Science Advances

AAAS

advances.sciencemag.org/cgi/content/full/3/10/eaao0476/DC1

Supplementary Materials for

Design of flexible polyphenylene proton-conducting membrane for next-generation fuel cells

Junpei Miyake, Ryunosuke Taki, Takashi Mochizuki, Ryo Shimizu, Ryo Akiyama, Makoto Uchida, Kenji Miyatake

Published 25 October 2017, *Sci. Adv.* **3**, eaao0476 (2017)
DOI: 10.1126/sciadv.aao0476

This PDF file includes:

Supplementary Figures

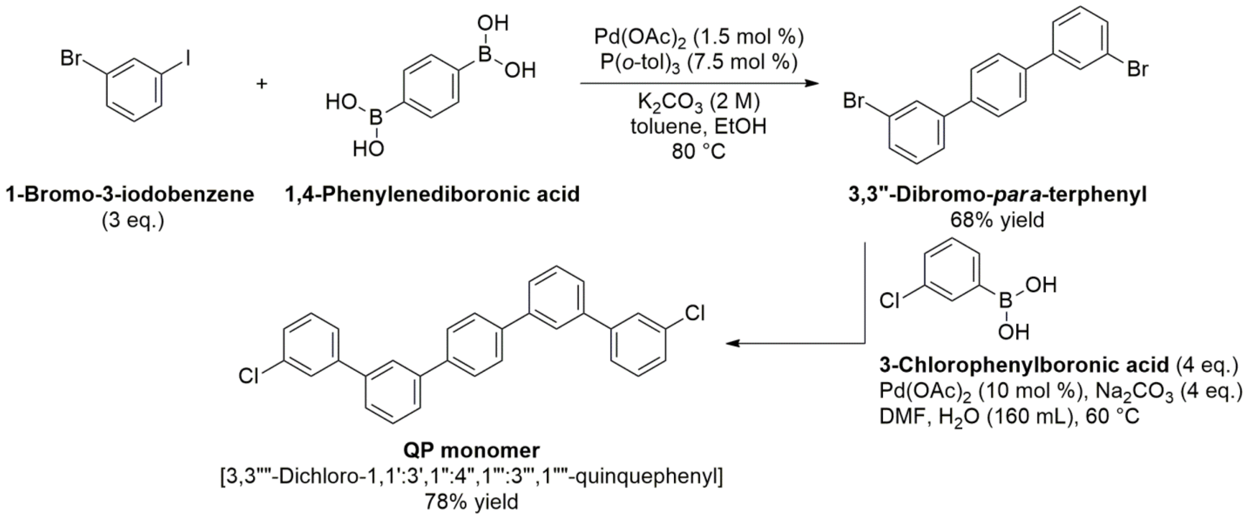


fig. S1. Synthesis of QP monomer.

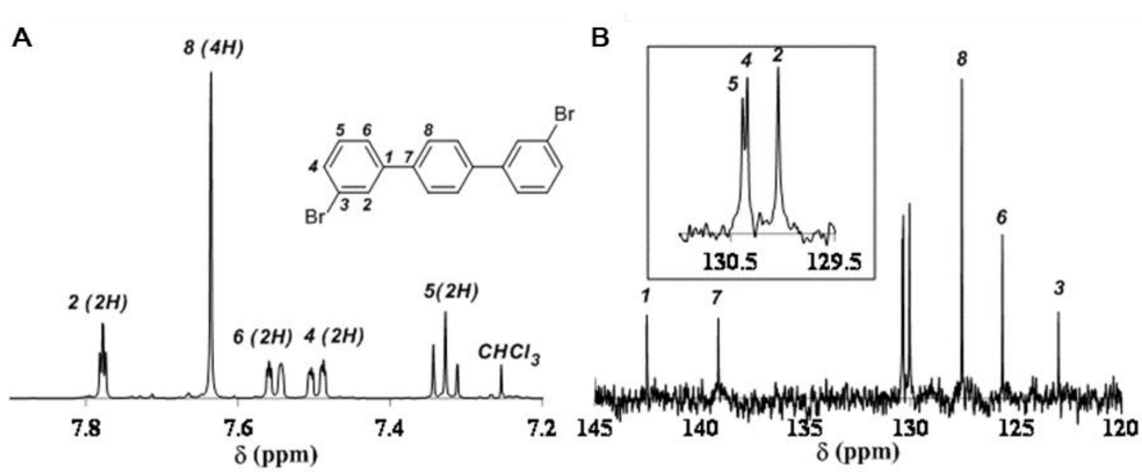


fig. S2. NMR assignment of 3,3″-dibromo-*para*-terphenyl. (**A**) ^{1}H NMR (500 MHz, $CDCl_3$) spectrum; δ 7.33 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.48−7.51 (m, 2H), 7.54−7.57 (m, 2H), 7.64 (s, 4H), 7.78 (m, 2H). (**B**) ^{13}C NMR (125 MHz, $CDCl_3$) spectrum; δ 123.0, 125.6, 127.6, 130.0, 130.3, 139.1, 142.5.

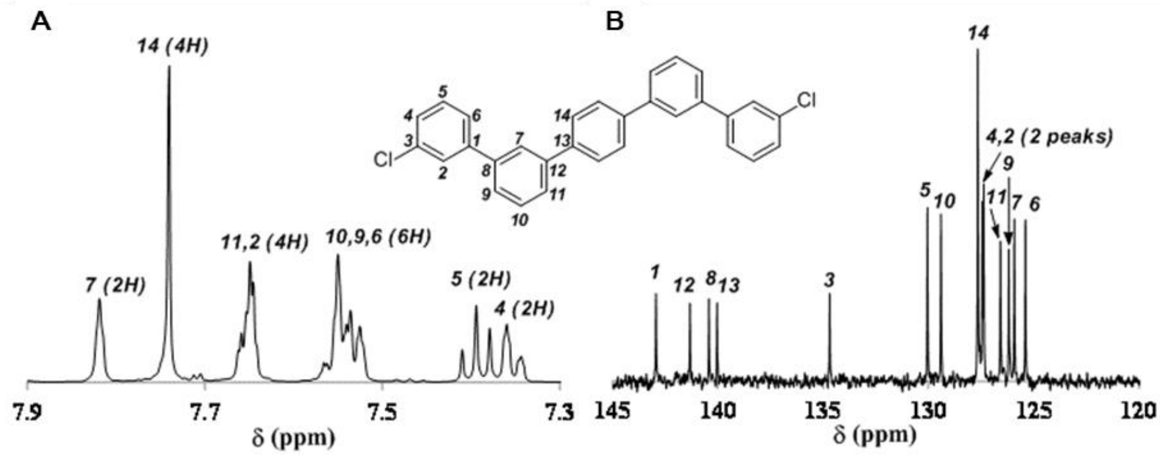


fig. S3. NMR assignment of QP monomer. (**A**) ^{1}H NMR (500 MHz, $CDCl_3$) spectrum; δ 7.36−7.37 (m,. 2H), 7.41 (dd, J = 7.8, 7.8 Hz, 2H), 7.52−7.59 (m, 6H), 7.65−7.68 (m, 4H), 7.75 (s, 4H), 7.83 (m, 2H). (**B**) ^{13}C NMR (125 MHz, $CDCl_3$) spectrum; δ 125.4, 125.9, 126.1, 126.6, 127.37, 127.44, 127.6, 129.4, 130.0, 134.7, 140.0, 140.4, 141.3, 142.9.

