

Supporting Information

Conformational effects induced by guest encapsulation in an enantiopure water-soluble cryptophane

Aude Bouchet, Thierry Brotin, Mathieu Linares, Hans Ågren,
Dominique Cavagnat, and Thierry Buffeteau

Table of Contents

S1 : ^1H NMR spectrum of *rac*-**5** in CD_2Cl_2 solution.

S2 : ^{13}C NMR spectrum of *rac*-**5** in CD_2Cl_2 solution.

S3 : ^1H NMR spectra of *MM*-**1** and *PP*-**1** in D_2O /KOD solution (0.08 M).

S4 : ^{13}C NMR spectrum of *MM*-**1** in $\text{DMSO}-d_6$ solution.

S5 : UV-Vis spectra of empty *rac*-**1** as well as *rac*-**1** in presence of CH_2Cl_2 and CHCl_3 in (A) H_2O /LiOH, (B) H_2O /NaOH, (C) H_2O /KOH and (D) H_2O /CsOH solutions (0.1 M).

S6 : ECD spectra of *MM*-**1** in NaOH aqueous solutions at different pH values.

S7 : ECD spectra of *MM*-**1** in H_2O /NaOH (0.1 M) and MeOH solutions.

S8 : ECD spectra of empty *PP*-**1** as well as *PP*-**1** in presence of Xe and CH_3Cl in H_2O /NaOH solution (0.1M).

S9 : ECD spectra of empty *PP*-**1** as well as *PP*-**1** in presence of CH_3I , CH_2BrCl , CH_2Br_2 and CH_2ClI in H_2O /NaOH solution (0.1M).

S10 : ECD spectra of empty *PP*-**1** as well as *PP*-**1** in presence of Xe and CH_3Cl in H_2O /LiOH solution (0.1M).

S11 : ECD spectra of empty *PP*-**1** as well as *PP*-**1** in presence of CH_3I , CH_2BrCl and CH_2Br_2 in H_2O /LiOH solution (0.1M).

S12 : IR spectra of *rac*-**1** in D_2O /KOD solution at different concentrations. The concentration of host **1** was 0.030 M.

S13 : IR spectra of *rac*-**1** in D_2O /CsOD solution at different concentrations. The concentration of host **1** was 0.030 M.

S14 : (A) IR and (B) VCD spectra of empty *PP-1* as well as *PP-1* in presence of xenon, CD₂Cl₂ and CDCl₃ in D₂O using KOD solution (0.21 M). The concentration of host **1** was 0.030 M.

S15 : (A) IR and (B) VCD spectra of empty *PP-1* as well as *PP-1* in presence of CD₂Cl₂ in D₂O using CsOD solution (0.21 M). The concentration of host **1** was 0.030 M.

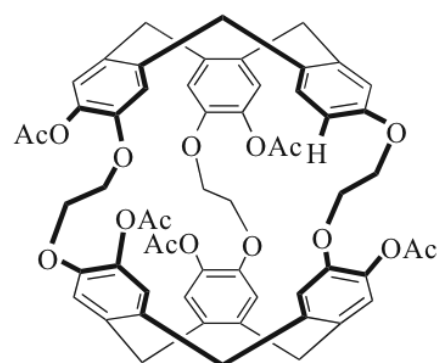
S16 : ¹H NMR (500 MHz) spectra of empty *rac-1* as well as *rac-1* in presence of CH₂Cl₂ recorded at 278 K in D₂O/KOD.

S17 : Distance (in Angströms), between the center of the cavity and the sodium cations, extracted from MD calculations of empty *PP-1*, starting from the *TTT* (A), *G_IG_IG_I* (B), and *G₂G₂G₂* (C) conformations of the linkers.

S18 : Distance (in Angströms), between the center of the cavity and the cesium cations, extracted from MD calculations of empty *PP-1*, starting from the *TTT* (A), *G_IG_IG_I* (B), and *G₂G₂G₂* (C) conformations of the linkers.

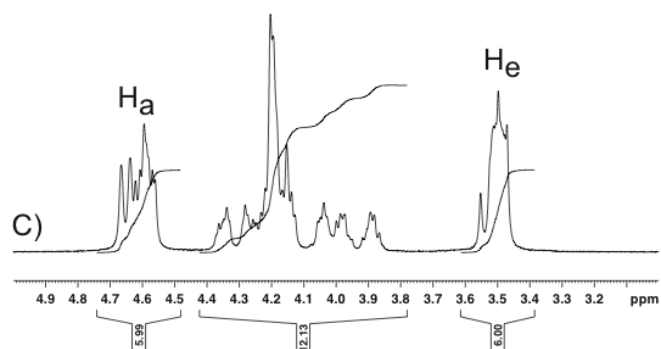
S19 : ECD spectra of empty *MM-1* in H₂O/CsOH solution (0.1 M) as well as *MM-1* in H₂O/LiOH (0.1 M) + CsOH (2 10⁻⁴ M) solution in presence (saturated solution) or not of CHCl₃.

