# Structure of Self-Assembled Multilayers Prepared from Water-Soluble Polythiophenes

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# SUPPORTING INFORMATION

**Contents**

**Viinikanoja et al : Supplemetary Information S1**

$^{1}$H NMR and $^{13}$C NMR shifts (δ) in DMSO/$D_2O$ and their assignments for the alkoxythiophene monomers (3TOPIM, 3TOHIM, 4Me-3TOEIM, 4Me-3TOHIM).

**3TOPIM:**

$^{1}$H NMR (DMSO/$D_2O$): 8.60 (1H, s), 7.40 (1H, s), 7.33 (1H, s), 7.27 (1H, dd), 6.67 (1H, dd), 6.42 (1H, t), 4.31 (2H, t), 3.99 (2H, t), 3.76 (3H, s), 2.25 (2H, s)

$^{13}$C NMR: 156, 136, 126, 124, 122, 119, 99, 67, 47, 36, 29

See S2-S5 and S6-S8 for $^{1}$H NMR and $^{13}$C NMR spectra, respectively.

**3TOHIM:**

$^{1}$H NMR($D_2O$/DMSO): 8.57(1H, s), 7.38(1H, s), 7.33 (1H, m), 7.27 (1H, dd), 6.71 (1H, d), 6.44(1H, d), 4.09 (2H, t), 3.94 (2H, t), 3.77(3H,d) 1.79 (2H, m), 1.66 (2H, m), 1.38 (2H, m), 1.25(2H, m)

$^{13}$C NMR ($D_2O$): 157, 138, 126, 124, 122, 119, 99, 71, 49, 38, 29, 28, 25, 24

See S9-S12 and S13-S15 for $^{1}$H NMR and $^{13}$ C NMR spectra, respectively.

**4Me-3TOEIM:**

$^{1}$H NMR (DMSO/$D_2O$): 9.07 (1H, s), 7.71 (1H, t), 7.64 (1H, t), 7.02 (1H, dd), 6.52 (1H, d), 4.56 (2H, t), 4.24 (2H, t), 3.83 (3H, s), 1.94 (3H, s)

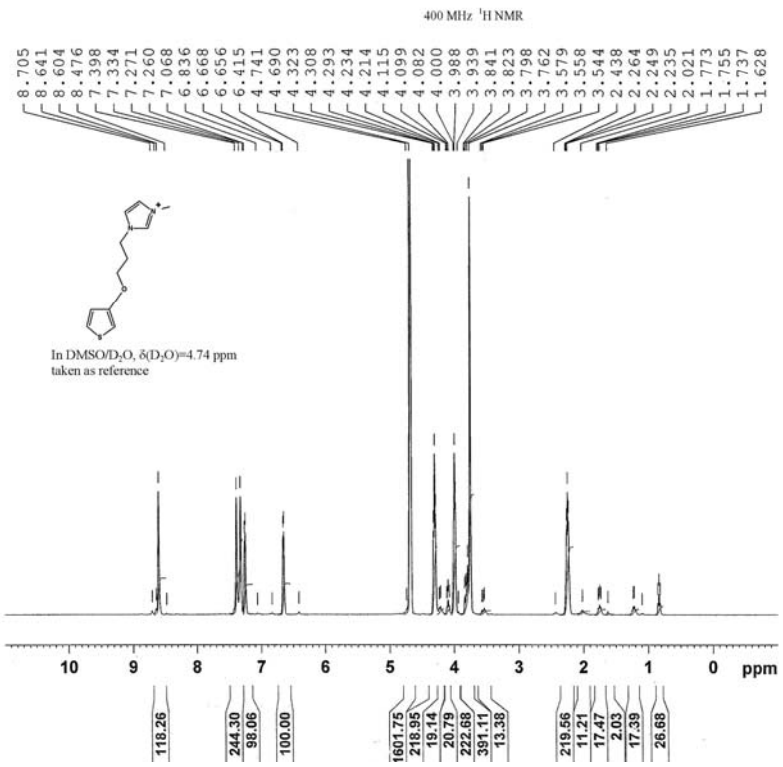
See S16-S19 for $^{1}$H NMR spectra.

**4Me-3TOHIM:**

$^{1}$H NMR (DMSO/$D_2O$): 8.60 (1H, s), 7.33 (2H, d), 6.81 (1H, d), 6.27 (1H, d), 4.06 (2H, t), 3.86 (2H, d), 3.77 (3H, s), 1.92 (3H, s), 1.75 (2H, m), 1.64 (2H, m), 1.35 (2H, m), 1.23 (2H, m)

See S20-S23 for $^{1}$H NMR spectra.

**Viinikanoja et al : Supplementary Information S2**







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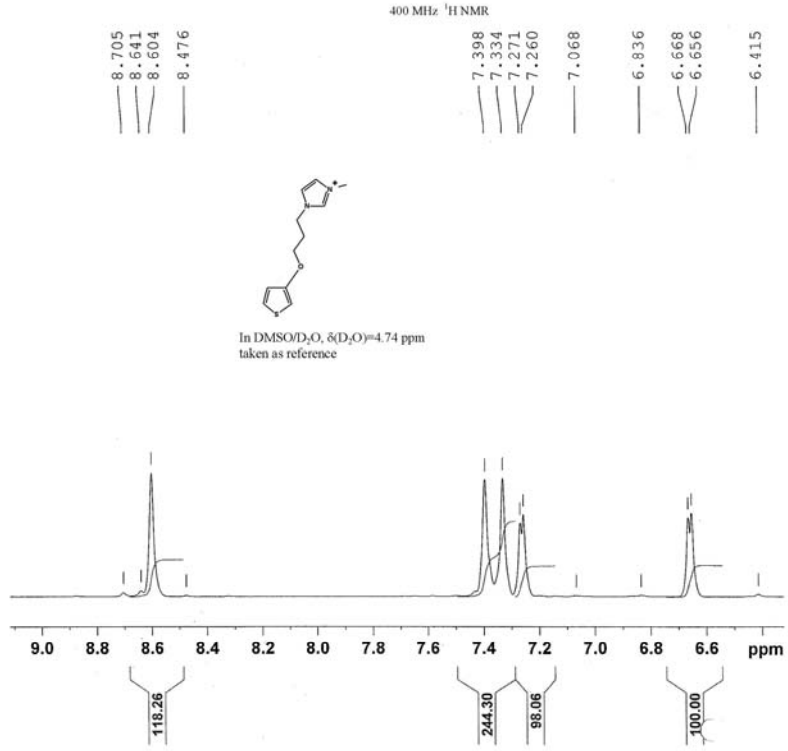



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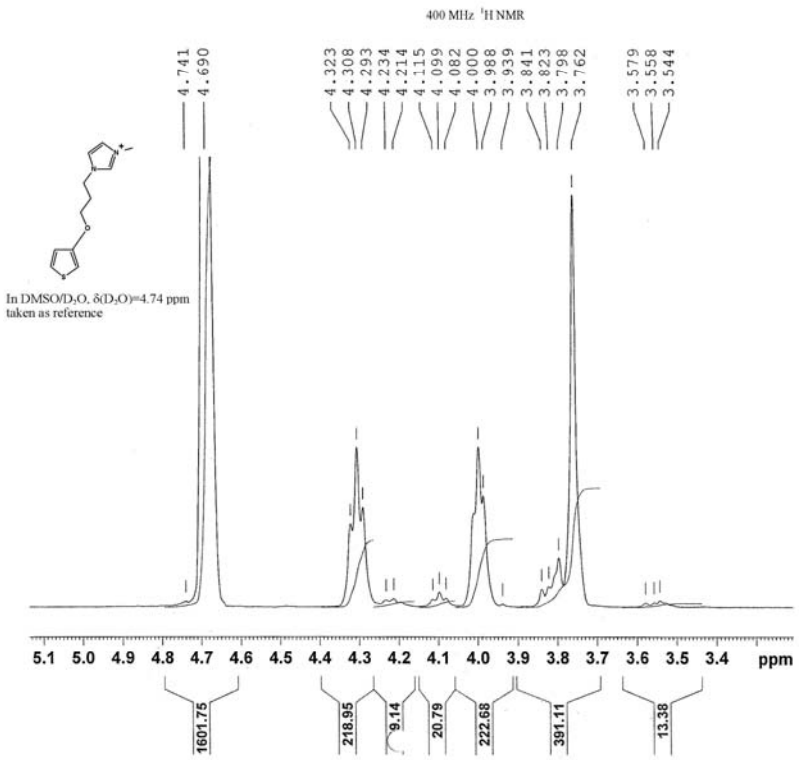


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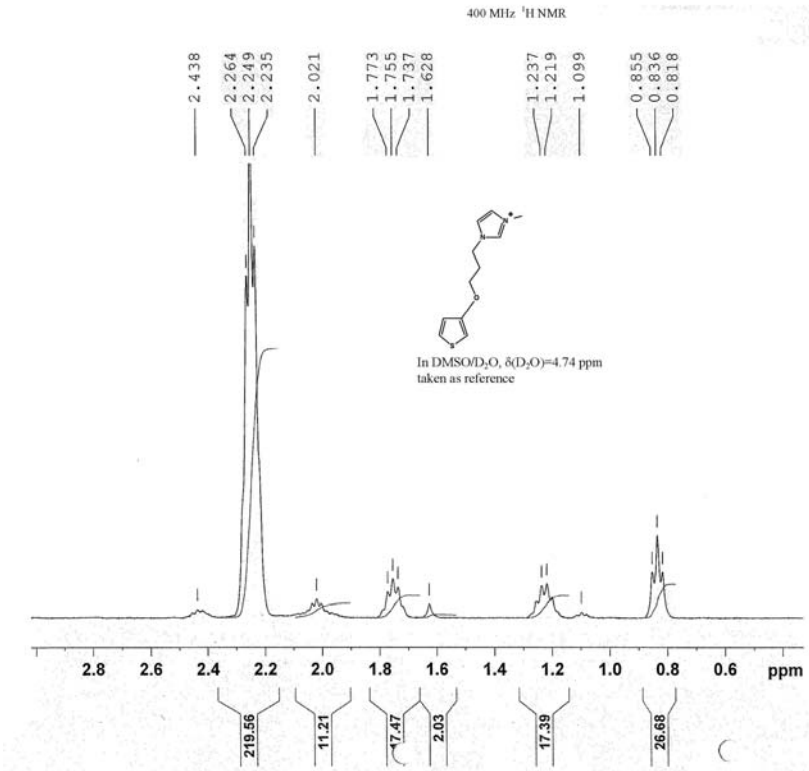