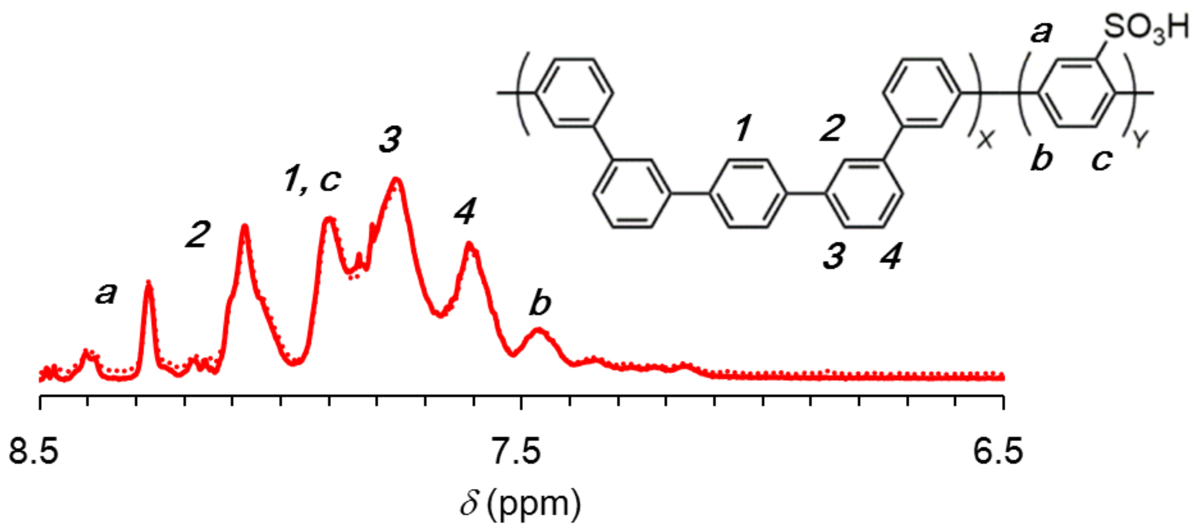


fig. S4. ^{1}H NMR assignment of SPP-QP (titrated IEC = 2.4 mmol g^{-1}) copolymer. Comparison of before (**solid line**) and after (**dotted line**) the oxidative stability test in Fenton's solution (aqueous solution containing 3% H_2O_2 and 2ppm Fe^{2+}) at 80 °C for 1 h. The ^{1}H NMR measurement was conducted at 80 °C in DMSO-d_6.

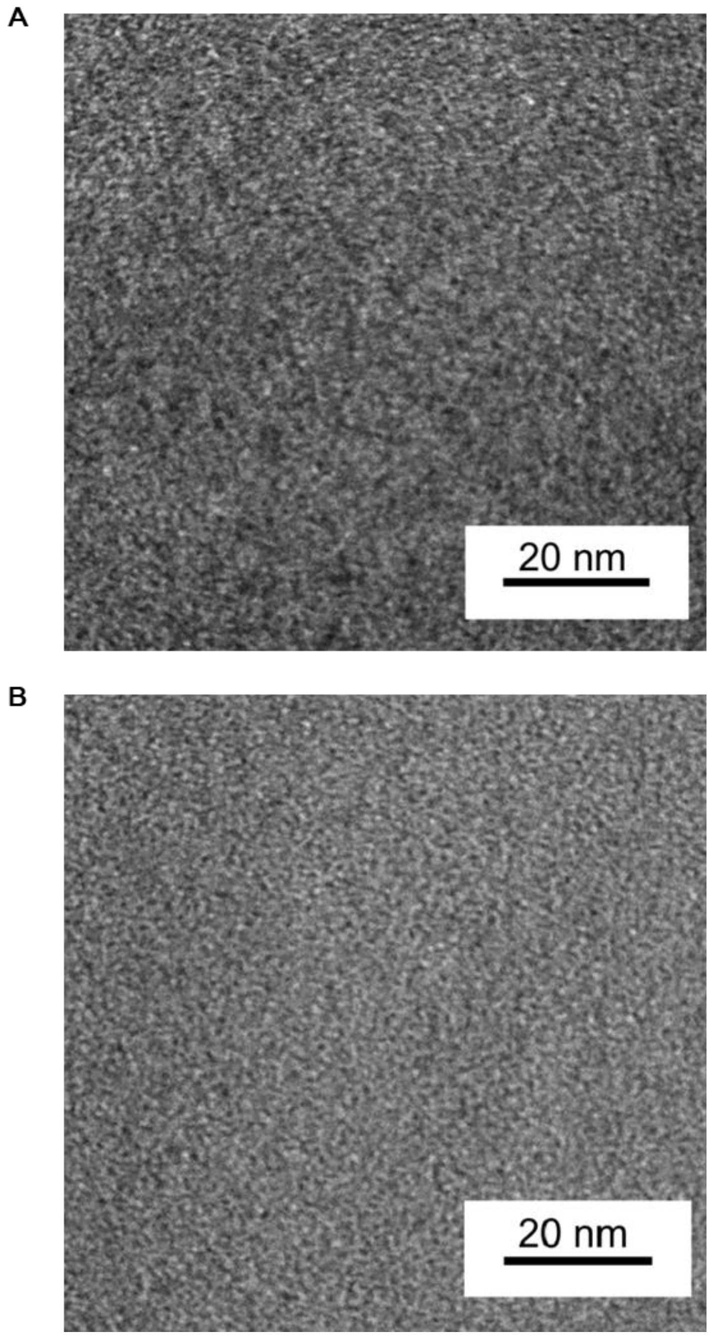


fig. S5. Morphology of SPP-QP (titrated IEC = 2.4 mmol g^{-1}) membrane. TEM images of (**A**) before and (**B**) after the oxidative stability test in Fenton's solution (aqueous solution containing 3% H_2O_2 and 2ppm Fe^{2+}) at 80 °C for 1 h. The samples were stained with lead ions (Pb^{2+}) prior to the observation.

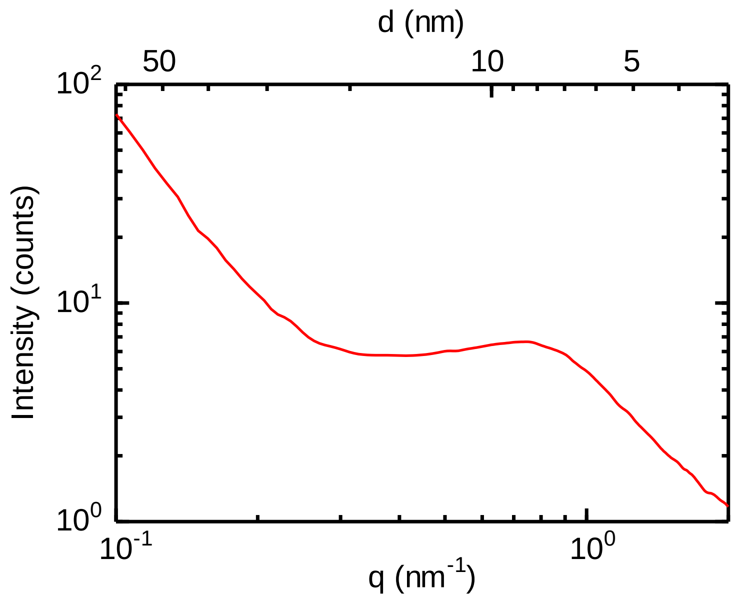


fig. S6. SAXS profile. The measurement was conducted with the SPP-QP membrane (titrated IEC = 2.7 mmol g^{-1}) at 80 °C and 30% RH.