S20 : Full list of authors of reference 17.

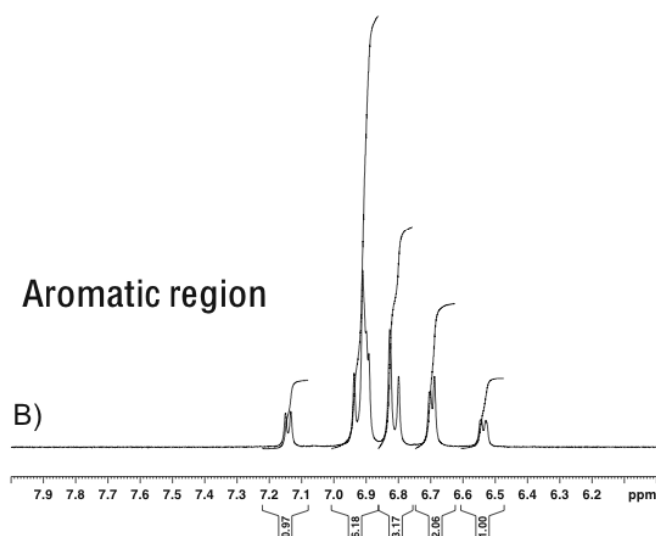


(-)-PP-5

Only one enantiomer is shown



Aliphatic region



Aromatic region

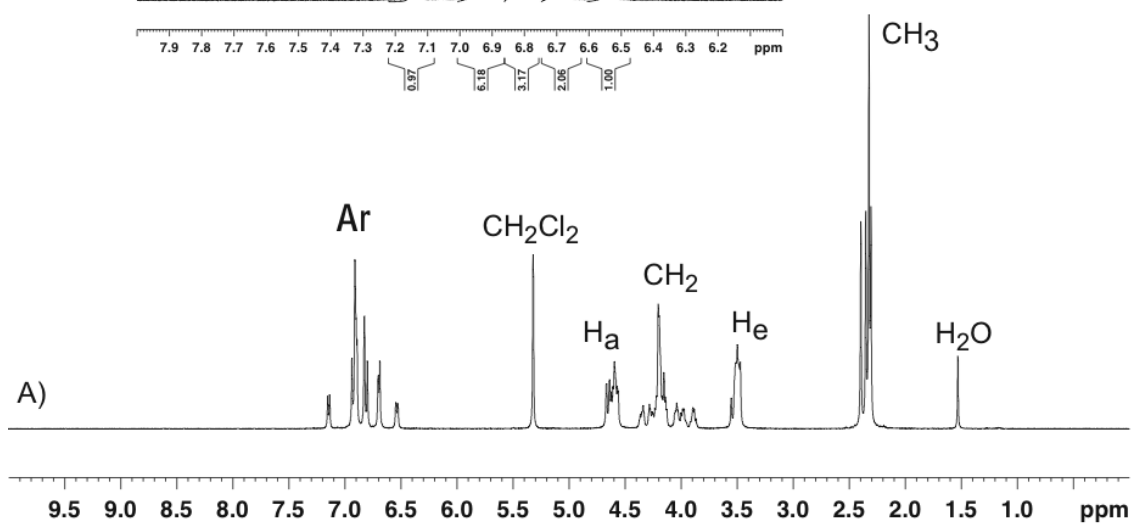
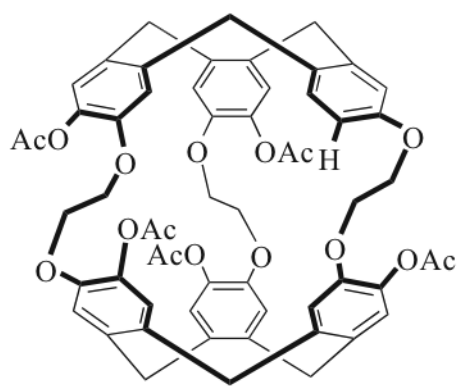


Figure S1 : ^1H NMR spectrum of *rac*-**5** in CD_2Cl_2 solution.



