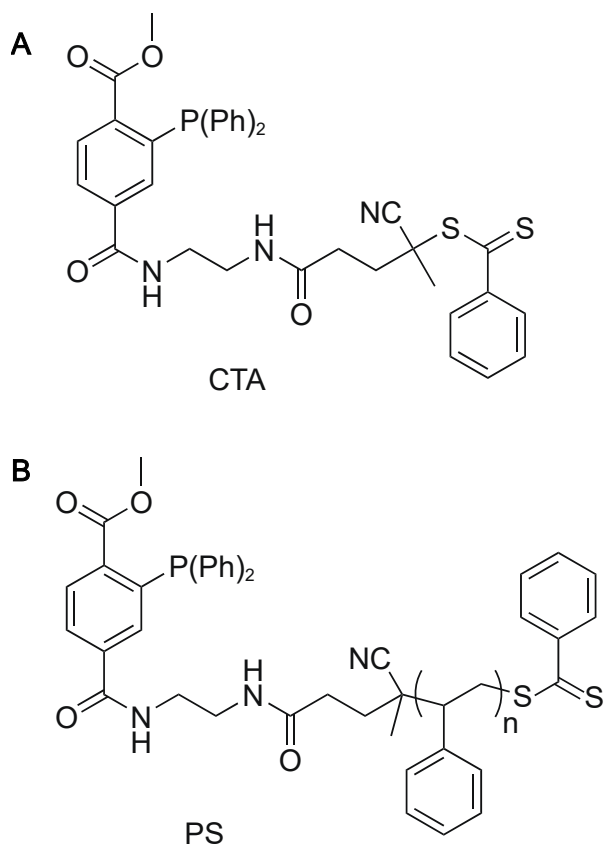in Figure S3. Specifically, Freshly vaccum distilled styrene (2.86 mL, 2.6g, 25 mmol, 1000 eq.), CTA (16.6 mg, 25 μmol, 1 eq.) and AIBN (0.8 mg, 5 μmol, 0.2 eq.) were fully mixed in a flame-dried schlenk tube. The freeze-pump-thaw cycles were applied to remove the oxygen and the tube was protected by argon atmosphere. The reaction was in an oil bath of 70 - 75 °C for 72 h -96 h until the liquid became hard solid in the tube. Then the reaction was quenched and the tube was cooled to room temperature. The solid was dissolved by the small amount of THF to prepare highly concentrated PS solution. Such concentrated solution was added into large amount of methanol in the clean beaker, drop by drop and with magneton stirring. Then the methanol was filtered and the precipitated PS polymer was washed by methanol several times. The final polymer was vaccum distilled to remove the residual methanol to obtain the dried the PS polymer.

In order to mix PS and salt, The PS (100 mg) is dissolved in THF (20 mL), then the water is gradually added into solution until the PS begins to separate out. The mixture is vapored under vacuum to remove THF and water is supplemented timely. After that, the aqueous solution containing 0.5 mmol LiCl is added into the abovementioned mixture of PS and water and vapored several times with water.

It's difficult to control the hydration level in our sample. We left PS+LiCl sample unsealed for 20 min and seal again. (Singapore annual average humidity 84%). We observed after 20 min exposure to the air, weight of the sample does not increase any more.

Thermal test

Differential scanning calorimetry (DSC) (TA, Q10) was conducted in an atmosphere of flowing nitrogen in hermetic aluminium holders over a temperature range from 40°C to 120°C, with a heating rate of 10°C/min.

Computational Method

All geometries are calculated with Gaussian 09, Revision E.01. [5] The M062X [6] functional and the basis set Def2-TZVP [7-8] are used in the geometry optimization. Vibrational frequency calculations are performed on the optimized geometries to validate these geometries are local minima and also to produce the thermodynamical data in 298.15 K in gas phase.