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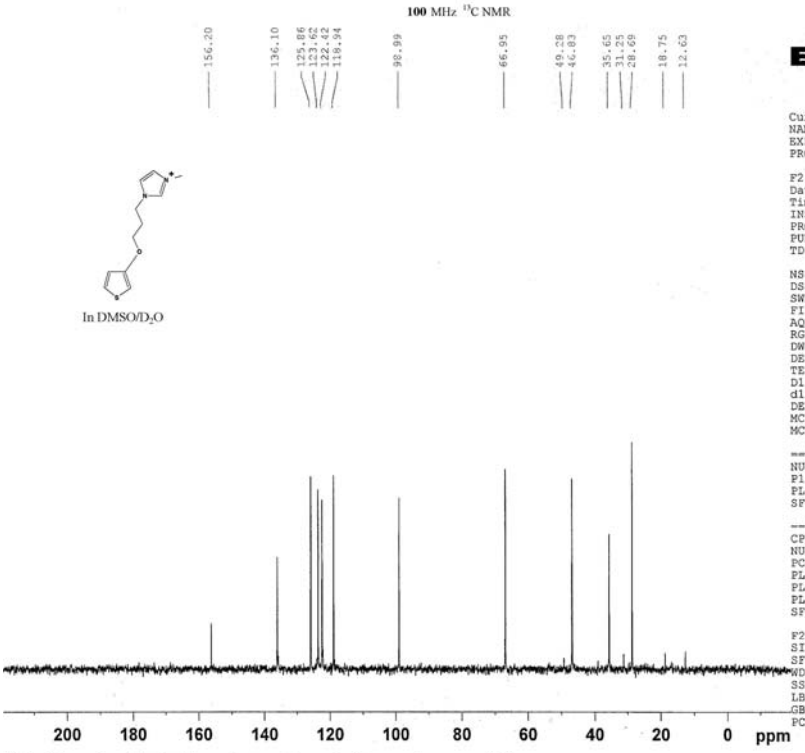
**Viinikanoja et al : Supplementary Information S6**

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PL1                 0.00 dB
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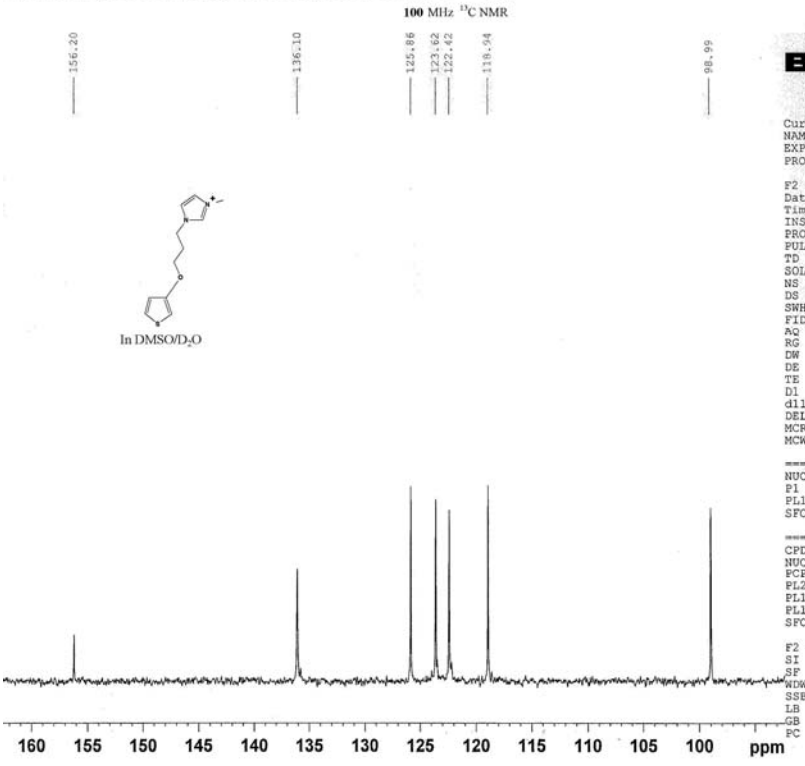
**Viinikanoja et al : Supplementary Information S7**

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P1                  7.60 usec
PL1                 0.00 dB
SFO1         100.5272692 MHz

======== CHANNEL f2 ========
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NUC2                 1H
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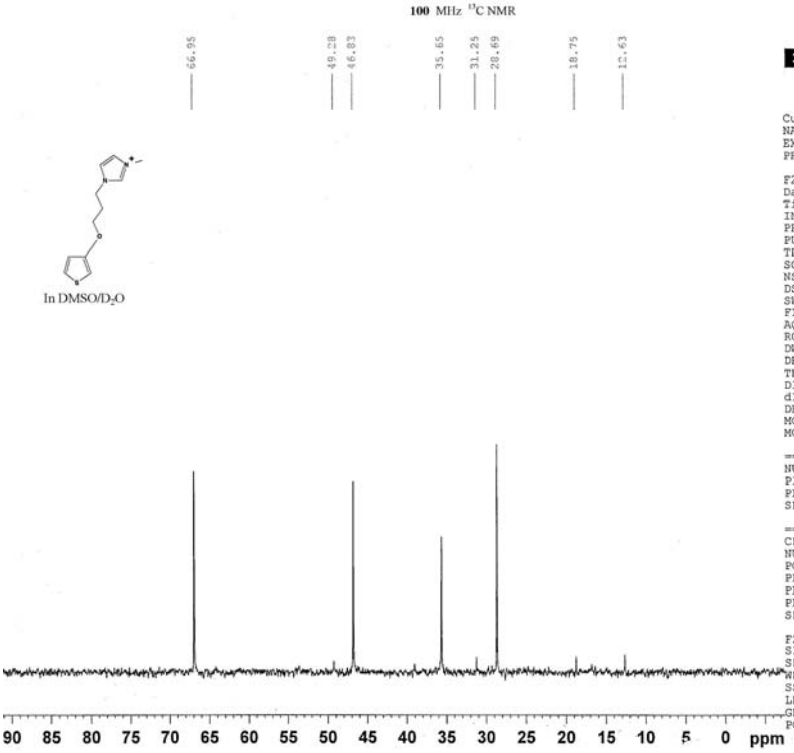


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======== CHANNEL f2 ========
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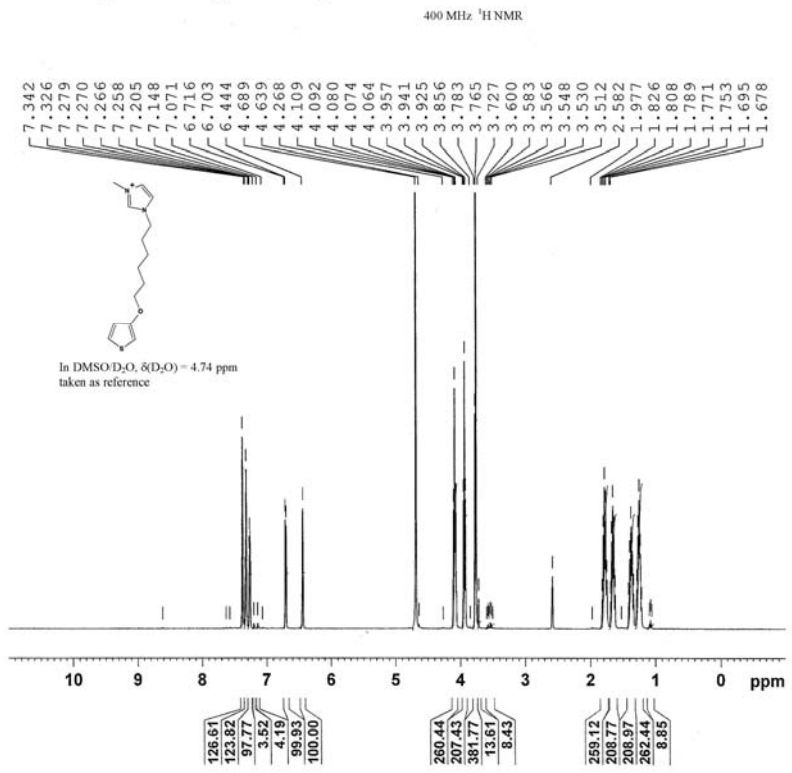


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======== CHANNEL f1 ========
NUC1                   1H
P1                   8.10 usec
PL1                 -1.00 dB
SFO1          399.7524686 MHz