Only one enantiomer is shown

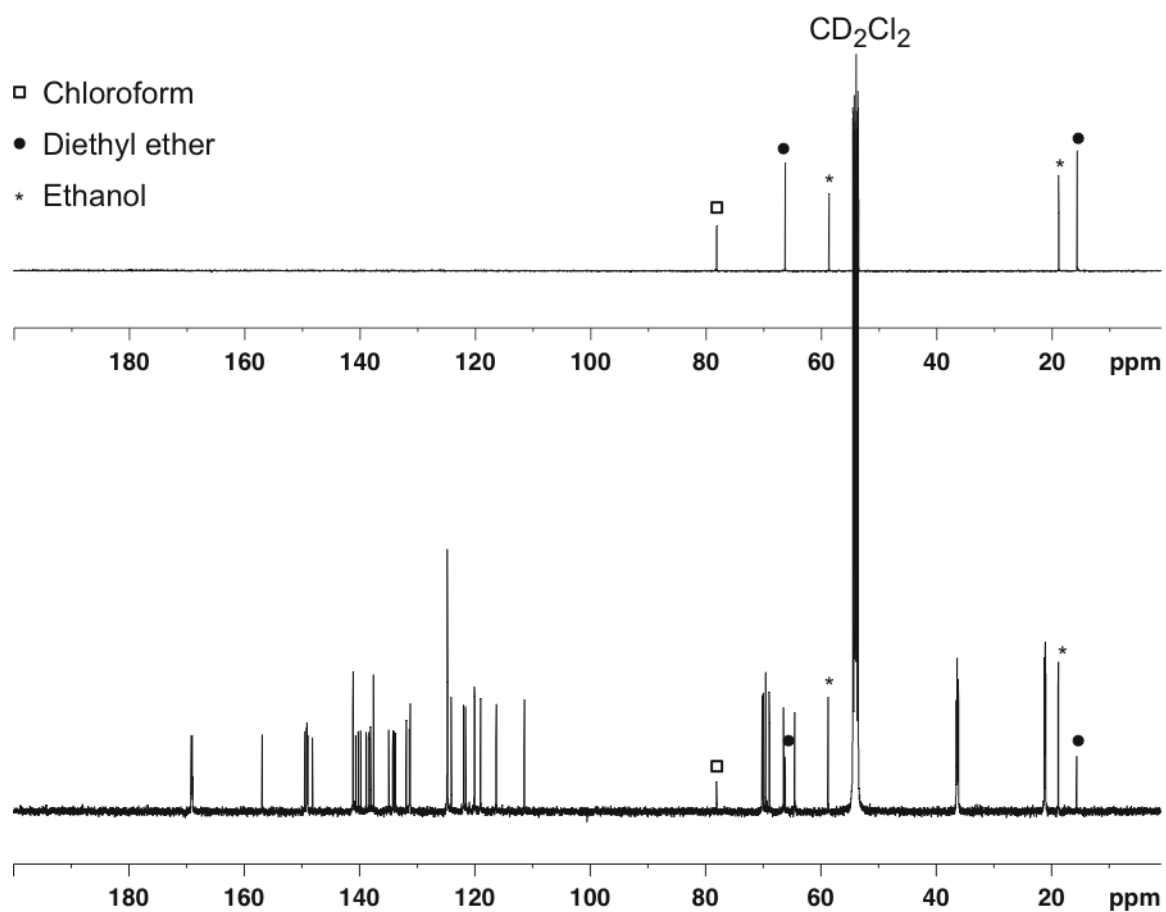


Figure S2 : ^{13}C NMR spectrum of *rac*-5 in CD_2Cl_2 solution.