Results and Discussion

Table S1. The Formation Gibbs Free Energies for Chemicals from the calculations at 298.15 K in gas phase

Chemical	$\Delta G_f^{\emptyset}(298.15\ K)$ (Hartree)
Li^+	-7.2956
H_2O	-76.4227
C_6H_6	-232.1509
Li^+- H_2O Complex	-83.7649
Li^+- C_6H_6 Complex	-239.4968
C_6H_6-Li^+- H_2O Complex	-315.9507

C$_6$H$_6$-Li$^+$-4H$_2$O Complex	-545.2544
C$_6$H$_6$-Li$^+$-4H$_2$O Complex 2	-545.2552

Table S2 The Gibbs Free Energy changes of the several complexation processes at 298.15 K in gas phase

| Complexation Process	$\Delta G_r^{\emptyset}(298.15\ K)$ (kJ/mol)
Li$^+$ + H$_2$O → Li$^+$- H$_2$O Complex	-122.3
Li$^+$ + C$_6$H$_6$ → Li$^+$- C$_6$H$_6$ Complex	-132.1
Li$^+$ + C$_6$H$_6$ + H$_2$O → C$_6$H$_6$-Li$^+$- H$_2$O Complex	-214.0
Li$^+$ + C$_6$H$_6$ + 4 H$_2$O → C$_6$H$_6$-Li$^+$- 4H$_2$O Complex	-307.4
Li$^+$ + C$_6$H$_6$ + 4 H$_2$O → C$_6$H$_6$-Li$^+$- 4H$_2$O Complex 2	-309.5

The free energy calculations show that all the Li$^+$ cation complexation with either water or benzene are spontaneous, which is well expected as the positive charge ion can be stabilized by the electron lone pair in water or pi-electron clouds in benzene ring through electrostatic interaction. Geometry optimization results show that with the increase of the water molecule's number, Li$^+$ cation moves away from the benzene ring and is solvated in the water cage.

Li$^+$
Sum of electronic and zero-point Energies=   -7.282882 Hartree
Sum of electronic and thermal Energies=   -7.281466 Hartree
Sum of electronic and thermal Enthalpies=   -7.280522 Hartree
Sum of electronic and thermal Free Energies=   -7.295630 Hartree

H$_2$O
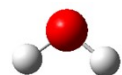

```
O     -0.000000   0.116235  -0.000001
H      0.764251  -0.464941   0.000003
H     -0.764251  -0.464941   0.000003
```
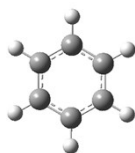
Sum of electronic and zero-point Energies=   -76.404570 Hartree
Sum of electronic and thermal Energies=   -76.401734 Hartree
Sum of electronic and thermal Enthalpies=   -76.400790 Hartree
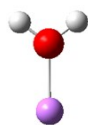Sum of electronic and thermal Free Energies=   -76.422860 Hartree

C$_6$H$_6$

C	-1.051409	-0.906841	0.000017
C	-1.311064	0.457082	0.000042
C	-0.259661	1.363928	0.000057
C	1.051409	0.906841	0.000044
C	1.311063	-0.457082	0.000019
C	0.259661	-1.363929	0.000007
H	-1.871000	-1.613905	-0.000206
H	-2.333149	0.813481	-0.000173
H	-0.462202	2.427243	-0.000146
H	1.870999	1.613906	-0.000168
H	2.333150	-0.813479	-0.000203
H	0.462202	-2.427243	-0.000215

Sum of electronic and zero-point Energies=   -232.123443 Hartree
Sum of electronic and thermal Energies=   -232.119071 Hartree
Sum of electronic and thermal Enthalpies=   -232.118127 Hartree
Sum of electronic and thermal Free Energies=   -232.150887 Hartree

Li^+- H_2O Complex

Li	1.490959	-0.000115	0.000001
O	-0.331030	-0.000088	-0.000001
H	-0.913120	-0.771190	0.000003
H	-0.911518	0.772237	0.000003

Sum of electronic and zero-point Energies=   -83.743109 Hartree
Sum of electronic and thermal Energies=   -83.739637 Hartree
Sum of electronic and thermal Enthalpies=   -83.738693 Hartree
Sum of electronic and thermal Free Energies=   -83.764878 Hartree