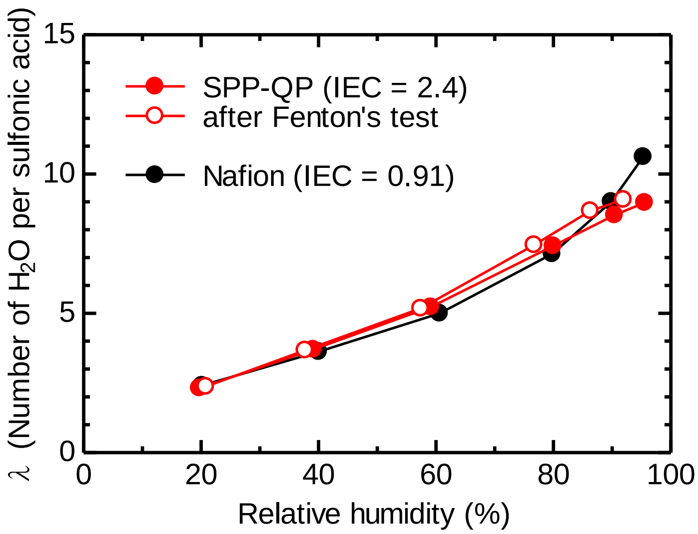


fig. S7. Number of absorbed water molecules per sulfonic acid group (λ). The *λ* values of PEMs at 80 °C as a function of relative humidity (RH). The IEC values (mmol g^{-1}) in parentheses were determined by acid-base titration. Fenton's test was conducted by immersing the membrane in Fenton's solution (aqueous solution containing 3% H_2O_2 and 2ppm Fe^{2+}) at 80 °C for 1 h. The solid lines are guides for the eye.

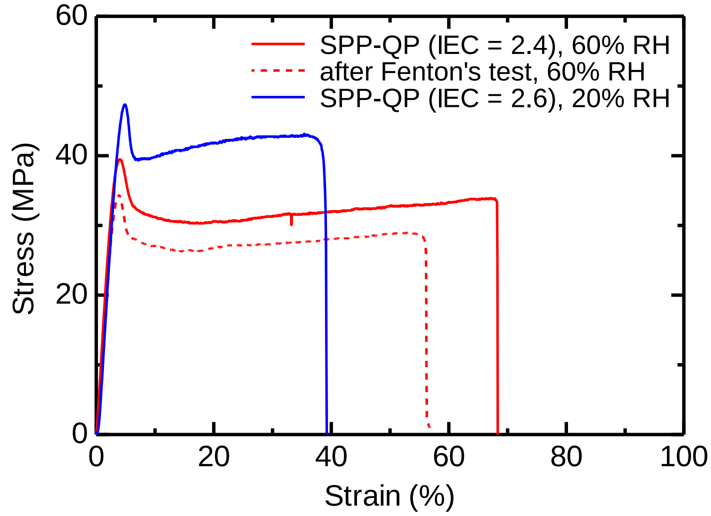


fig. S8. Stress versus strain curves. The measurement was conducted at 80 °C and 60% RH or 20% RH. Fenton's test was conducted by immersing the membrane in Fenton's solution (aqueous solution containing 3% H_2O_2 and 2ppm Fe^{2+}) at 80 °C for 1 h.

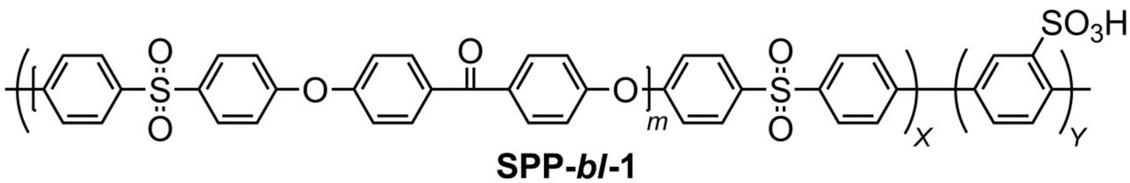


fig. S9. Chemical structure of the SPP-*bl*-1 copolymer.

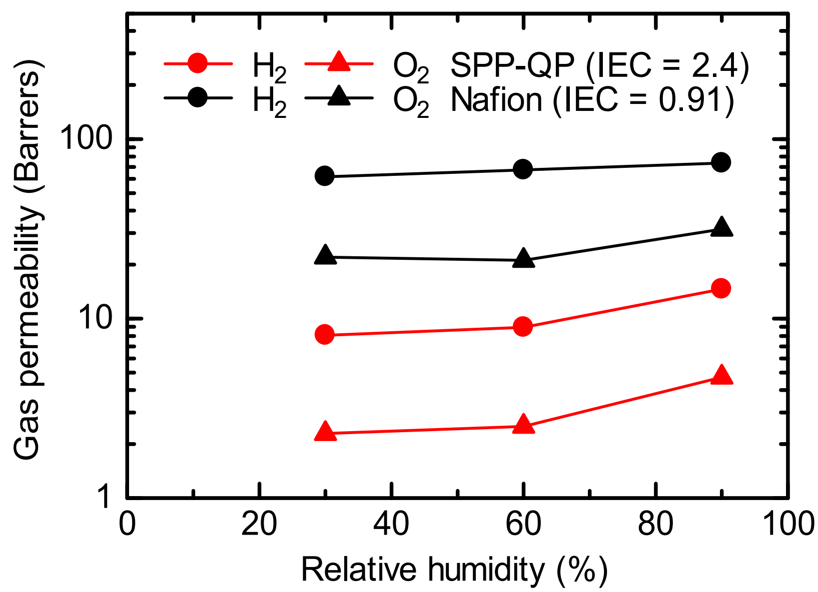


fig. S10. Hydrogen and oxygen permeability. The measurement was conducted at 80 °C as a function of RH. The solid lines are guides for the eye. 1 Barrer = 10^{-10} cm^3 (STD) cm cm^{-2} s^{-1} $cmHg^{-1}$.

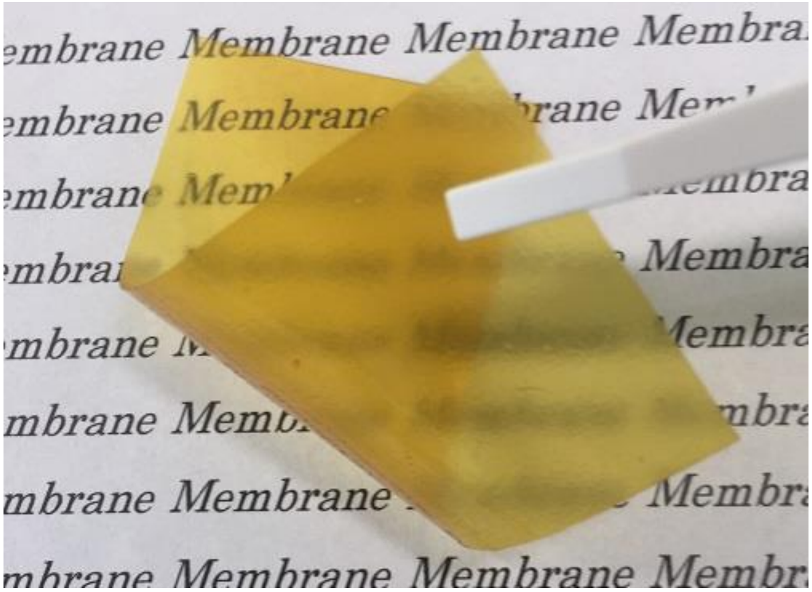


fig. S11. Membrane durability and flexibility. The picture was taken after immersing the SPP-QP membrane (titrated IEC = 2.4 mmol g^{-1}) in Fenton's solution (aqueous solution containing 3% H_2O_2 and 2ppm Fe^{2+}) at 80 °C for 1 h.