F2 - Processing parameters
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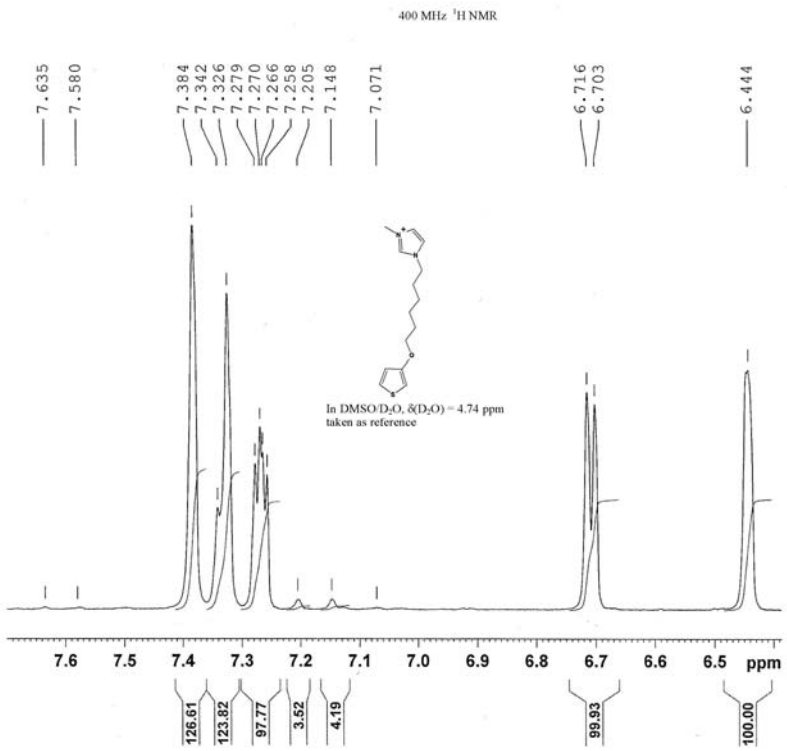
**Viinikanoja et al : Supplementary Information** **S10**





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DS 2
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AQ 3.9715922 sec
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DW 60.600 usec
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TE 295.0 K
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======== CHANNEL f1 ========
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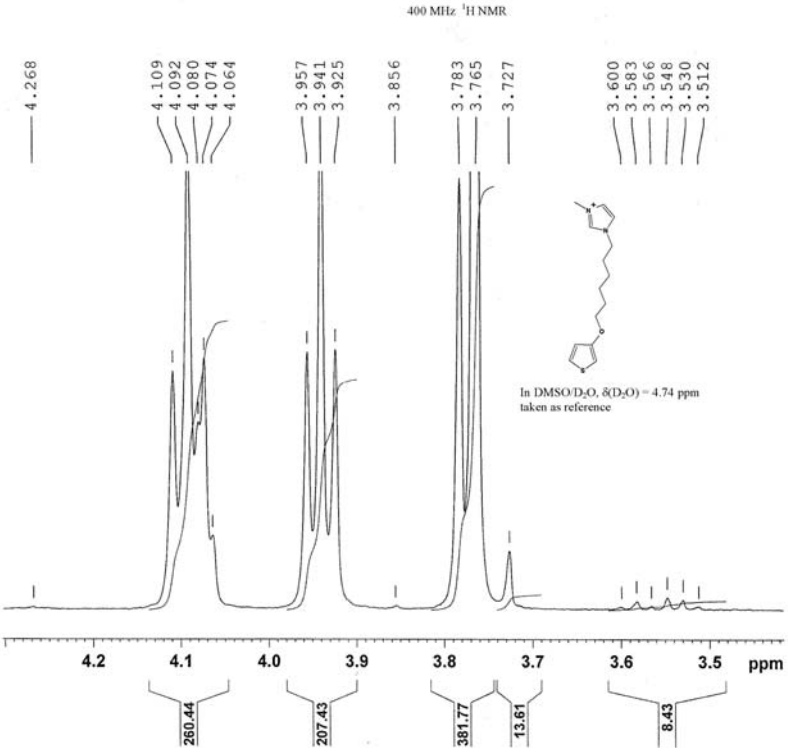
**Viinikanoja et al : Supplementary Information** **S11**





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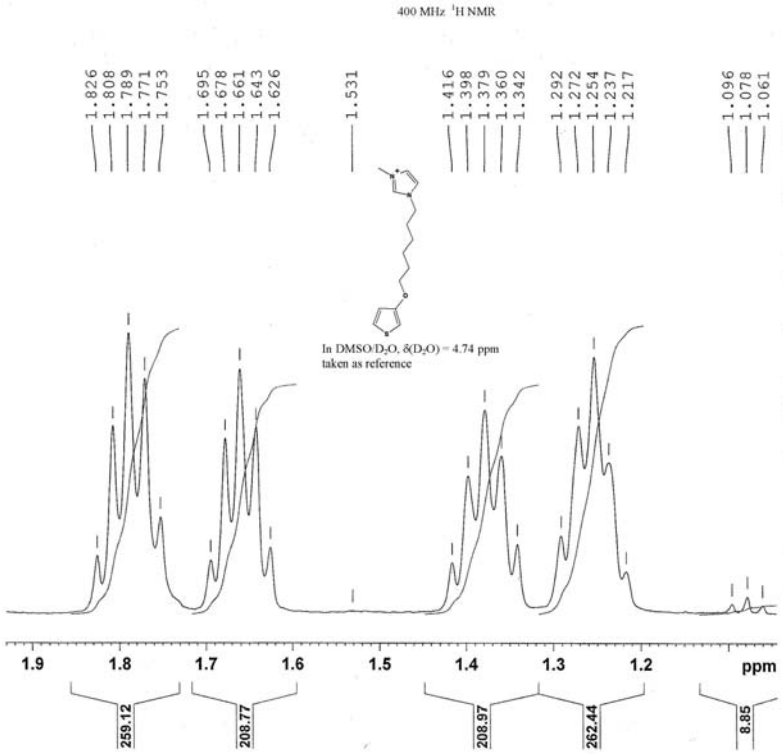


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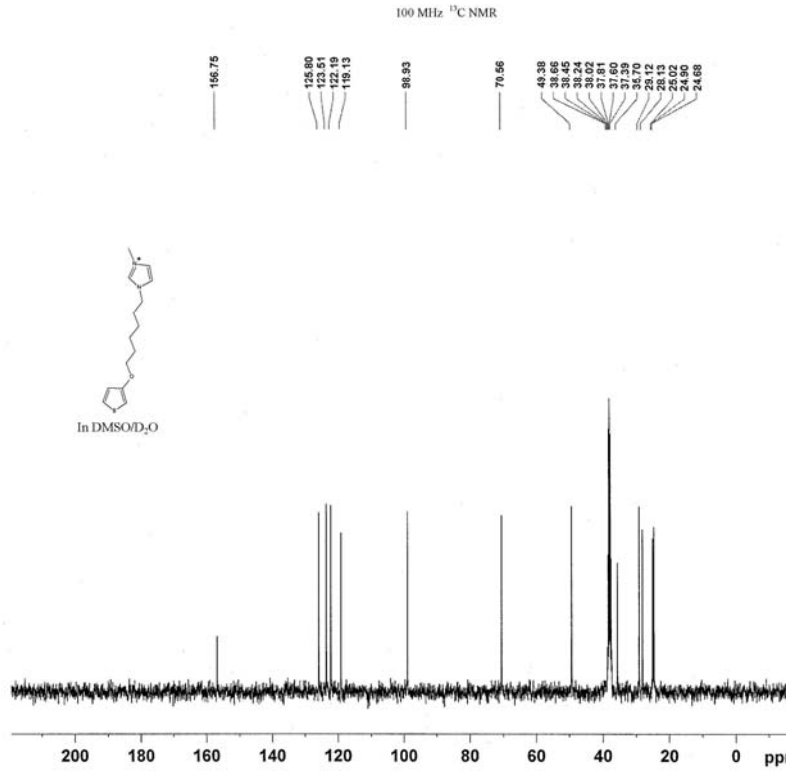


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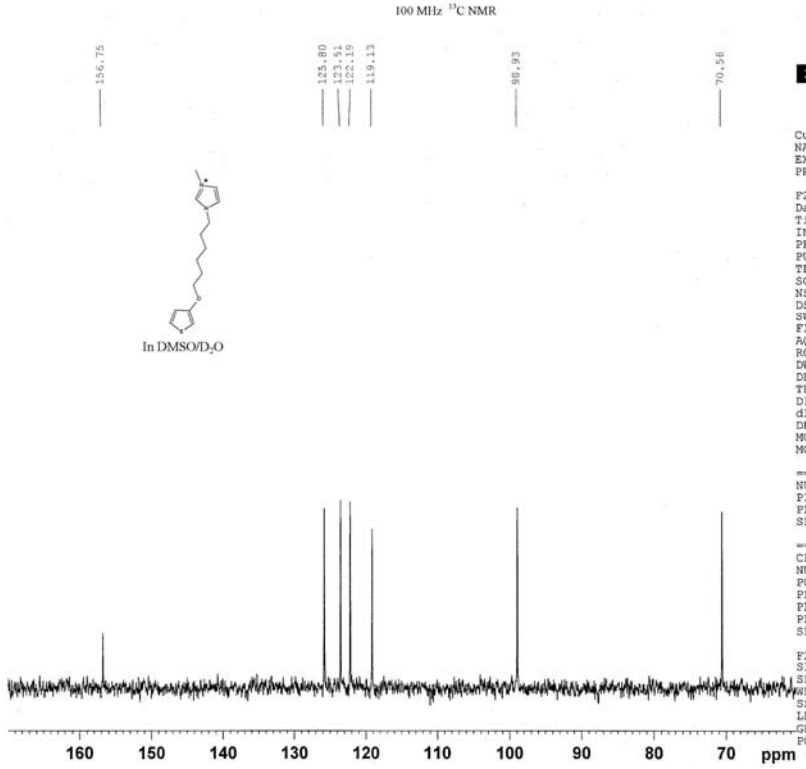
100 MHz $^{13}$C NMR