Li^+- C_6H_6 Complex
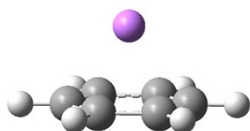
C	1.240792	0.641142	-0.119474
C	0.065160	1.395143	-0.119448
C	-1.175690	0.753999	-0.119414
C	-1.240824	-0.641142	-0.119422
C	-0.065169	-1.395115	-0.119503
C	1.175681	-0.753990	-0.119530
H	2.202162	1.137846	-0.124960
H	0.115706	2.476056	-0.125068
H	-2.086532	1.338192	-0.125321

```
H     -2.202195  -1.137831  -0.125009
H     -0.115730  -2.476036  -0.125027
H      2.086522  -1.338181  -0.125126
Li     0.000124  -0.000087   1.683753
```

Sum of electronic and zero-point Energies=   -239.468403 Hartree
Sum of electronic and thermal Energies=   -239.462951 Hartree
Sum of electronic and thermal Enthalpies=   -239.462007 Hartree
Sum of electronic and thermal Free Energies=   -239.496805 Hartree

C_6H_6-Li^+- H_2O Complex
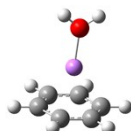

```
C      0.77995    0.70835   -1.20839
C      0.82044   -0.68619   -1.20824
C      0.83935   -1.38327    0.00042
C      0.81857   -0.68603    1.20894
C      0.77808    0.70852    1.20885
C      0.75819    1.40549    0.00017
H      0.77123    1.24907   -2.14543
H      0.84263   -1.22673   -2.14518
H      0.87746   -2.46460    0.00052
H      0.83910   -1.22644    2.14600
H      0.76771    1.24935    2.14581
H      0.73417    2.48723    0.00007
Li    -1.06656   -0.04328   -0.00090
O     -2.92439   -0.03469   -0.00097
H     -3.50763   -0.80221   -0.00138
H     -3.49732    0.74053   -0.00051
```

Sum of electronic and zero-point Energies=   -315.915489 Hartree
Sum of electronic and thermal Energies=   -315.906366 Hartree
Sum of electronic and thermal Enthalpies=   -315.905422 Hartree
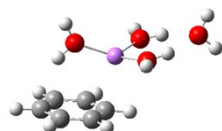Sum of electronic and thermal Free Energies=   -315.950737 Hartree

C_6H_6-Li^+-4H_2O Complex


```
C     -1.37711   -1.20306   -0.92047
C     -0.79779    0.00455   -1.29938
C     -1.37914    1.20878   -0.91311
C     -2.54892    1.20547   -0.16265
C     -3.13518   -0.00209    0.20409
C     -2.54684   -1.20636   -0.17003
H     -0.93138   -2.13843   -1.23367
H      0.09340    0.00720   -1.91656
H     -0.93510    2.14685   -1.22061
H     -3.01379    2.14073    0.12041
H     -4.05990   -0.00461    0.76716
```

H	-3.01011	-2.14414	0.10725
Li	0.77926	-0.00049	0.62347
O	1.96664	1.41709	0.23031
H	2.88118	1.20636	-0.01610
H	1.90509	2.36329	0.38425
O	1.96656	-1.41749	0.22736
H	2.88097	-1.20787	-0.02036
O	-0.43058	-0.00519	2.05594
H	-0.35071	-0.00524	3.01342
H	1.90371	-2.36378	0.38023
H	-1.37287	-0.00343	1.83641
O	4.32449	0.00046	-0.42942
H	5.09325	-0.00075	0.15271
H	4.67148	0.00253	-1.32916

Sum of electronic and zero-point Energies=   -545.206923 Hartree
Sum of electronic and thermal Energies=   -545.188652 Hartree
Sum of electronic and thermal Enthalpies=   -545.187708 Hartree
Sum of electronic and thermal Free Energies=   -545.254352 Hartree

C_6H_6-Li^+-$4H_2O$ Complex 2
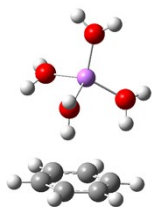
C	2.15286	-1.37622	0.18785
C	2.47606	-0.44569	1.17241
C	2.38220	0.91514	0.90529
C	1.98011	1.34582	-0.35508
C	1.65240	0.41740	-1.33723
C	1.73205	-0.94370	-1.06383
H	2.24572	-2.43472	0.39398
H	2.82280	-0.78221	2.14140
H	2.64658	1.63678	1.66691
H	1.96204	2.40661	-0.57826
H	1.36171	0.75140	-2.32549
H	1.50153	-1.66472	-1.83751
Li	-2.07749	0.10538	-0.00081
O	-0.81260	-0.46189	1.31035
H	-1.04727	-0.48168	2.24344
H	0.15558	-0.45711	1.26974
O	-2.14125	-1.51405	-1.02910
H	-2.44483	-1.74995	-1.90994
O	-1.34717	1.70536	-0.70681
H	-1.64720	2.40268	-1.29631
H	-1.51078	-2.18777	-0.75452
H	-0.39136	1.80120	-0.60586
O	-3.81800	0.30547	0.75989
H	-4.47675	-0.39555	0.73551
H	-4.24728	1.08329	1.12827