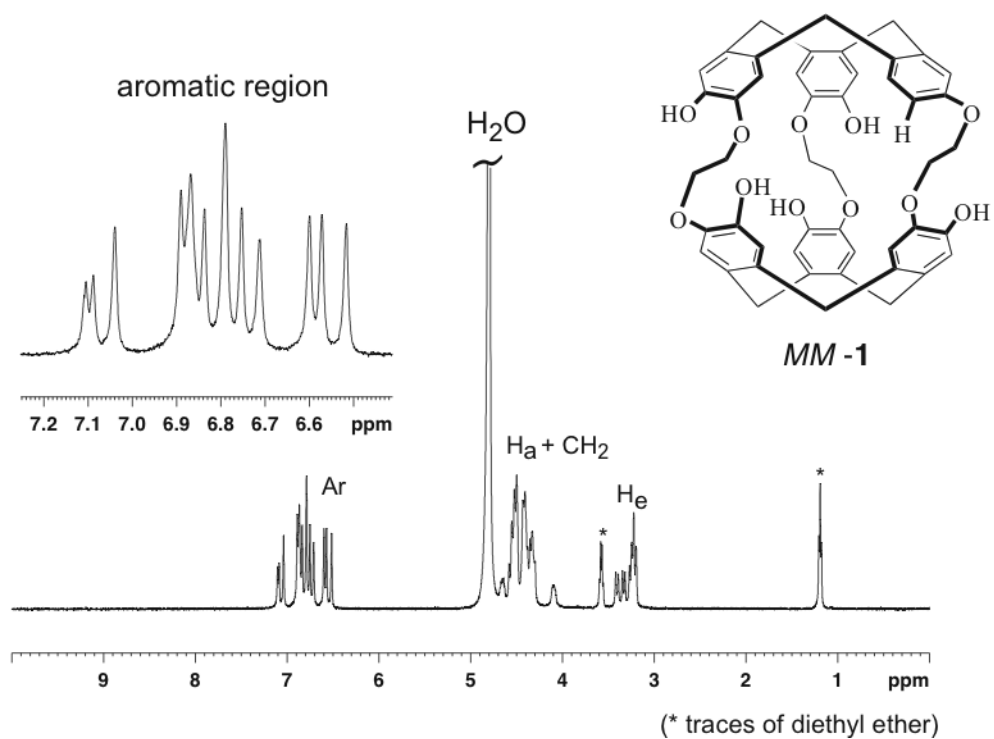
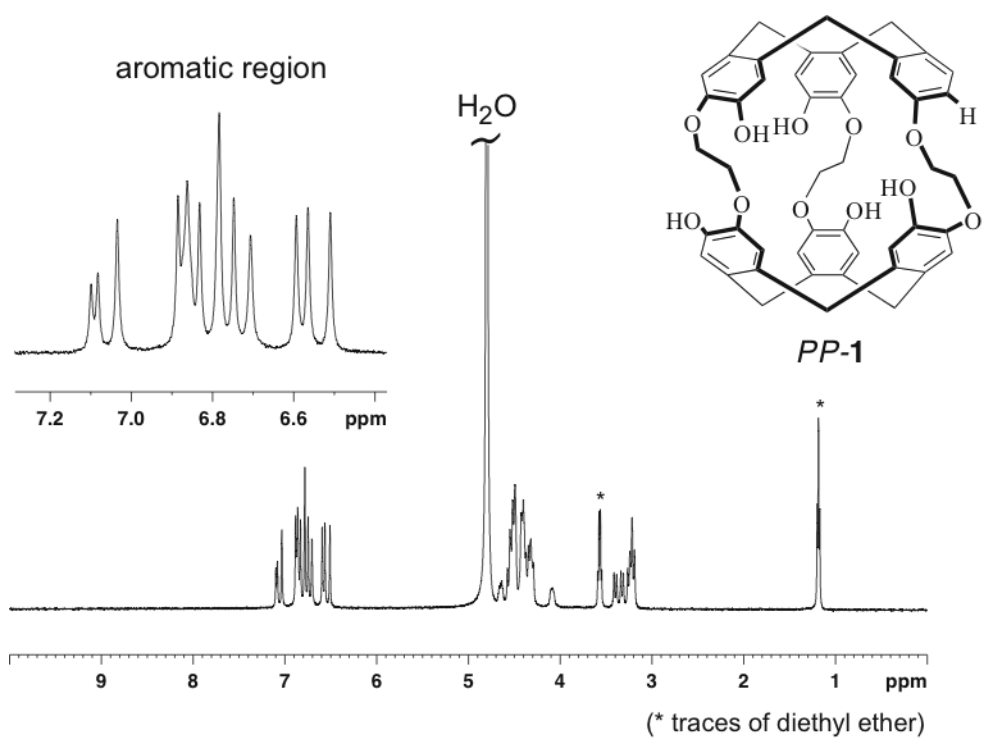
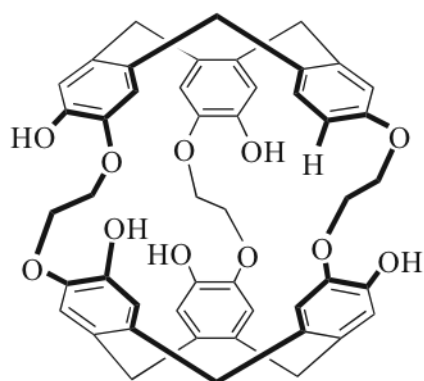


Figure S3 : 1H NMR spectra of *MM-1* and *PP-1* in D_2O/KOD solution (0.08 M).



(only one enantiomer is shown)