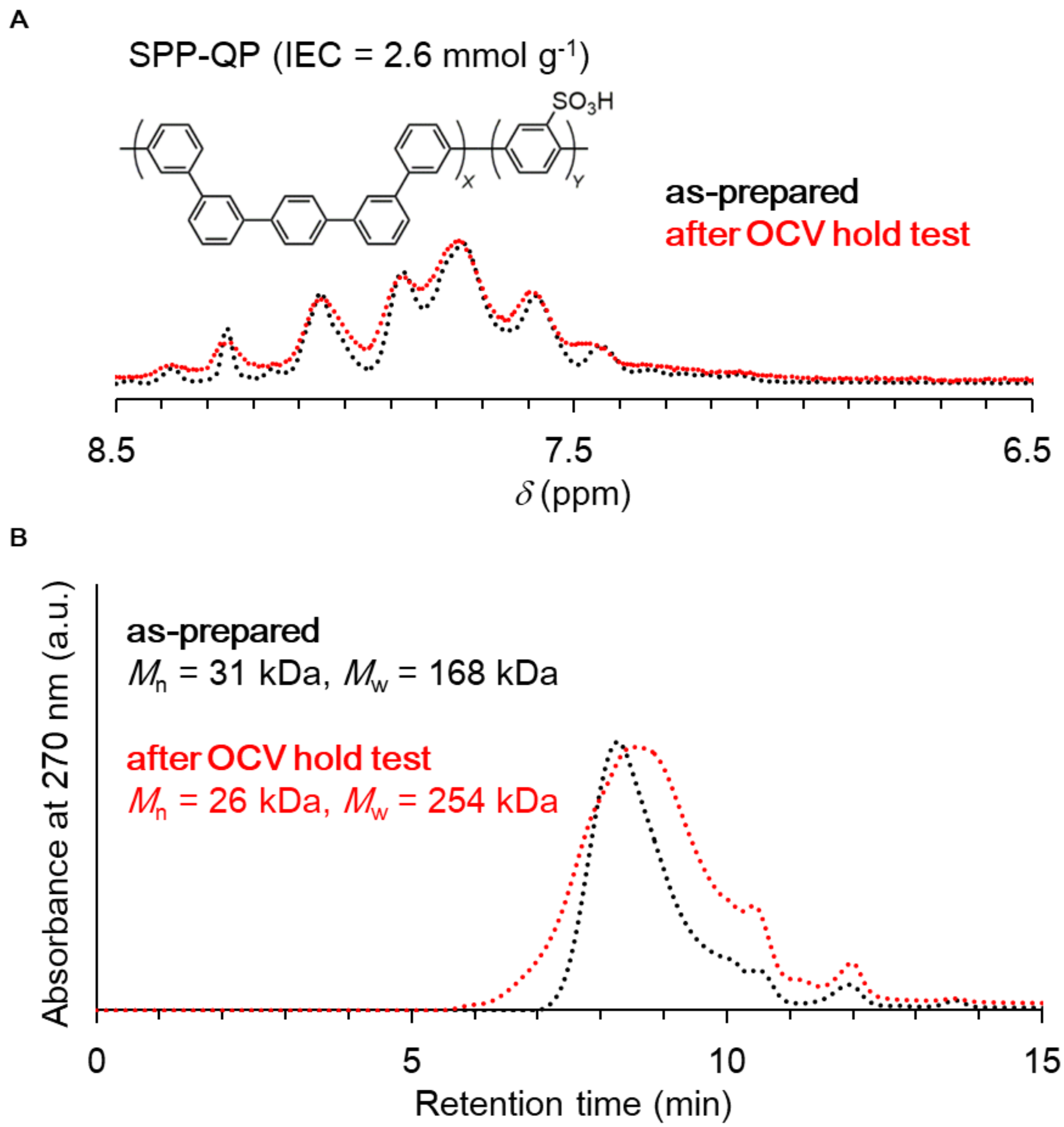


fig. S12. The effect of the OCV hold test on the molecular structure of the SPP-QP membrane (IEC = 2.6 mmol g^{-1}). (**A**) ^{1}H NMR spectra at 80 °C in DMSO-d_6. (**B**) GPC profiles. OCV hold test: 30% RH, H_2/air, 80 °C, 1000 h.

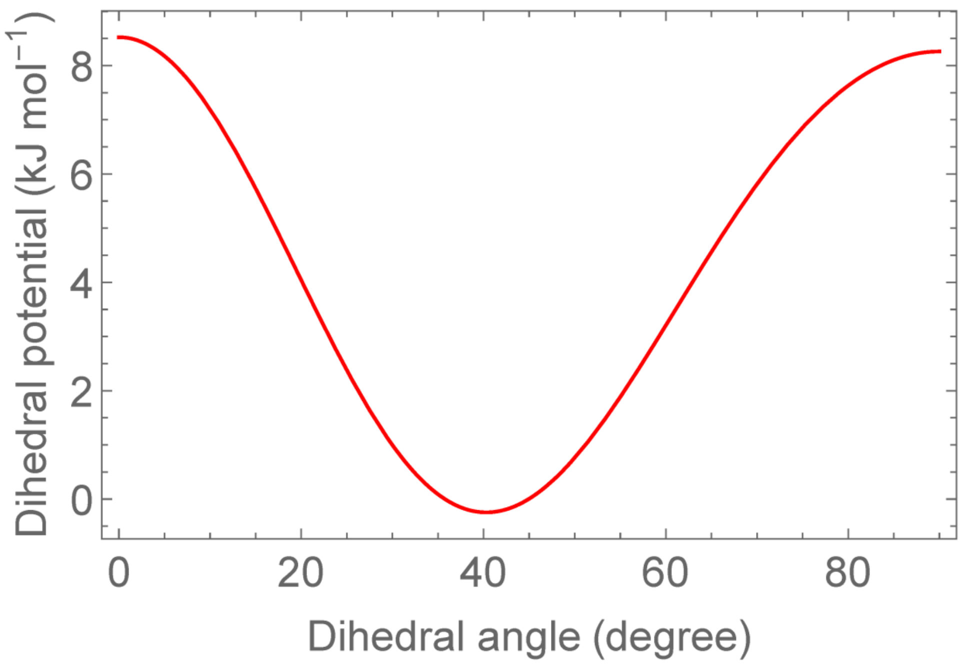
Mathematica Notebook

・**Torsional potential of biphenyl**

bpfitf[x_]=4.184*1.003626-4.184*0.155120 Cos[2Pi (x) / 180]+4.184*1.002066 Cos[4Pi (x) / 180]+4.184*0.186577 Cos[6Pi (x) / 180]

4.19917 -0.649022 Cos[(π x)/90]+4.19264 Cos[(π x)/45]+0.780638 Cos[(π x)/30]

Plot[bpfitf[x],{x,0,90},PlotStyle->{Red,Thickness[0.004]},PlotRange->All,Frame->True,Axes->False,FrameTicks->True,FrameLabel->{"Dihedral angle (degree)","Dihedral potential (kJ mol^{-1})"},LabelStyle->Directive[FontFamily->"Arial",16]]