Sum of electronic and zero-point Energies=   -545.208159 Hartree
Sum of electronic and thermal Energies=   -545.190358 Hartree
Sum of electronic and thermal Enthalpies=   -545.189413 Hartree
Sum of electronic and thermal Free Energies=   -545.255154 Hartree

Reference:

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8.   Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Physical Chemistry Chemical Physics* **2006,** *8* (9).

Topspin Code for the ion suppressed HETCORE measurement

```
;cp HETCOR
;
;TS3.5pl6, 2018.06.19
;
```

```
;
;Avance III version
;parameters:
;p3 : proton 90 at power level PLW12
;p15 : contact time at PLW1(f1) and SPW0(f2)
;pl1 : X power level during contact
;pl2 : 1H 90 power level, used
;pl12 : decoupling power level (if not PLW13)
;sp0 : proton power level during contact
;sp1 : X power level during contact
;cnst21 : on resonance, usually = 0
;cpdprg2 : e.g. cw, spinal64 (at PLW12)
;d1 : recycle delay
;pcpd2 : pulse length in decoupling sequence (e.g. 180deg)
;spnam0 : use e.g. ramp.100 or ramp90100.100 for variable amplitude CP
;zgoptns : -Dfslg, -Dlacq, -Dlcp15, or blank
;
;
;$CLASS=Solids
;$DIM=1D
;$TYPE=cross polarisation
;$SUBTYPE=simple 1D
;$COMMENT=basic cp experiment, arbitrary contact and decoupling schemes


#include <Avancesolids.incl>
#include <trigg.incl>
     ; definition of external trigger output

"acqt0=-(p1*2/3.1416)-0.5u"

"in0=inf1"              ;#######################
"d0=1u"                ;#   t1_init => 0, 0    #
"in30=inf1"             ;#######################

define delay ONTIME        ;######################

"l0=0"

Prepare, ze

"ONTIME=aq+d0+p15"

#ifndef lcp15
#include <p15_prot.incl>
               ;make sure p15 does not exceed 10 msec
               ;let supervisor change this pulseprogram if
               ;more is needed
#endif
#ifndef lacq
               ;disable protection file for long acquisition change decoupling
power !!! or you risk probe damage
               ;if you set the label lacq (ZGOPTNS -Dlacq), the protection is disabled

#include <ONTIME_prot.incl>
     ;total RF deposition restriction

#include <aq_prot.incl>
               ;allows max. 50 msec acquisition time, supervisor
               ;may change  to max. 1s at less than 5 % duty cycle
```

```
                    ;and reduced decoupling field
#endif

#include <t1_prot.incl>
       ;check d0 and d30


;#######################################################
;#          Start of Active Pulse Program          #
;#######################################################

Start, 30m  do:f2
 d1

 trigg
 1u fq=0.0:f2                  ;set 1H on resonance

if "l0>0"
{
 "d51=d0-2u"
}

 (p3 pl2 ph1):f2
;#####a t2 filter#####
d3
(p3*2 pl2 ph0):f2
d3
;####################




;#######################################################
;#               t1 evolution                 #
;#######################################################

if "l0>0"
{
 0.5u
 d51
 0.5u
}
;################suppression#########

 (p3 pl2 ph3):f2          ; brings magn. to z

 0.5u cpds4:f1 pl13:f1
 d19*0.25
 0.5u do:f1

 0.5u cpds5:f1
 d19*0.25
 0.5u do:f1

 0.5u cpds4:f1
 d19*0.25
 0.5u do:f1

 0.5u cpds5:f1
 d19*0.25
 0.5u do:f1
```

```
 (p3 pl2 ph4):f2          ; brings magn. to y
;#################################

 (p15:sp1 ph2):f1 (p15:sp0 ph10):f2
; (p15:sp1 ph5):f1 (p15:sp0 ph11):f2
;d3
;(p1*2 pl1 ph6):f1
;d3
 (0.5u pl12):f2
 0.5u cpds2:f2            ;pl12 is used here with tppm, spinal, pl13 with cwlg, cwlgs
 gosc ph31
 1m do:f2
lo to Start times ns

30m mc #0 to Start
 F1PH(calph(ph1, +90), caldel(d0, +in0) & caldel(d30, -in30) & calclc(l0, 1))

HaltAcqu, 1m
exit

ph0= 0
ph1= 1 3 1 3 3 1 3 1
    3 1 3 1 1 3 1 3
;ph1= 1 3
ph2= 0 0 2 2 1 1 3 3
;ph2 = 0 0 2 2 1 1 3 3
ph3= 1
ph4= 3
ph5=2 2 0 0 3 3 1 1
ph6=1 1 1 1 2 2 2 2
ph10= 0
ph11= 2
ph31= 0 2 2 0 3 1 1 3
    2 0 0 2 1 3 3 1
;ph31 = 0 2 2 0 1 3 3 1

;$id: $
```