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======== CHANNEL f1 ========
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P1                   7.60 usec
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======== CHANNEL f2 ========
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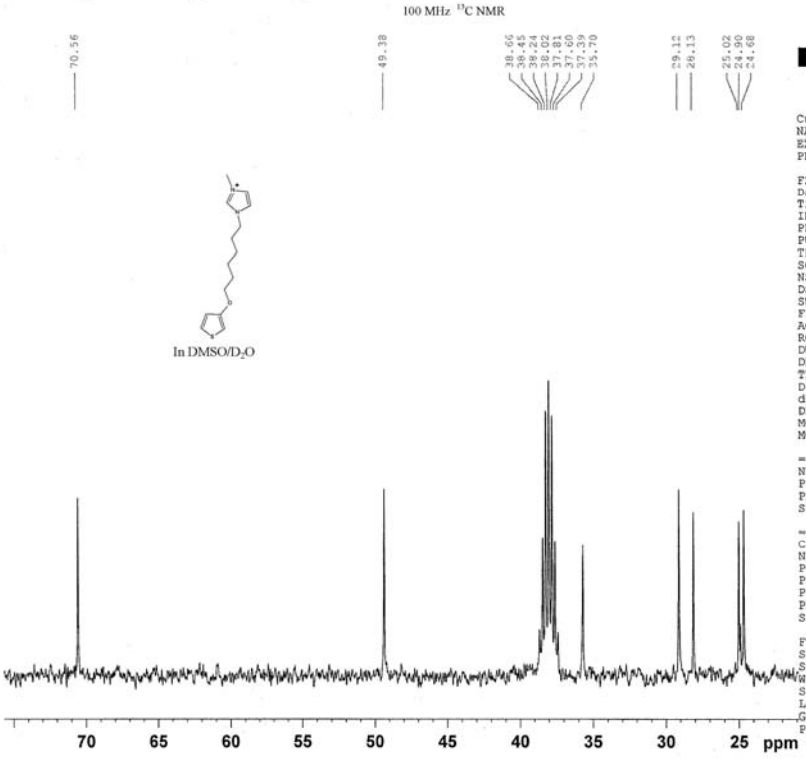
100 MHz $^{13}$C NMR

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MCWRK          0.01500000 sec

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P1                   7.60 usec
PL1                  0.00 dB
SFO1         100.5272692 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2               80.00 usec
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PL12                18.00 dB
PL13                18.00 dB
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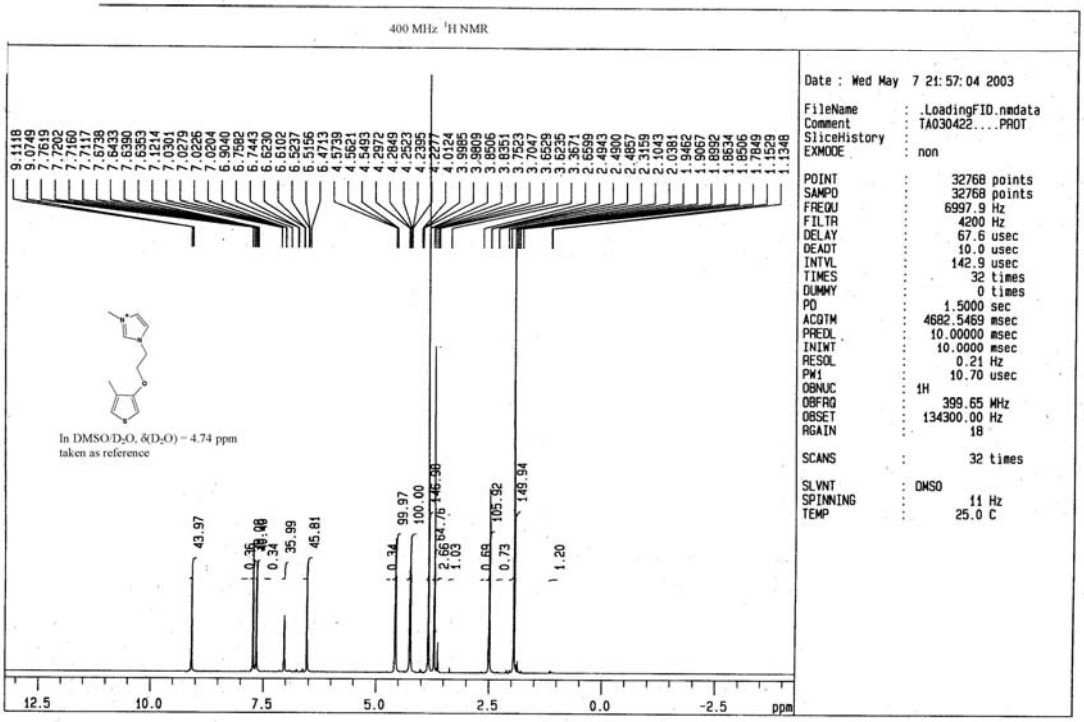
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taken as reference
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40.40
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35.99
45.81
0.34
99.97
100.00
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10.0
7.5
5.0
2.5
0.0
-2.5
ppm
Date : Wed May 7 21:57:04 2003
FileName : .LoadingFID.nmdata
Comment : TA030422....PROT
SliceHistory :
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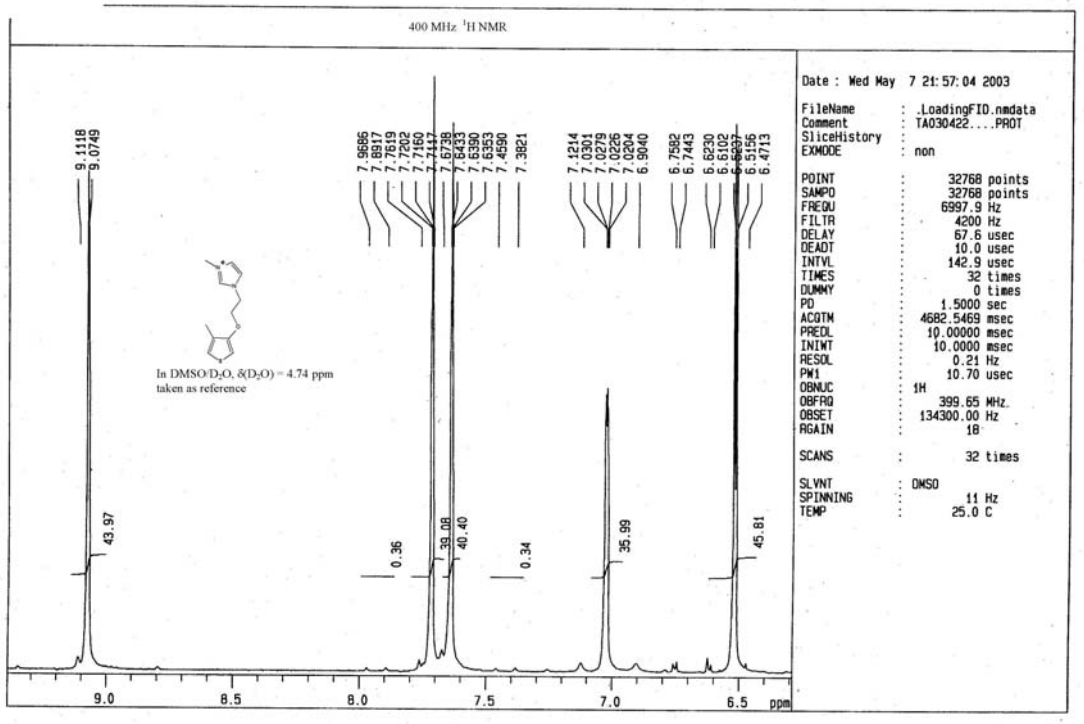
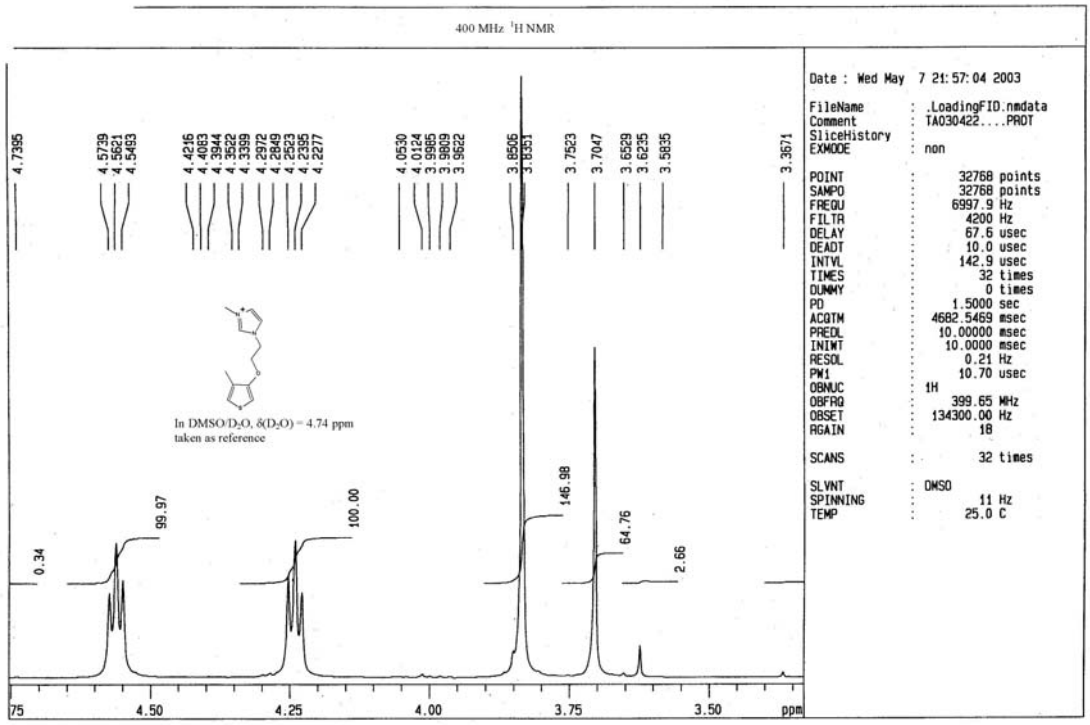
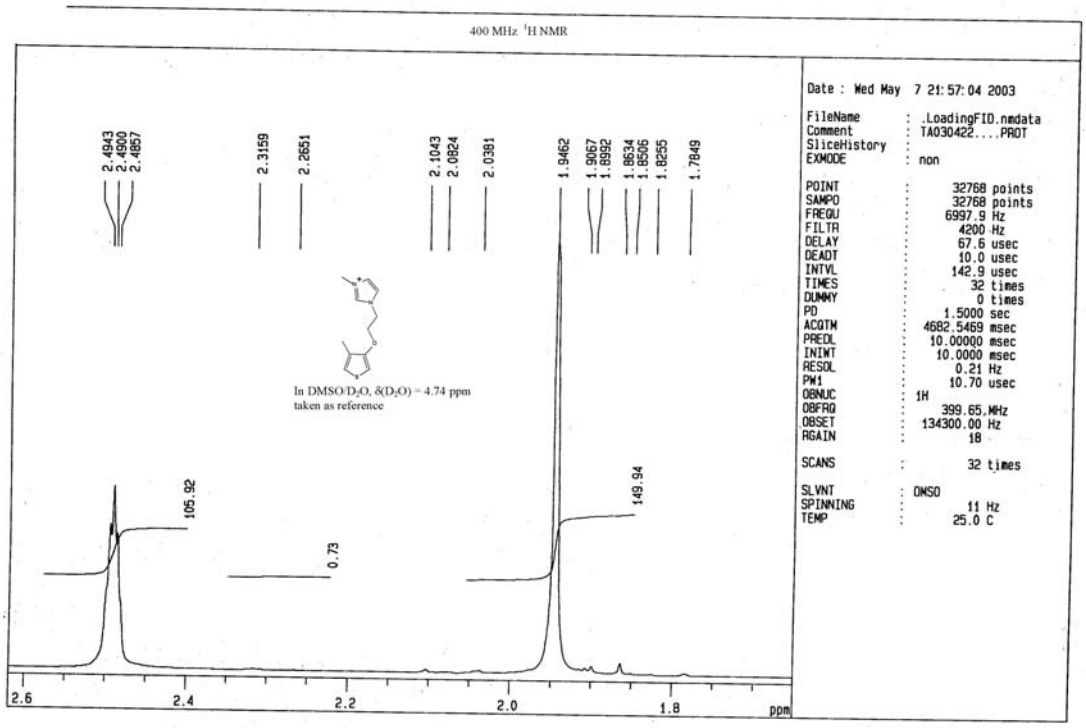
POINT : 32768 points
SAMPO : 32768 points
FREQU : 6997.9 Hz
FILTR : 4200 Hz
DELAY : 67.6 usec
DEADT : 10.0 usec
INTVL : 142.9 usec
TIMES : 32 times
DUMMY : 0 times
PD : 1.5000 sec
ACQTM : 4682.5469 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 0.21 Hz
PW1 : 10.70 usec
OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134300.00 Hz
RGAIN : 18
SCANS : 32 times
SLVNT : DMSO
SPINNING : 11 Hz
TEMP : 25.0 C