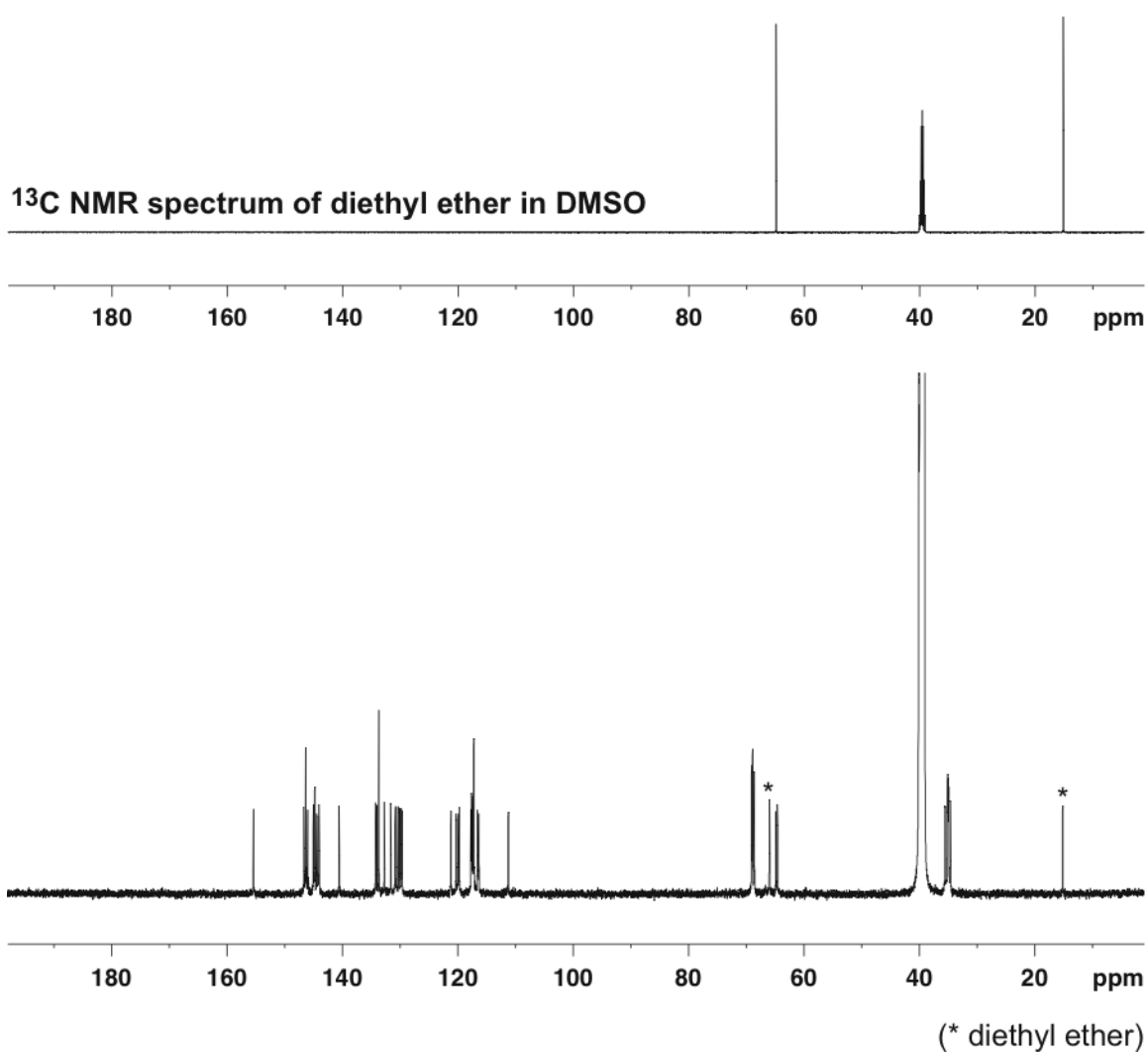


Figure S4 : ^{13}C NMR spectrum of *MM-1* in $\text{DMSO-}d_6$ solution.