Solid state NMR simulation, SIMPSON Code:

```
spinsys {
  channels 7Li 1H
  nuclei 7Li 1H
  dipole 1 2 -17014.1 0 0 0
}

par {
  spin_rate       20000
  proton_frequency 600e6
  crystal_file    zcw986
  gamma_angles    8
  sw              spin_rate/gamma_angles
  np              16
  start_operator  I2x
  detect_operator I1p
```

```
    method         direct
#   verbose        1101
    variable nmr     50
    variable tsw     50
}

proc pulseq {} {
  global par
#  reset
#  acq_block {pulse $par(tsw) 60000 x 40000 x}
reset
pulse $par(tsw) 65000 x 45000 x
acq
}

proc main {} {
global par

set fp [ open "1.4A.dat" "w"]
set NN 300
for {set nmr1 1} {$nmr1 <= $NN} {incr nmr1} {
set par(nmr) [expr $nmr1]
set par(tsw) [expr $par(nmr)*2]
set f [fsimpson]
#fsave $f $par(name).fid
set val [fmaxheight $f -abs]
#set val [findex $f 1 -re]
#puts "[expr $par(tsw)] [lindex $val 0]"
puts $fp "[expr $par(tsw)] [lindex $val 0]"

funload $f
}
close $fp
}
```

RFDR simulation

```
spinsys {
  channels 1H
  nuclei 1H 1H
  shift 1 7p 0 0 0 0 0
  shift 2 0p 0 0 0 0 0
  dipole 1 2 -3056.2 0 0 0
}

par {
  spin_rate        80000
  proton_frequency 800e6
  crystal_file     rep30
  gamma_angles     1
  sw               spin_rate/8*gamma_angles
  np               100
  start_operator   I1z
```

```
  detect_operator  I2p
  method          direct
# verbose          1101
  variable nmr    50
}

proc pulseq [5] {
  global par

  set tr [expr 1.0e6/$par(spin_rate)]
  set tr2 [expr $tr/2.0-0.8]
  reset
  delay $tr2
  pulse 1.6 312500 x
  delay $tr2
  store 1

  reset
  delay $tr2
  pulse 1.6 312500 y
  delay $tr2
  store 2

  reset
foreach i {1 2 1 2 2 1 2 1} {
 prop $i
}
  store 8

reset
prop 8 $par(nmr)
pulseid 1 250000 y
acq
}

proc main [5] {
global par

set fp [ open "3.4A.dat" "w"]
set NN 30
for {set nmr1 0} {$nmr1 <= $NN} {incr nmr1} {
set par(nmr) [expr $nmr1]
set f [fsimpson]
#fsave $f $par(name).fid
set val [fmaxheight $f -abs]
#set val [findex $f 1 -re]
puts "[expr $nmr1] [lindex $val 0]"
puts $fp "[expr 8.0/$par(spin_rate)*$nmr1] [lindex $val 0]"

funload $f
}
close $fp
```