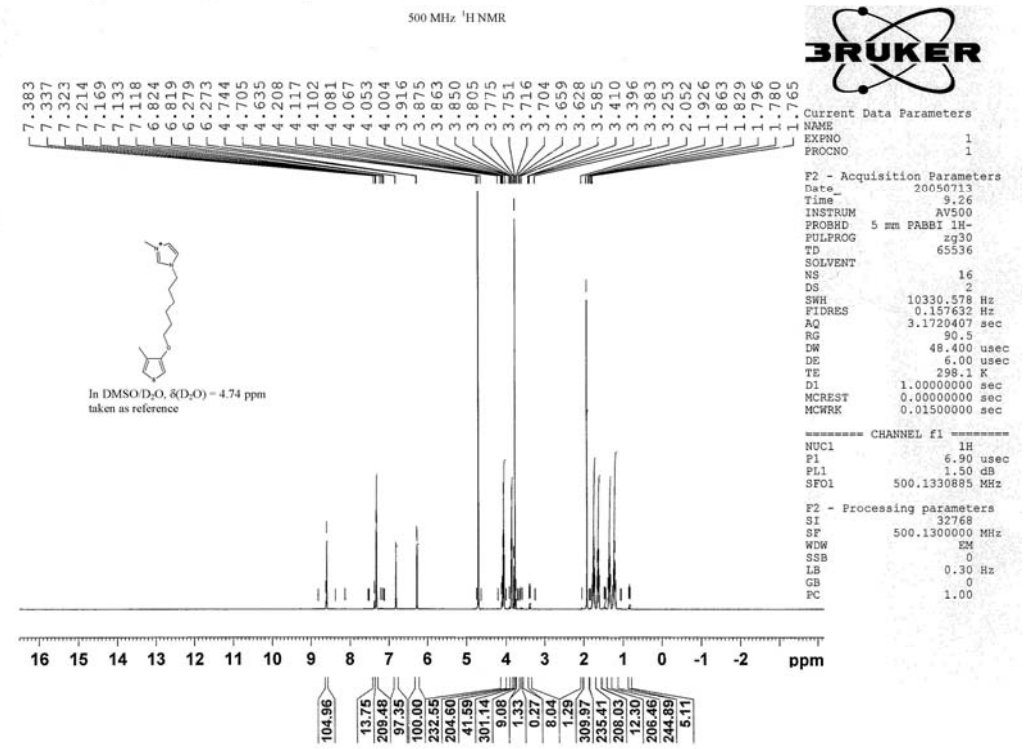



400 MHz ¹H NMR
9.1118
9.0749
7.9686
7.6917
7.7619
7.7202
7.7160
7.6738
7.6433
7.6390
7.6353
7.4590
7.3821
7.1214
7.0301
7.0279
7.0226
7.0204
6.9040
6.7582
6.7443
6.6230
6.6102
6.5237
6.5156
6.4713
In DMSO/D2O, δ(D2O) = 4.74 ppm
taken as reference
43.97
0.36
39.08
40.40
0.34
35.99
45.81
9.0
8.5
8.0
7.5
7.0
6.5
ppm
Date : Wed May 7 21:57:04 2003
FileName : .LoadingFID.nmdata
Comment : TA030422....PROT
SliceHistory :
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 6997.9 Hz
FILTR : 4200 Hz
DELAY : 67.6 usec
DEADT : 10.0 usec
INTVL : 142.9 usec
TIMES : 32 times
DUMMY : 0 times
PD : 1.5000 sec
ACQTM : 4682.5469 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 0.21 Hz
PW1 : 10.70 usec
OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134300.00 Hz
RGAIN : 18
SCANS : 32 times
SLVNT : DMSO
SPINNING : 11 Hz
TEMP : 25.0 C

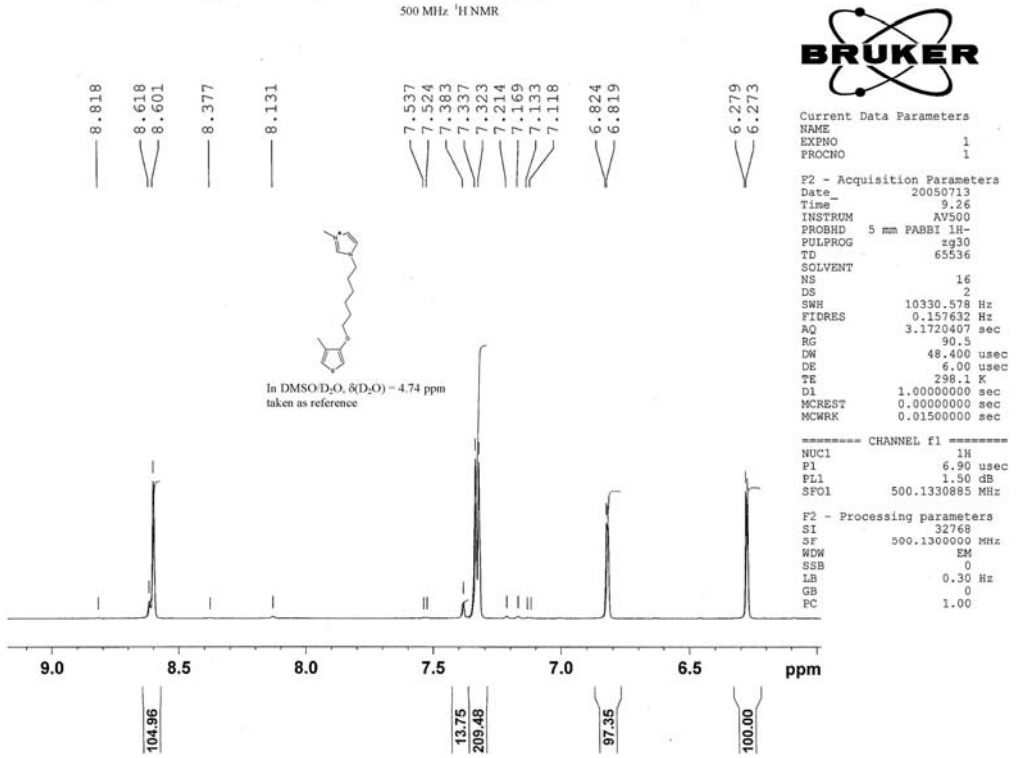

400 MHz $^1$H NMR
4.7395
4.5739
4.5621
4.5493
4.4216
4.4083
4.3944
4.3522
4.3399
4.2972
4.2849
4.2523
4.2396
4.2277
4.0530
4.0124
3.9985
3.9809
3.9622
3.8506
3.8351
3.7523
3.7047
3.6529
3.6235
3.5835
3.3671
In DMSO/$D_2O$, $\delta(D_2O)$ = 4.74 ppm
taken as reference
99.97
100.00
146.98
64.76
2.66
0.34
4.50
4.25
4.00
3.75
3.50
ppm
Date : Wed May 7 21:57:04 2003
FileName : .LoadingFID.nmdata
Comment : TA030422....PROT
SliceHistory :
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 6997.9 Hz
FILTR : 4200 Hz
DELAY : 67.6 usec
DEADT : 10.0 usec
INTVL : 142.9 usec
TIMES : 32 times
DUMMY : 0 times
PD : 1.5000 sec
ACQTM : 4682.5469 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 0.21 Hz
PW1 : 10.70 usec
OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134300.00 Hz
RGAIN : 18
SCANS : 32 times
SLVNT : DMSO
SPINNING : 11 Hz
TEMP : 25.0 C