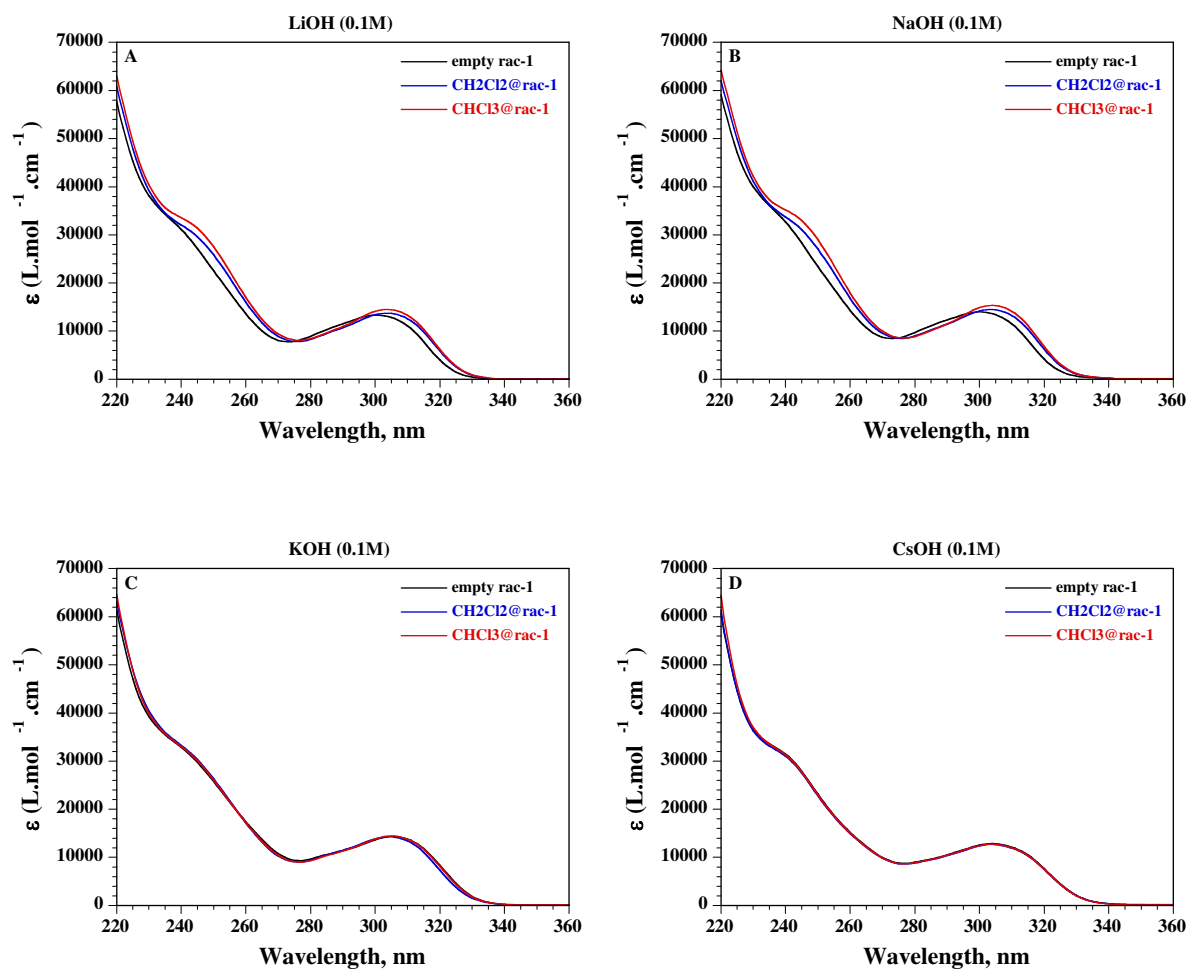


Figure S5 : UV-Vis spectra of empty *rac-1* as well as *rac-1* in presence of CH_2Cl_2 and CHCl_3 in (A) $\text{H}_2\text{O}/\text{LiOH}$, (B) $\text{H}_2\text{O}/\text{NaOH}$, (C) $\text{H}_2\text{O}/\text{KOH}$ and (D) $\text{H}_2\text{O}/\text{CsOH}$ solutions (0.1 M).

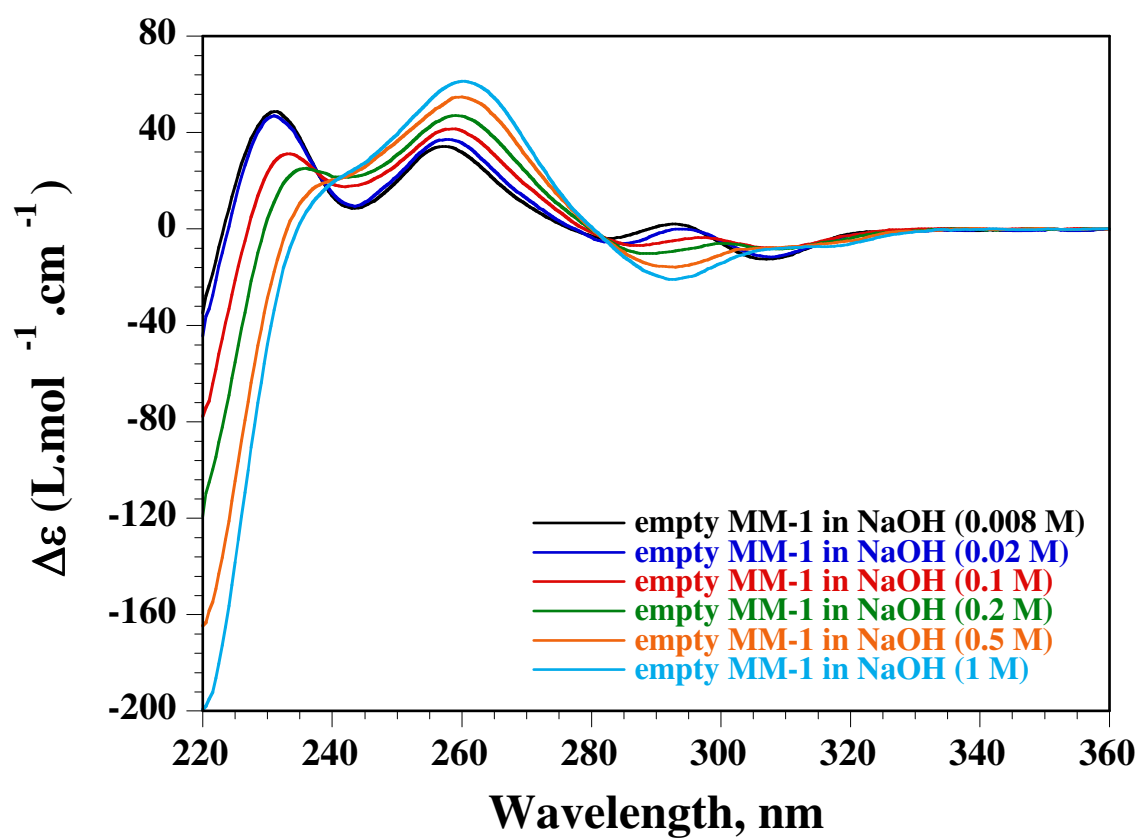


Figure S6 : ECD spectra of *MM-1* in NaOH aqueous solutions at different pH values.