・**Dihedral distribution of biphenyl using Boltzmann Factors**

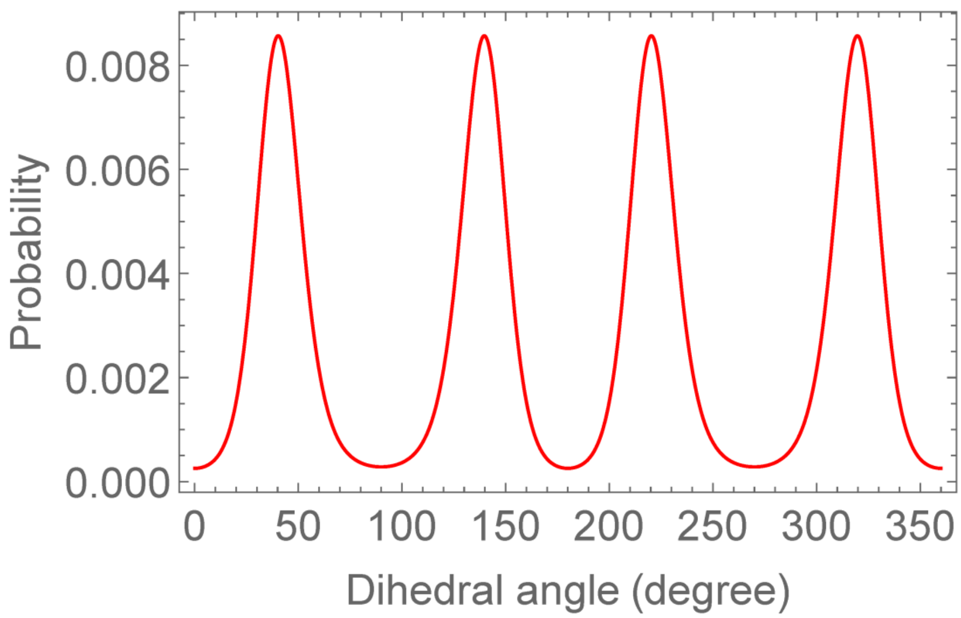
kTval=300 QuantityMagnitude["MolarGasConstant","Kilo""Joules"/("Kelvins" "Moles")]

2.49434

normVal=4 NIntegrate[Exp[-bpfitf[x]/kTval],{x,0,90}];

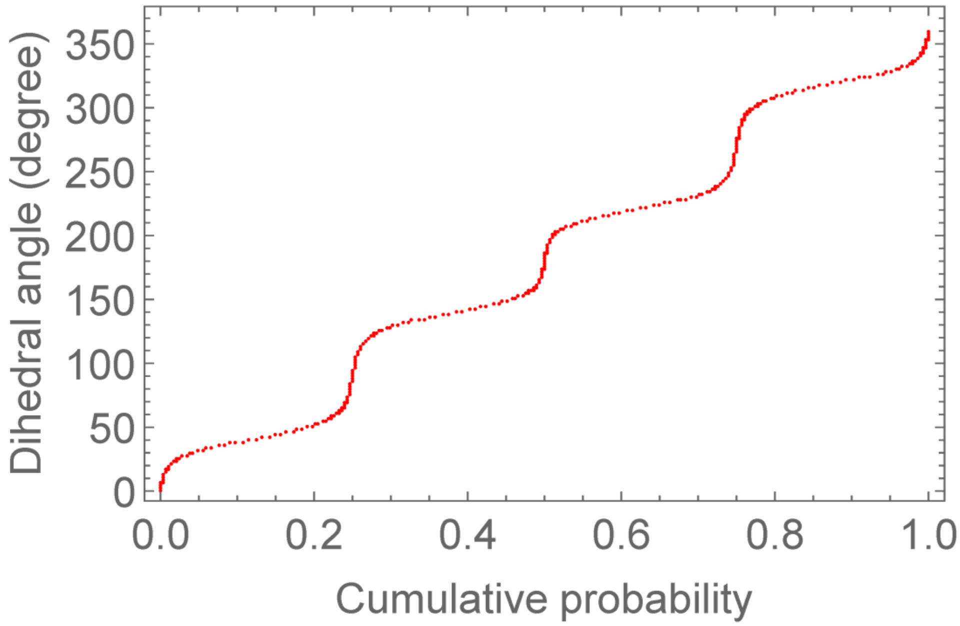
Clear[prob];

```
prob[x_]:=Exp[-bpfitf[x]/kTval]/normVal/;0<=x<=90;
prob[x_]:=prob[180-x]/;90<x<=180;
prob[x_]:=prob[x-180]/;180<x<=270;
prob[x_]:=prob[360-x]/;270<x<=360;
Plot[prob[x],{x,0,360},PlotStyle->{Red,Thickness[0.004]},PlotRange->All,Frame->True,FrameTicks->True,FrameLabel->{"Dihedral angle (degree)","Probability"},LabelStyle->Directive[FontFamily->"Arial",16]]
```



・**Cumulative probability for biphenyl**

```
pIntTable=Quiet[Table[{NIntegrate[prob[xp],{xp,0,x}],x},{x,0,360}]];
ListPlot[pIntTable,PlotStyle->{Red,PointSize[0.004]},Frame->True,FrameTicks->True,
 FrameLabel->{"Cumulative probability","Dihedral angle (degree)"},
 LabelStyle->Directive[FontFamily->"Arial",16]]
```

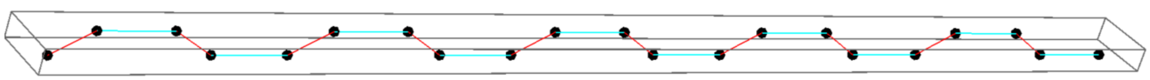



```
bp[prob_]=Interpolation[pIntTable][prob];
```

meta:100%

・**Molecular geometry**

```
lccc=2.42690;
lcc=1.48358;
e[1]=lccc{0,0,1};
e[2]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[3]=lccc{0,0,1};
e[4]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
chain[n_]:=Prepend[Accumulate[Table[e[Mod[k,4,1]],{k,1,n}]],{0,0,0}]
drawChain[pts_]:=Graphics3D[{PointSize[0.01],Point/@pts,
  Table[{Hue[(1/2)Mod[i,2]],Line[{pts[[i]],pts[[i+1]]}]},{i,1,Length[pts]-1}]}]
drawChain[chain[20]]
```



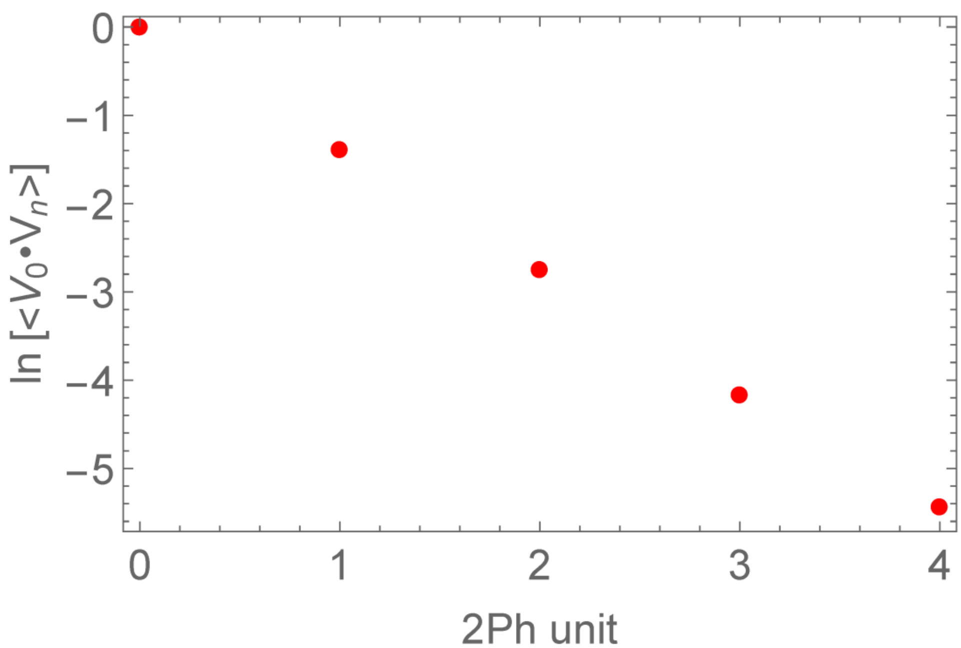
・**Rotation matrix to rotate a backbone dihedral angle**

```
dihedralRotate[pts_,nb_?EvenQ,theta_]:=Module[{},
 vec=pts[[nb+1]]-pts[[nb]];
 origin=pts[[nb]];
 rot=RotationMatrix[theta,vec];
 Join[Take[pts,nb],origin+(rot.(#-origin))&/@Drop[pts,nb]]]
```