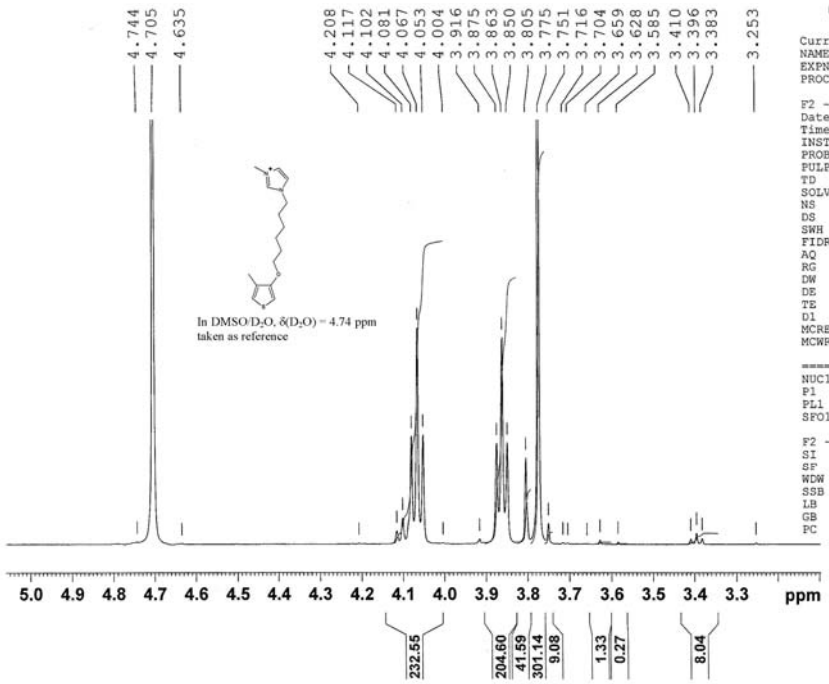

400 MHz $^1$H NMR
2.4943
2.4900
2.4857
2.3159
2.2651
2.1043
2.0824
2.0381
1.9462
1.9067
1.8992
1.8634
1.8506
1.8255
1.7849
In DMSO/$D_2O$, $\delta(D_2O)$ = 4.74 ppm
taken as reference
105.92
0.73
149.94
2.6
2.4
2.2
2.0
1.8
ppm
Date : Wed May 7 21:57:04 2003
FileName : .LoadingFID.nmdata
Comment : TA030422....PROT
SliceHistory :
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 6997.9 Hz
FILTR : 4200 Hz
DELAY : 67.6 usec
DEADT : 10.0 usec
INTVL : 142.9 usec
TIMES : 32 times
DUMMY : 0 times
PD : 1.5000 sec
ACQTM : 4682.5469 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 0.21 Hz
PW1 : 10.70 usec
OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134300.00 Hz
RGAIN : 18
SCANS : 32 times
SLVNT : DMSO
SPINNING : 11 Hz
TEMP : 25.0 C


500 MHz $^1$H NMR
7.383
7.337
7.323
7.214
7.169
7.133
7.118
6.824
6.819
6.279
6.273
4.744
4.705
4.635
4.208
4.117
4.102
4.081
4.067
4.053
4.004
3.916
3.875
3.863
3.850
3.805
3.775
3.751
3.716
3.704
3.659
3.628
3.585
3.410
3.396
3.383
3.253
2.052
1.926
1.863
1.829
1.796
1.780
1.765
In DMSO/$D_2O$, δ($D_2O$) = 4.74 ppm
taken as reference
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
104.96
13.75
209.48
97.35
100.00
232.55
204.60
41.59
301.14
9.08
1.33
0.27
8.04
1.29
309.97
235.41
208.03
12.30
206.46
244.89
5.11
Current Data Parameters
NAME
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050713
Time 9.26
INSTRUM AV500
PROBHD 5 mm PABBI 1H-
PULPROG zg30
TD 65536
SOLVENT
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 90.5
DW 48.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.90 usec
PL1 1.50 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00




500 MHz $^1$H NMR
8.818
8.618
8.601
8.377
8.131
7.537
7.524
7.383
7.337
7.323
7.214
7.169
7.133
7.118
6.824
6.819
6.279
6.273
In DMSO/$D_2O$, δ($D_2O$) = 4.74 ppm
taken as reference
9.0 8.5 8.0 7.5 7.0 6.5 ppm
104.96
13.75
209.48
97.35
100.00
Current Data Parameters
NAME
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050713
Time 9.26
INSTRUM AV500
PROBHD 5 mm PABBI 1H-
PULPROG zg30
TD 65536
SOLVENT
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 90.5
DW 48.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.90 usec
PL1 1.50 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

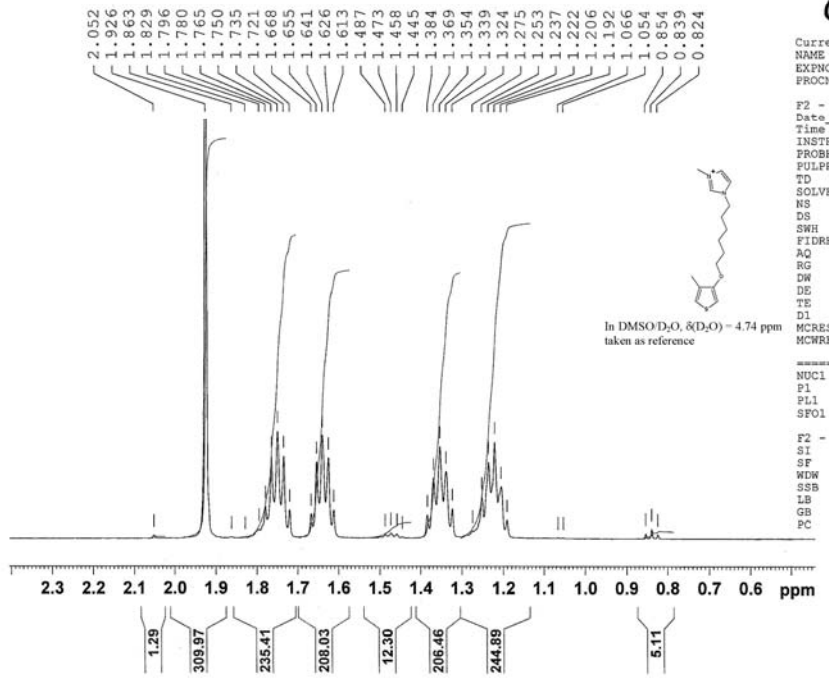
500 MHz $^1$H NMR




```
Current Data Parameters
NAME
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050713
Time               9.26
INSTRUM           AV500
PROBHD   5 mm PABBI 1H-
PULPROG            zg30
TD                65536
SOLVENT
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1720407 sec
RG                 90.5
DW               48.400 usec
DE                6.00 usec
TE               298.1 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.90 usec
PL1                1.50 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



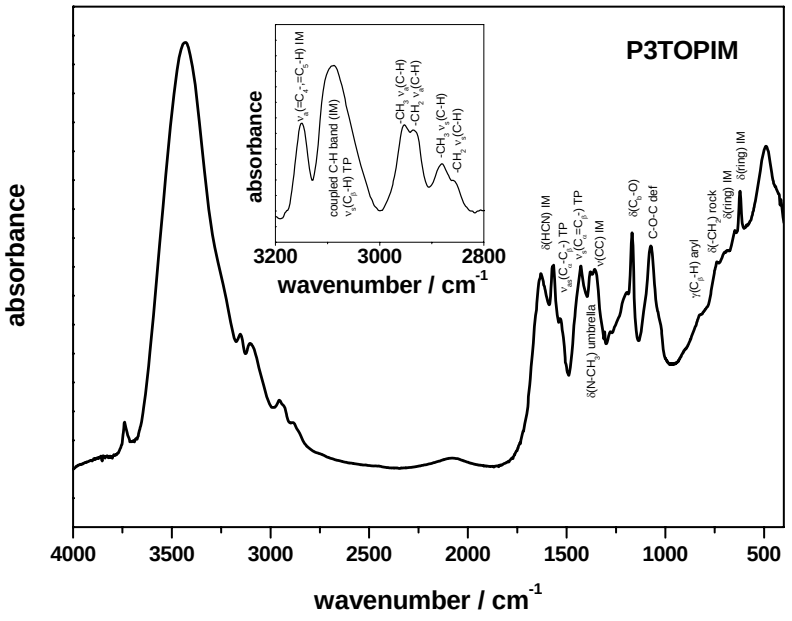
500 MHz $^1$H NMR




```
Current Data Parameters
NAME
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050713
Time               9.26
INSTRUM           AV500
PROBHD   5 mm PABBI 1H-
PULPROG            zg30
TD                65536
SOLVENT
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1720407 sec
RG                 90.5
DW               48.400 usec
DE                6.00 usec
TE               298.1 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.90 usec
PL1                1.50 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

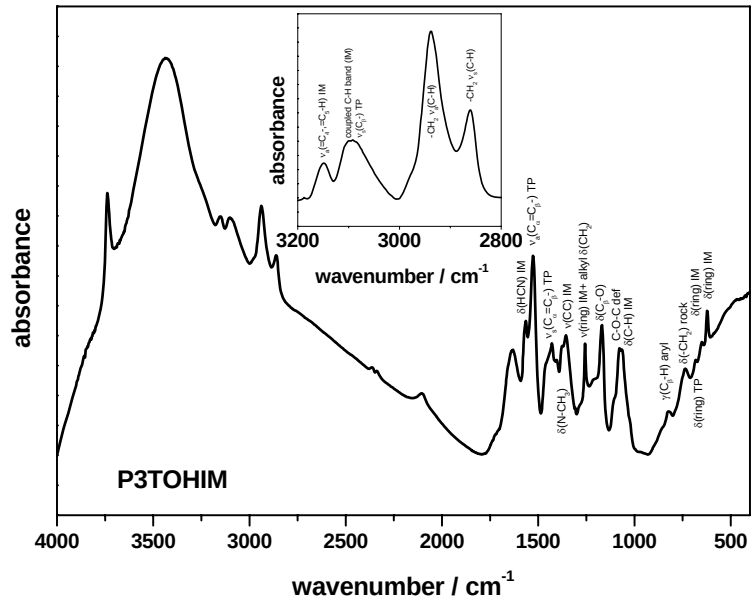
**Viinikanoja et al : Supplementary Information S24**

IR-spectrum (in KBr) of P3TOPIM and the tentative assignment of the some major bands (peak positions in S29). The inset shows the region 3200-2800 $cm^{-1}$ after the background correction.