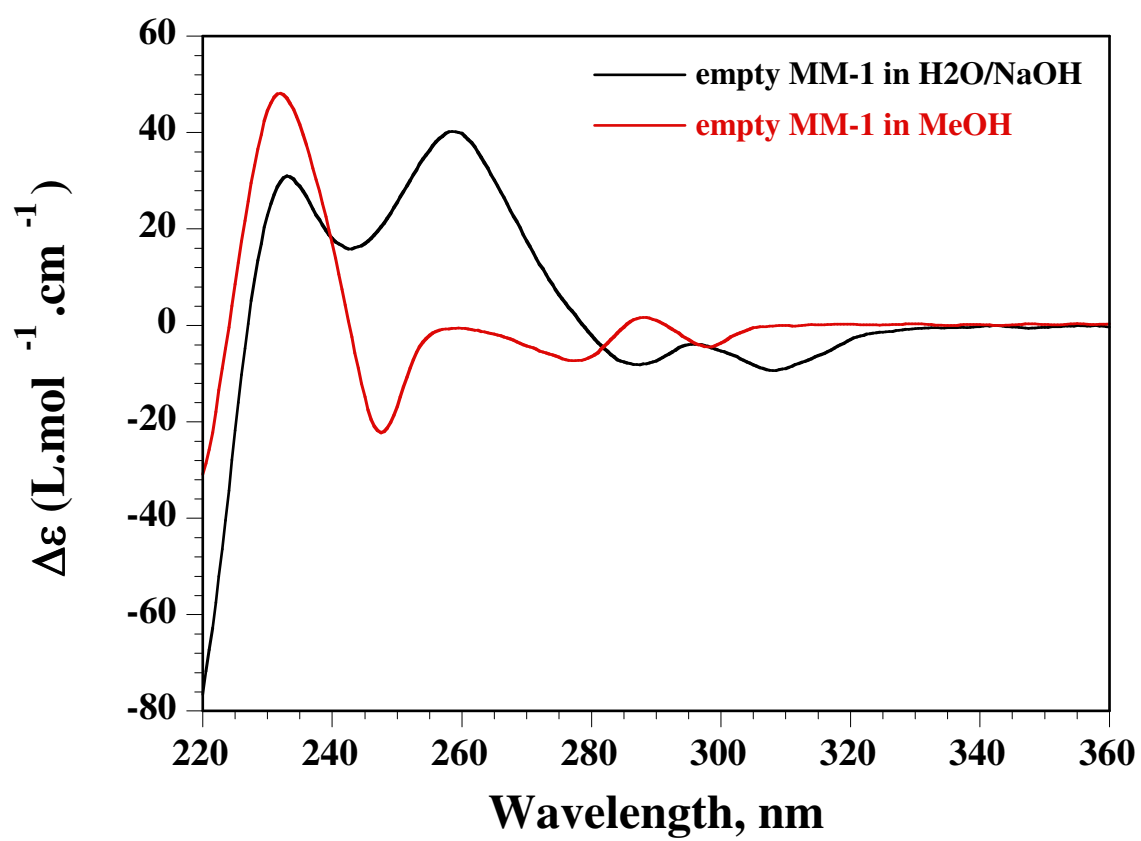


Figure S7 : ECD spectra of *MM-1* in H₂O/NaOH (0.1 M) and MeOH solutions.