・**Tangent-tangent correlation function**

```
cosVals[pts_]:=Table[(pts[[k]]-pts[[k-1]]).(pts[[3]]-pts[[2]])/
  (Norm[pts[[k]]-pts[[k-1]]]Norm[pts[[3]]-pts[[2]]]),{k,3,Length[pts],4}]
```

```
randomRotate[pts_]:=Module[{},
  newpts=pts;
  Do[newpts=dihedralRotate[newpts,k,bp[RandomReal[]]],{k,2,Length[pts],2}];
  newpts]
Clear[ch];
ch=chain[40];
cosList=ParallelTable[cosVals[randomRotate[ch]],{100000}];
corr=Plus@@cosList/100000;
ListPlot[Table[{i-1,Log[corr[[i]]]},{i,1,5}],
 PlotStyle->{Red,PointSize[0.02]},Frame->True,FrameTicks->True,
 FrameLabel->{"2Ph unit","ln [<V₀•Vₙ>]"},
 LabelStyle->Directive[FontFamily->"Arial",16]]
```



・**Calculation of persistence length (lp)**

logFitallmetaPh2[x_]=Fit[Log[corr[[1;;4]]],{1,x},x]

1.38649 -1.38475 x

-1/logFitallmetaPh2'[x]

0.722152

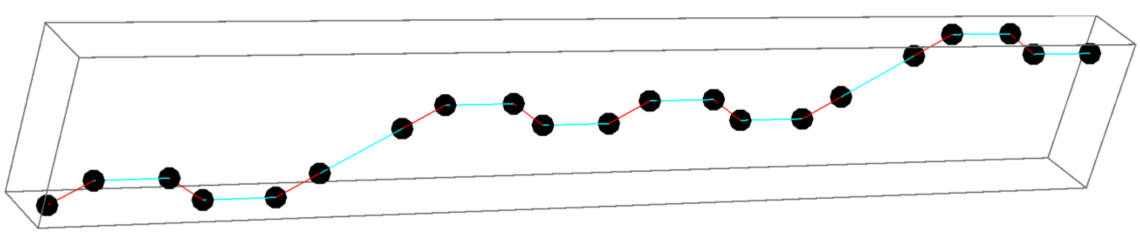
lp=Norm[$\sum_{i=1}^{4} e[i]$]*0.722152/10

0.536085

meta:80%

・**Molecular geometry**

```
lccc=2.42690;
lcc=1.48358;
lcccc=2.80996;
e[1]=lccc{0,0,1};
e[2]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[3]=lccc{0,0,1};
e[4]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[5]=lcccc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[6]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[7]=lccc{0,0,1};
e[8]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[9]=lccc{0,0,1};
e[10]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
chain[n_]:=Prepend[Accumulate[Table[e[Mod[k,10,1]],{k,1,n}]],{0,0,0}]
drawChain[pts_]:=Graphics3D[{PointSize[0.02],Point/@pts,
  Table[{Hue[(1/2)Mod[i,2]],Line[{pts[[i]],pts[[i+1]]}]},{i,1,Length[pts]-1}]}]
drawChain[chain[20]]
```

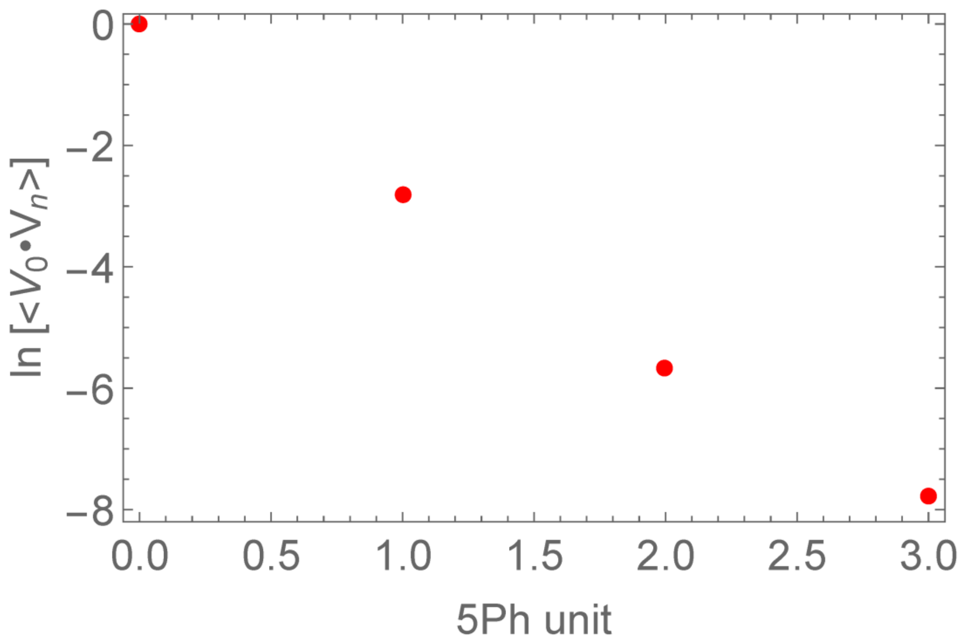


・**Rotation matrix to rotate a backbone dihedral angle**

```
dihedralRotate[pts_,nb_?EvenQ,theta_]:=Module[{},
  vec=pts[[nb+1]]-pts[[nb]];
  origin=pts[[nb]];
  rot=RotationMatrix[theta,vec];
  Join[Take[pts,nb],origin+(rot.(#-origin))&/@Drop[pts,nb]]]
```

・**Tangent-tangent correlation function**

```
cosVals[pts_]:=Table[(pts[[k]]-pts[[k-1]]).(pts[[3]]-pts[[2]])/
   (Norm[pts[[k]]-pts[[k-1]]]Norm[pts[[3]]-pts[[2]]]),{k,3,Length[pts],10}]
randomRotate[pts_]:=Module[{},
  newpts=pts;
  Do[newpts=dihedralRotate[newpts,k,bp[RandomReal[]]],{k,2,Length[pts],2}];
  newpts]
Clear[ch];
ch=chain[100];
cosList=ParallelTable[cosVals[randomRotate[ch]],{100000}];
corr=Plus@@cosList/100000;
ListPlot[Table[{i-1,Log[corr[[i]]]},{i,1,4}],
 PlotStyle->{Red,PointSize[0.02]},Frame->True,FrameTicks->True,
 FrameLabel->{"5Ph unit","ln [<V0•Vn>]"},
 LabelStyle->Directive[FontFamily->"Arial",16]]
```



・**Calculation of persistence length (lp)**

logFitQP[x_]=Fit[Log[corr[[1;;3]]],{1,x},x]

2.83261 -2.82565 x

-1/logFitQP'[x]