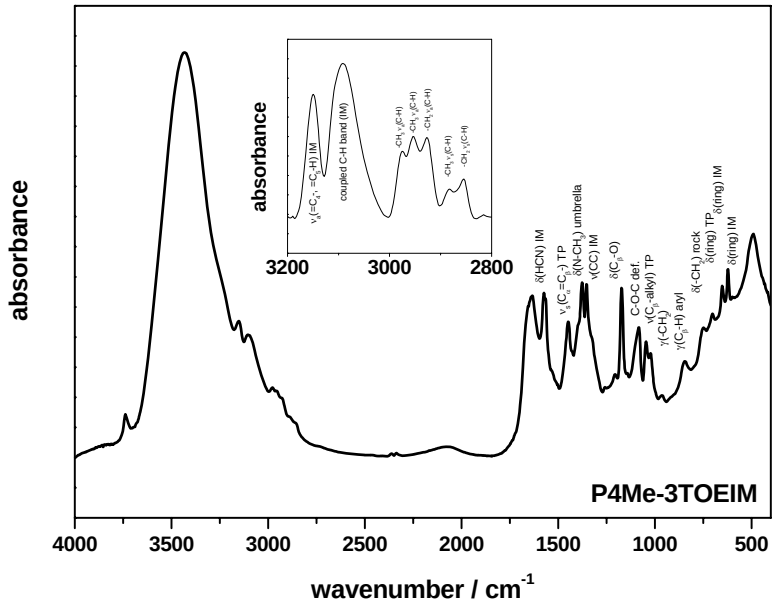

**Viinikanoja et al : Supplementary Information S25**

IR-spectrum (in KBr) of P3TOHIM and the tentative assignment of the some major bands (peak positions in S29). The inset shows the region 3200-2800 $cm^{-1}$ after the background correction.



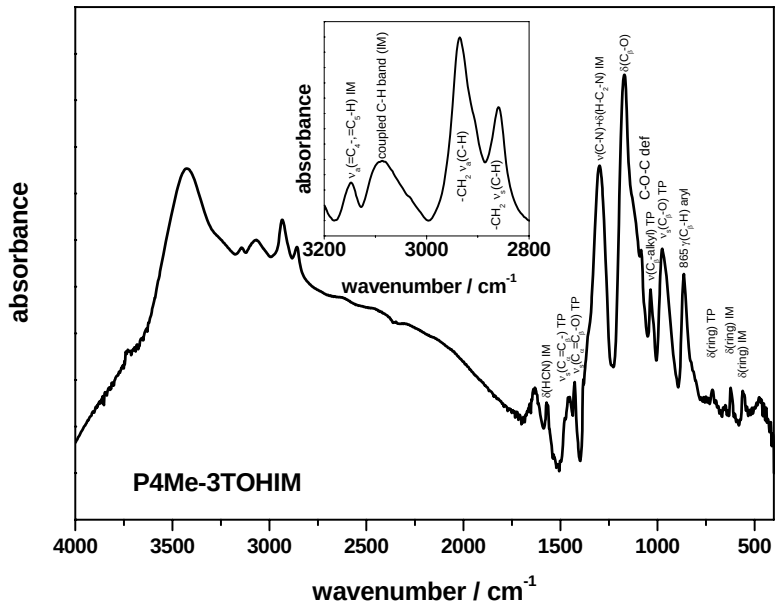
**Viinikanoja et al : Supplementary Information S26**

IR-spectrum (in KBr) of P4Me-3TOEIM and the tentative assignment of the some major bands (peak positions in S29). The inset shows the region 3200-2800 $cm^{-1}$ after the background correction.




**Viinikanoja et al : Supplementary Information S27**

IR-spectrum (in KBr) of P4Me-3TOHIM and the tentative assignment of the some major bands (peak positions in S29). The inset shows the region 3200-2800 $cm^{-1}$ after the background correction.



PM-IRRAS spectra of $(PT/PSS)_{10}$ alkyl C-H stretching region. In addition to methyl and methylene bands of film constituents, Fermi resonance bands (FR) and a band indicating structure with an all-trans arrangement is shown.

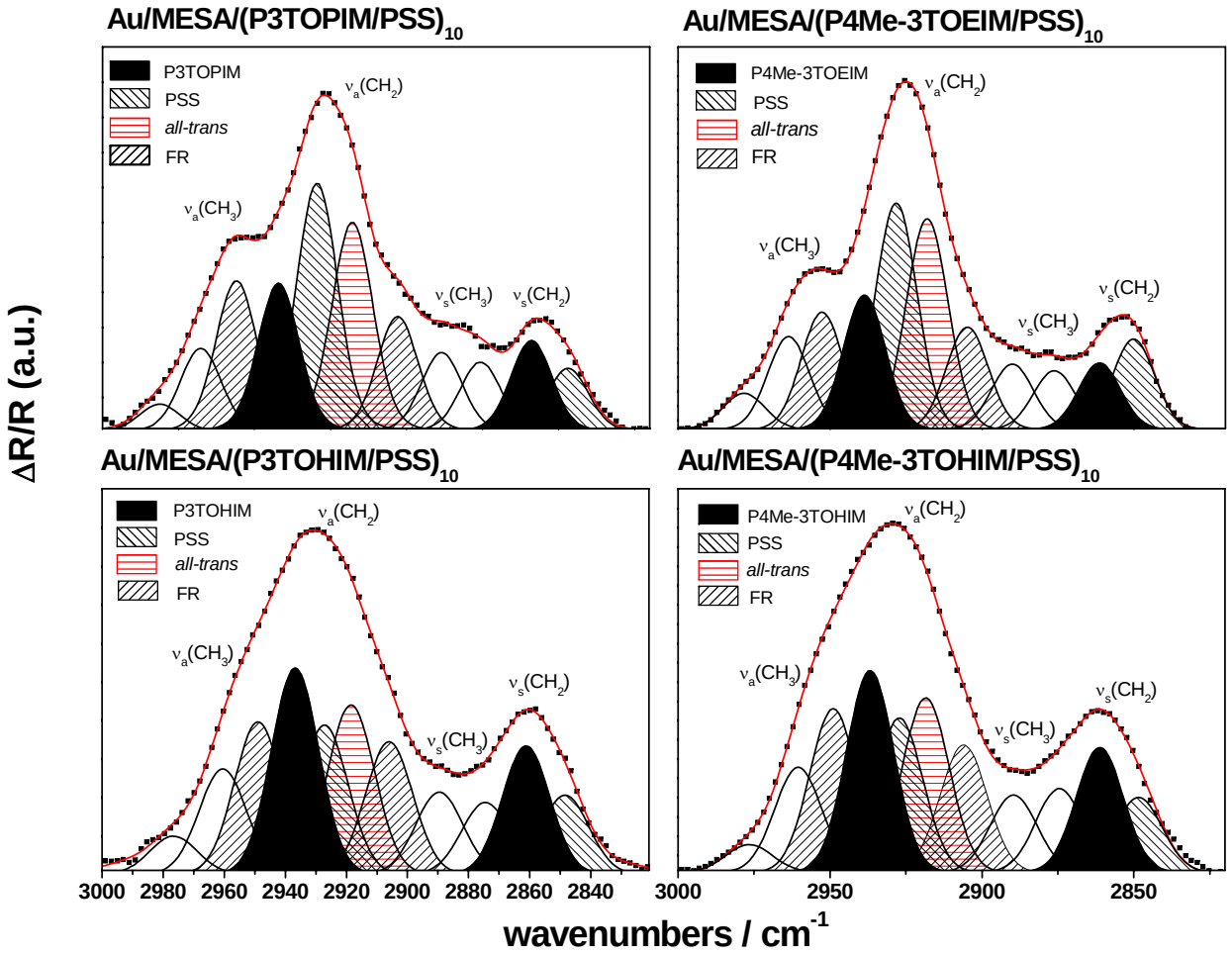


**Table 1.** Peak positions ($cm^{-1}$) and tentative assignments for P4Me-3TOEIM, P3TOPIM, P3TOHIM and P4Me-3TOHIM in bulk samples (in KBr) and in the $(PT/PSS)_{10}$ films (FTIR and PM-IRRAS spectra, respectively).