0.353901

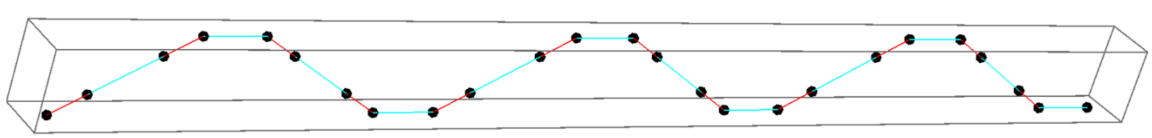
lp=Norm[$\sum_{i=1}^{10} e[i]$]*0.353901/10

0.661402

meta:50%

・**Molecular geometry**

```
lccc=2.42690;
lcc=1.48358;
lcccc=2.80996;
e[1]=lccc{0,0,1};
e[2]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[3]=lcccc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[4]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[5]=lccc{0,0,1};
e[6]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[7]=lcccc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[8]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
chain[n_]:=Prepend[Accumulate[Table[e[Mod[k,8,1]],{k,1,n}]],{0,0,0}]
drawChain[pts_]:=Graphics3D[{PointSize[0.01],Point/@pts,
  Table[{Hue[(1/2)Mod[i,2]],Line[{pts[[i]],pts[[i+1]]}]},{i,1,Length[pts]-1}]}]
drawChain[chain[24]]
```



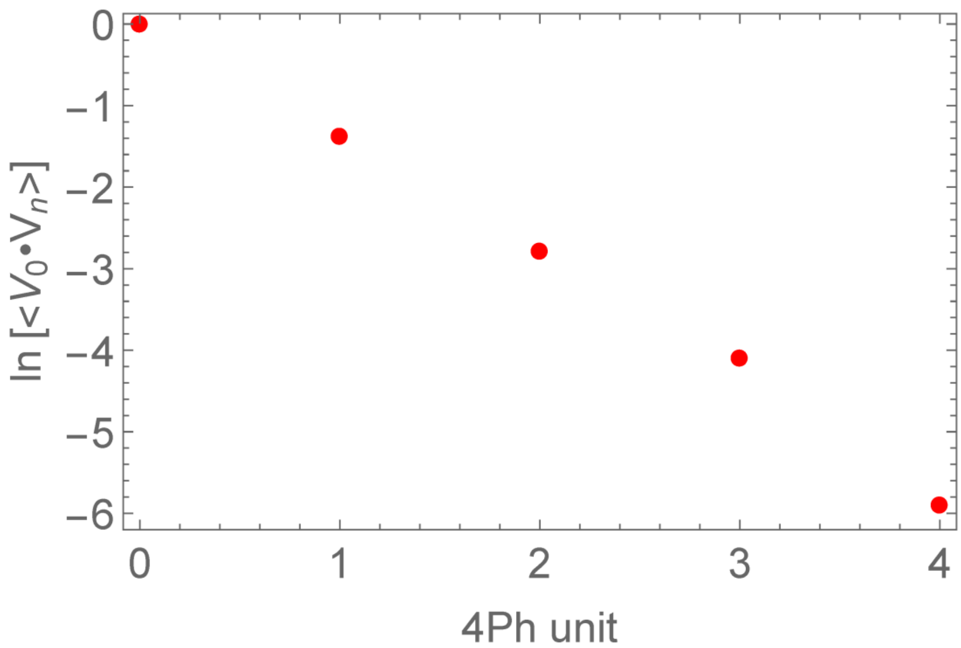
・**Rotation matrix to rotate a backbone dihedral angle**

```
dihedralRotate[pts_,nb_?EvenQ,theta_]:=Module[{},
 vec=pts[[nb+1]]-pts[[nb]];
 origin=pts[[nb]];
```

```
  rot=RotationMatrix[theta,vec];
  Join[Take[pts,nb],origin+(rot.(#-origin))&/@Drop[pts,nb]]]
```

• **Tangent-tangent correlation function**

```
cosVals[pts_]:=Table[(pts[[k]]-pts[[k-1]]).(pts[[3]]-pts[[2]])/
   (Norm[pts[[k]]-pts[[k-1]]]Norm[pts[[3]]-pts[[2]]]),{k,3,Length[pts],8}]
randomRotate[pts_]:=Module[{},
  newpts=pts;
  Do[newpts=dihedralRotate[newpts,k,bp[RandomReal[]]],{k,2,Length[pts],2}];
  newpts]
Clear[ch];
ch=chain[80];
cosList=ParallelTable[cosVals[randomRotate[ch]],{100000}];
corr=Plus@@cosList/100000;
ListPlot[Table[{i-1,Log[corr[[i]]]},{i,1,5}],
 PlotStyle->{Red,PointSize[0.02]},Frame->True,FrameTicks->True,
 FrameLabel->{"4Ph unit","ln [<V0•Vn>]"},
 LabelStyle->Directive[FontFamily->"Arial",16]]
```



・**Calculation of persistence length (lp)**

logFitm1p1Ph4[x_]=Fit[Log[corr[[1;;3]]],{1,x},x]

1.3978 -1.39148 x

-1/logFitm1p1Ph4'[x]

0.718658

lp=Norm[$\sum_{i=1}^{8} e[i]$]*0.718658/10

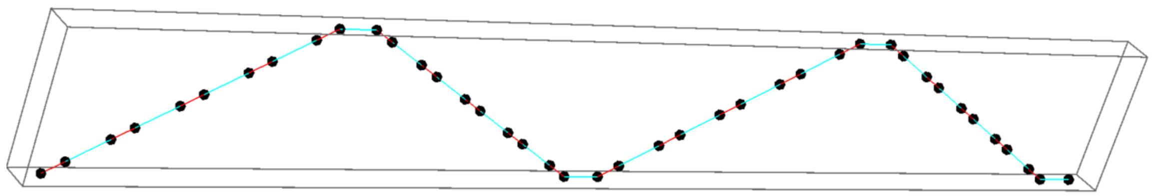
1.06793

meta:20%

・**Molecular geometry**

```
lccc=2.42690;
lcc=1.48358;
lcccc=2.80996;
e[1]=lccc{0,0,1};
e[2]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[3]=lcccc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[4]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[5]=lcccc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[6]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[7]=lcccc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[8]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[9]=lcccc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[10]=lcc{Sin[Pi/6.],0,Cos[Pi/6.]};
e[11]=lccc{0,0,1};
e[12]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[13]=lcccc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[14]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[15]=lcccc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[16]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[17]=lcccc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[18]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[19]=lcccc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
e[20]=lcc{Sin[-Pi/6.],0,Cos[-Pi/6.]};
chain[n_]:=Prepend[Accumulate[Table[e[Mod[k,20,1]],{k,1,n}]],{0,0,0}]
drawChain[pts_]:=Graphics3D[{PointSize[0.01],Point/@pts,
```

```
  Table[{Hue[(1/2)Mod[i,2]],Line[{pts[[i]],pts[[i+1]]}]},{i,1,Length[pts]-1}]}]
drawChain[chain[40]]
```



・Rotation matrix to rotate a backbone dihedral angle

```
dihedralRotate[pts_,nb_?EvenQ,theta_]:=Module[{},
  vec=pts[[nb+1]]-pts[[nb]];
  origin=pts[[nb]];
  rot=RotationMatrix[theta,vec];
  Join[Take[pts,nb],origin+(rot.(#-origin))&/@Drop[pts,nb]]]
```

・Tangent-tangent correlation function

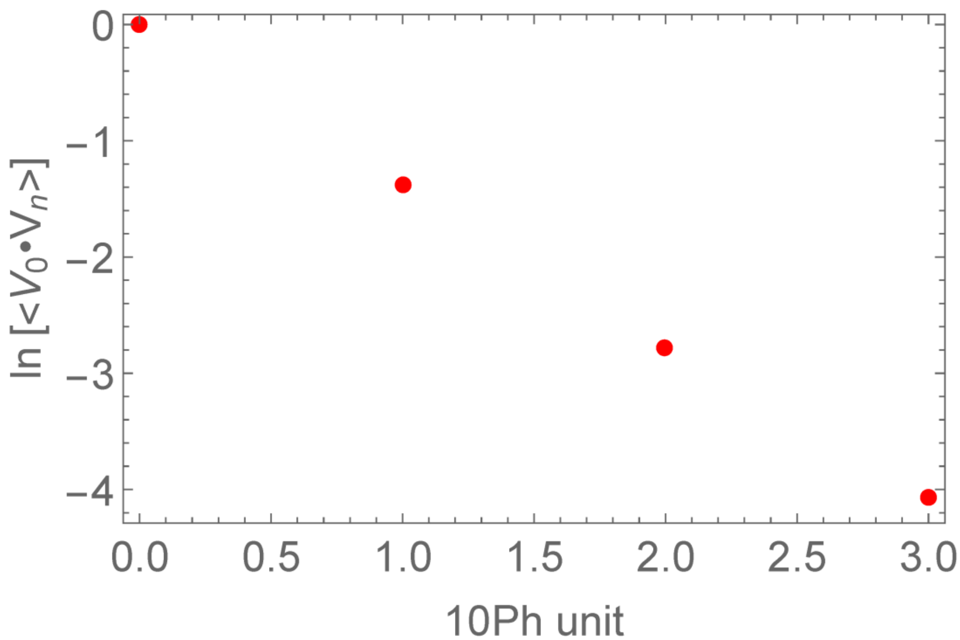
```
cosVals[pts_]:=Table[(pts[[k]]-pts[[k-1]]).(pts[[3]]-pts[[2]])/
   (Norm[pts[[k]]-pts[[k-1]]]Norm[pts[[3]]-pts[[2]]]),{k,3,Length[pts],20}]
randomRotate[pts_]:=Module[{},
  newpts=pts;
  Do[newpts=dihedralRotate[newpts,k,bp[RandomReal[]]],{k,2,Length[pts],2}];
  newpts]
Clear[ch];
ch=chain[200];
cosList=ParallelTable[cosVals[randomRotate[ch]],{100000}];
corr=Plus@@cosList/100000;
```

ListPlot[Table[{i-1,Log[corr[[i]]]},{i,1,4}],

PlotStyle->{Red,PointSize[0.02]},Frame->True,FrameTicks->True,

FrameLabel->{"10Ph unit","ln [<V_0•V_n>]"},

LabelStyle->Directive[FontFamily->"Arial",16]]



・**Calculation of persistence length (lp)**

logFitm1p4Ph10[x_]=Fit[Log[corr[[1;;3]]],{1,x},x]

1.39169 -1.38967 x

-1/logFitm1p4Ph10'[x]

0.719597

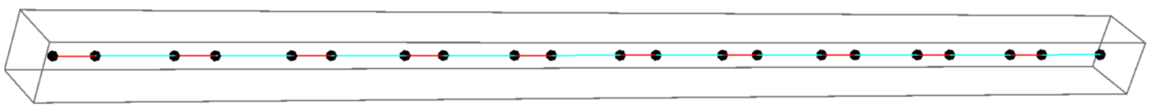
lp=Norm[$\sum_{i=1}^{20} e[i]$]*0.719597/10

2.67474

meta:0%

・**Molecular geometry**

```
lcccc=2.80996;
lcc=1.48358;
e[1]=lcccc{0,0,1};
e[2]=lcc{0,0,1};
chain[n_]:=Prepend[Accumulate[Table[e[Mod[k,2,1]],{k,1,n}]],{0,0,0}]
drawChain[pts_]:=Graphics3D[{PointSize[0.01],Point/@pts,
  Table[{Hue[(1/2)Mod[i,2]],Line[{pts[[i]],pts[[i+1]]}]},{i,1,Length[pts]-1}]}]
drawChain[chain[20]]
```



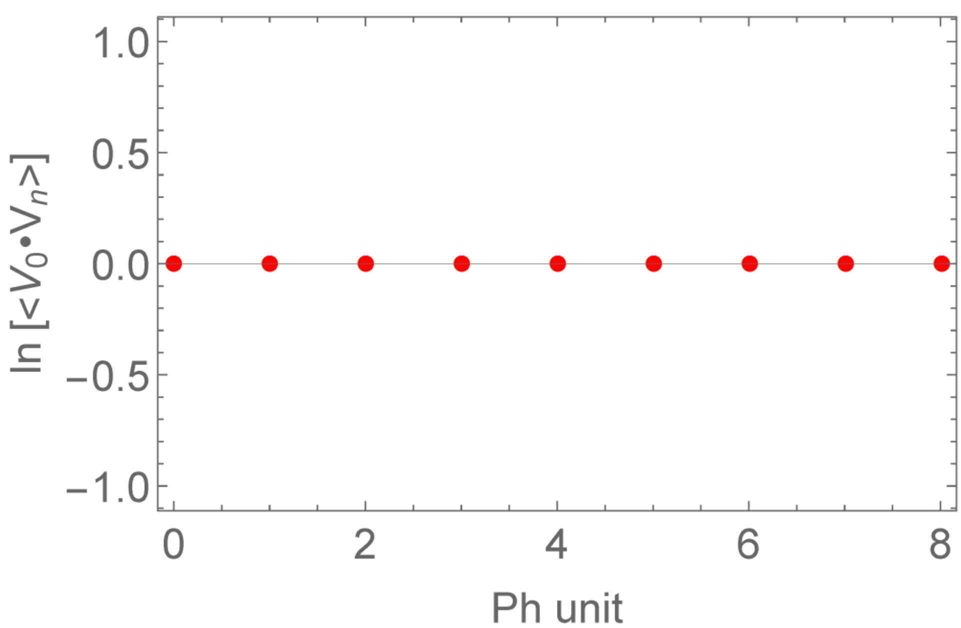
・**Rotation matrix to rotate a backbone dihedral angle**

```
dihedralRotate[pts_,nb_?EvenQ,theta_]:=Module[{},
 vec=pts[[nb+1]]-pts[[nb]];
 origin=pts[[nb]];
 rot=RotationMatrix[theta,vec];
 Join[Take[pts,nb],origin+(rot.(#-origin))&/@Drop[pts,nb]]]
```

・**Tangent-tangent correlation function**

```
cosVals[pts_]:=Table[(pts[[k]]-pts[[k-1]]).(pts[[3]]-pts[[2]])/
  (Norm[pts[[k]]-pts[[k-1]]]Norm[pts[[3]]-pts[[2]]]),{k,3,Length[pts],2}]
randomRotate[pts_]:=Module[{},
 newpts=pts;
```

```
 Do[newpts=dihedralRotate[newpts,k,bp[RandomReal[]]],{k,2,Length[pts],2}];
 newpts]
Clear[ch];
ch=chain[20];
cosList=ParallelTable[cosVals[randomRotate[ch]],{100000}];
corr=Plus@@cosList/100000;
ListPlot[Table[{i-1,Log[corr[[i]]]},{i,1,9}],
 PlotStyle->{Red,PointSize[0.02]},Frame->True,FrameTicks->True,
 FrameLabel->{"Ph unit","ln [<V0•Vn>]"},
 LabelStyle->Directive[FontFamily->"Arial",16]]
```



・**Calculation of persistence length (lp)**

```
logFitallparaPh1[x_]=Fit[Log[corr[[1;;8]]],{1,x},x]
0.
```

Thus, lp is calculated to be infinity.