| P4Me-3TOEIM | | P3TOPIM | | P3TOHIM | | P4Me-3TOHIM | | Assignment* |
|---|---|---|---|---|---|---|---|---|
| Bulk | film | bulk | film | bulk | film | bulk | film | |
| 3432 | 3467 | 3429 | 3470 | 3438 | 3461 | 3428 | 3474 | ν(O...H) in the hydrogen bridges broad |
| 3149 | 3150 | 3149 | 3149 | 3148 | 3149 | 3147 | 3149 | $\nu_{as}(C_4\text{-},C_5\text{-H})$ [a]IM |
| 3105 | 3103 | 3107 | 3106 | 3109 | 3105 | 3108 | 3105 | $\nu_s(=C_2\text{-H})$ IM |
| 3091 | 3094 | 3088 | 3093 | 3091 | 3097 | 3087 | 3094 | ν(C-H) [b]TP + bonded ν(C-H) IM broad |
| | 3060 | | 3065 | | 3061 | | 3058 | $\nu_s$(C-H) PSS |
| | 3023 | | 3025 | | 3020 | | 3024 | $\nu_s$(C-H) PSS |
| 2977 | | | | 2979 | | 2963 | | N-$CH_3$ $\nu_{as}$(C-H) |
| 2954 | 2953 | 2955 | 2960 | 2950 | 2960 | 2955 | 2960 | -$CH_3$ $\nu_{as}$(C-H) IM/TP |
| | | | 2943 | | 2945 | | 2944 | FR, -$CH_2$ $\nu_{as}$(C-H) |
| 2937 | 2932 | 2936 | 2933 | 2939 | 2933 | 2938 | 2931 | -$CH_2$ $\nu_{as}$(C-H) |
| 2924 | 2926 | 2927 | 2926 | 2929 | 2924 | 2927 | 2924 | -$CH_2$ $\nu_{as}$(C-H) |
| 2917 | 2918 | 2912 | 2917 | 2913 | 2918 | 2914 | 2917 | -$CH_2$ $\nu_{as}$(C-H) *trans* |
| 2905 | | | | | | 2906 | | FR, -$CH_2$ $\nu_s$(C-H) |
| 2898 | 2892 | 2899 | 2899 | 2899 | 2889 | 2895 | 2889 | FR, -$CH_2$ $\nu_s$(C-H) |
| 2884 | 2886 | 2880 | 2881 | 2882 | 2881 | 2882 | 2879 | FR, -$OCH_2$ $\nu_s$ (C-H)*ip* |
| 2870 | 2878 | 2868 | 2871 | | 2876 | 2877 | 2872 | -$CH_3$ $\nu_s$(C-H) |
| 2853 | 2860 | 2854 | 2860 | 2859 | 2864 | 2858 | 2864 | -$CH_2$ $\nu_s$(C-H) |
| | 2852 | | 2853 | | 2857 | | 2853 | -$CH_2$ $\nu_s$(C-H) |
| 1641 | 1668 | 1631 | 1662 | 1631 | 1668 | 1630 | 1673 | δ($H_2O$) |
| | 1599 | | 1599 | | 1599 | | 1599 | ν(C=C) PSS |
| 1575 | 1575 | 1573 | 1575 | 1573 | 1572 | 1573 | 1573 | δ(HCN) IM |
| 1563 | 1562 | 1564 | 1563 | 1564 | 1562 | 1562 | 1562 | |
| 1529 | 1539 | 1535 | 1537 | 1526 | 1536 | 1540 | 1543 | $\nu_{as}(C_\alpha{=}C_\beta\text{-})$ TP |
| | 1494 | | 1495 | | 1495 | | 1496 | ν(C=C) PSS |
| 1452 | 1451 | 1452 | 1453 | 1453 | 1455 | 1459 | 1451 | $\nu_s(C_\alpha{=}C_\beta\text{-})$ TP |
| 1446 | | | 1442 | 1442 | 1446 | 1450 | 1448 | δ($CH_2$) |
| 1424 | 1430 | 1427 | 1429 | 1428 | 1429 | 1427 | 1427 | $\nu_s(C_\alpha{=}C_\beta\text{-O})$ TP |
| | 1408 | | 1413 | | 1408 | | 1409 | ν(C=C) PSS |
| 1400 | | 1402 | | 1402 | | 1410 | | δ(-$CH_2$) alkyl |
| 1379 | 1380 | 1381 | 1381 | 1382 | 1376 | | 1377 | δ(N-$CH_3$) umbrella |
| | | 1358 | 1359 | 1355 | 1362 | 1362 | 1360 | ν(C-C) IM *ip* |
| 1353 | 1352 | 1344 | 1348 | 1339 | 1352 | 1351 | 1354 | δ(-$CH_2$) *wagg*. |
| | | | | | | | 1336 | $C_\beta$-$C_\beta$ str. TP |
| | 1294 | 1320 | | 1322 | 1293 | 1295 | 1294 | ν(C-N) + δ(H-$C_2$-N) IM |
| | 1281 | 1281 | | 1290 | | | | δ(-$CH_2$) *wagg.* |

| P4Me-3TOEIM | | P3TOPIM | | P3TOHIM | | P4Me-3TOHIM | | Assignment |
|---|---|---|---|---|---|---|---|---|
| **bulk** | **film** | **bulk** | **film** | **bulk** | **film** | **bulk** | **film** | |
| 1260 | 1265 | | | 1257 | 1264 | 1260 | | IM ν(ring) + alkyl δ($CH_2$) |
| | 1222 | | 1222 | | 1223 | | 1221 | **$\nu_{as}(SO_3^-)$ PSS** |
| | 1199 | | 1201 | | 1202 | | 1202 | |
| 1172 | 1172 | 1167 | 1165 | 1166 | 1163 | 1164 | 1167 | δ($C_\beta$-O) |
| | 1126 | | 1125 | | 1126 | | 1125 | **ν(C=C) PSS** |
| 1096 | | 1102 | | 1110 | 1109 | 1104 | 1107 | IM δ(N-$CH_3$) + δ(CNC) |
| 1080 | 1085 | 1074 | 1077 | 1081 | 1086 | 1082 | 1087 | C-O-C def. TP |
| | 1056 | | 1051 | | 1058 | | 1046 | **$\nu_s(SO_3^-)$ PSS** |
| 1047 | | | | 1037 | | 1036 | | ν($C_\beta$-alkyl) TP |
| | 1036 | | 1036 | | 1036 | | 1036 | $\nu_s(SO_3^-)$ PSS |
| 1020 | | 1020 | | 1021 | | 1020 | | γ(-$CH_2$) |
| | 1011 | | 1009 | | 1011 | | 1010 | δ(C=C), *in plane* PSS |
| 965 | | | | | | 978 | | $\nu_s$($C_\beta$-O) all-*trans* |
| 848 | | 831 | | 829 | | 866 | | γ($C_\beta$-H) aryl |
| 752 | | 740 | | 740 | | 820 | | δ(-$CH_2$) *rock* |
| 704 | | 706 | | 683 | | 718 | | δ(ring) TP |
| 652 | | 648 | | 650 | | 653 | | δ(ring) IM |
| 622 | | 622 | | 623 | | 621 | | δ(ring) IM |

[a]IM = methyl imidazolium , [b]TP = thiophene, PSS modes

*References: TP[1], PSS[2], IM[3]


(1) (a) Pron, A.; Louarn, G.; Lapkowski, M.; Zagórska. M.; Glowczyk-Zubek, J.; Lefrant, S. *Macromolecules* **1995**, *28*, 4644 (b) Villa, E.; Agosti, E.; Castiglioni, C.; Gallazzi, M. C.; Zerbi, G. *J. Chem. Phys.* **1996**, *105*, 9461 (c) Louarn, G.; Buisson, J. P.; Lefrant, S.; Fichou, D. *J. Phys. Chem.* **1995**, *99,* 11399 (d) Garreau, S.; Louarn, G.; Buisson, J. P.; Froyer, G.; Lefrant, S. *Macromolecules* **1999,** *32,* 6807 (e) Louarn, G.; Mevellec, J. Y.; Buisson, J. P.; Lefrant, S. *Synth. Met.* **1993**, *55-57*, 587 (f) Zerbi, G.; Chierichetti, B.; Ingänas, O. *J. Chem. Phys.* **1991**, *94*, 4646 (g) Casado, J.; Katz, H. E.; Hernández, V.; López Navarrete, J. T. *Vib. Spectrosc.* **2002**, *30*, 175 (h) Liedberg, B.; Yang, Z.; Engquist, I.; Wirde, M.; Gelius, U.; Götz, G.; Bäuerle, P.; Rummel, R. –M.; Ziegler, Ch; Göpel, W. *J. Phys. Chem. B* **1997,** *101,* 5951 (i) Garreau, S.; Leclerc, M.; Errien, N.; Louarn, G. *Macromolecules* **2003**, *36*, 692 (j) Buga, K.; Kepczynska, K.; Kulszewicz-Bajer, I.; Zagórska, M.; Demadrille, R.; Pron, A.; Quillard, S.; Lefrant, S. *Macromolecules* **2004**, *37*, 769 (k) Garreau, S.; Louarn, G.; Buisson, J. P.; Froyer, G.; Lefrant, S. *Macromolecules* **1999**, *32*, 6807 (l) Louarn, G.; Trznadel, M.; Buisson, J. P.; Laska, J.; Pron, A.; Lapkowski, M.; Lefrant, S. *J. Phys. Chem.* **1996**, *100*, 12532

(2) Zundel, G. in *Hydration and Intermolecular Interaction*; Academic Press, New York, 1969

(3) (a) Cordes, M.; Walter, J. L. *Spectrochim. Acta* **1968**, *24A*, 237 (b) Sadlej, J.; Jaworski, A.; Miaskiewicz, K. *J. Mol. Struct.* **1992**, *274*, 247 (c) Bukowska, J.; Kudelski, A.; Jackowska, K. *J. Electroanal. Chem.* **1991**, *309*, 251 (d) Bellocq, A.-M.; Garrigou-Lagrange, C. *Spectrochim. Acta* **1971**, *27A*, 1091 (e) Dieter, K. M.; Dymek, C. J, Jr.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722 (f) Tait, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4352 (g) Elaiwi, A.; Hitchcock, P. B.; Seddon, K. R.;Srinivasan, N.; Tan, Y. M.; Welton, T.; Zora, J. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3467 (h) Kölle, P.; Dronskowski, R. *Inorg. Chem.* **2004**, *43*, 2803

Density of PT-based aggregates in $(PT/PSS)_{10}$ multilayers (125-200 nm range).

| Film | Density (particles/$\mu m^2$) |
|---|---|
| $(P3TOPIM/PSS)_{10}$ | 32 |
| $(P4Me\text{-}3TOEIM/PSS)_{10}$ | 26 |
| $(P3TOHIM/PSS)_{10}$ | 35 |
| $(P4Me\text{-}3TOHIM/PSS)_{10}$ | 125 |