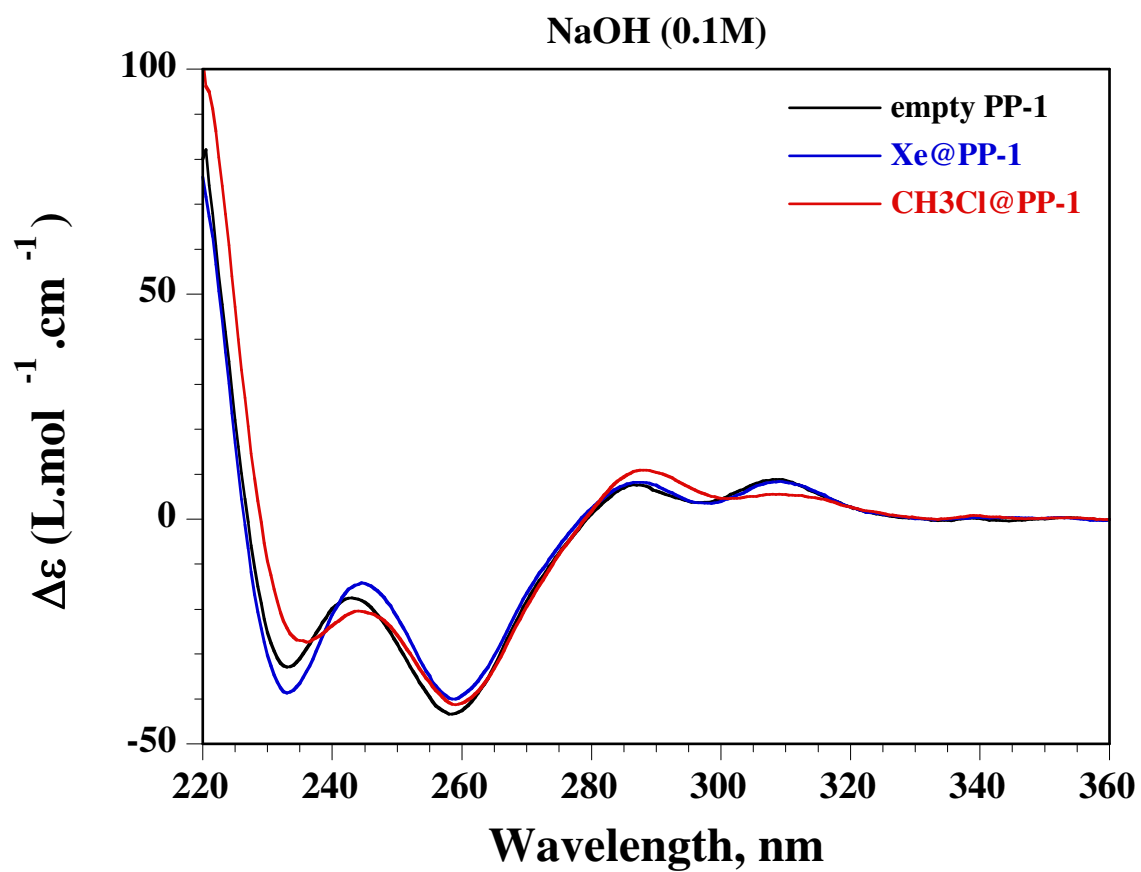


Figure S8 : ECD spectra of empty *PP-1* as well as *PP-1* in presence of Xe and CH₃Cl in H₂O/NaOH solution (0.1M).

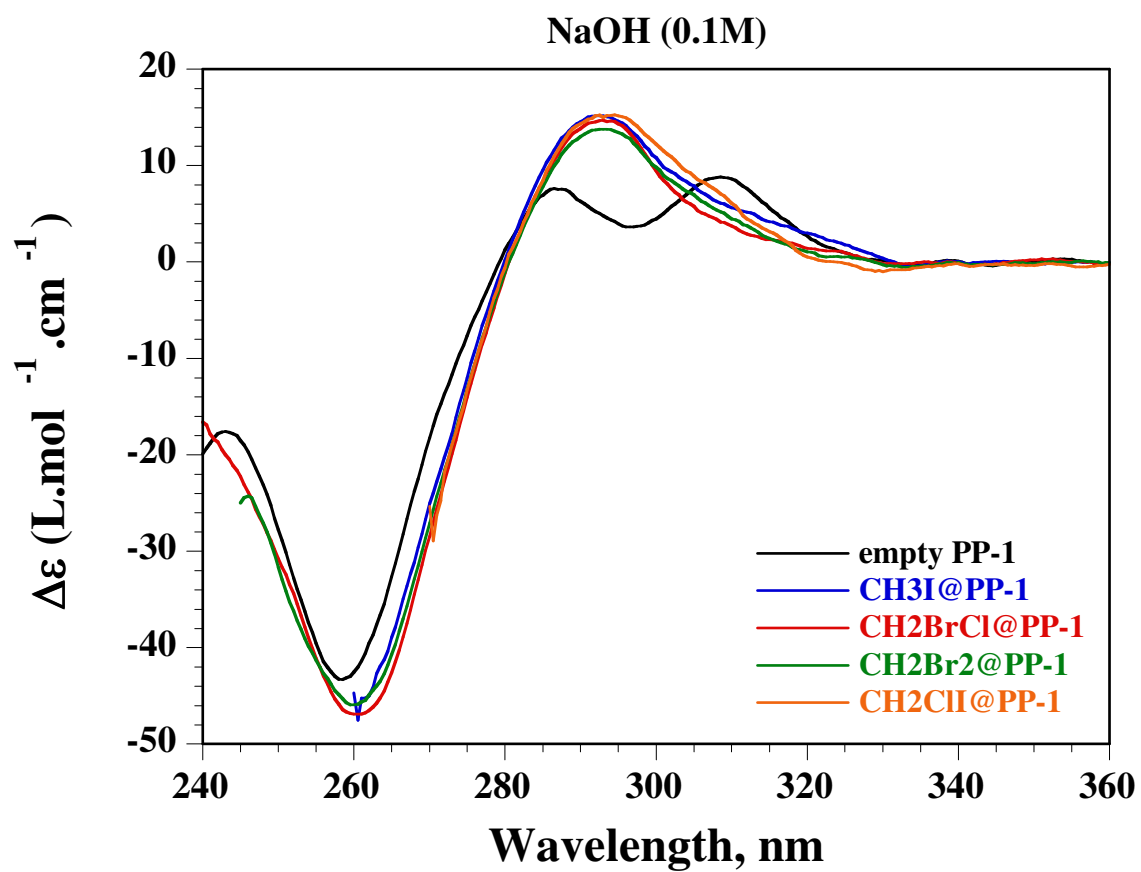


Figure S9 : ECD spectra of empty *PP-1* as well as *PP-1* in presence of CH₃I, CH₂BrCl, CH₂Br₂ and CH₂ClI in H₂O/NaOH solution (0.1M).

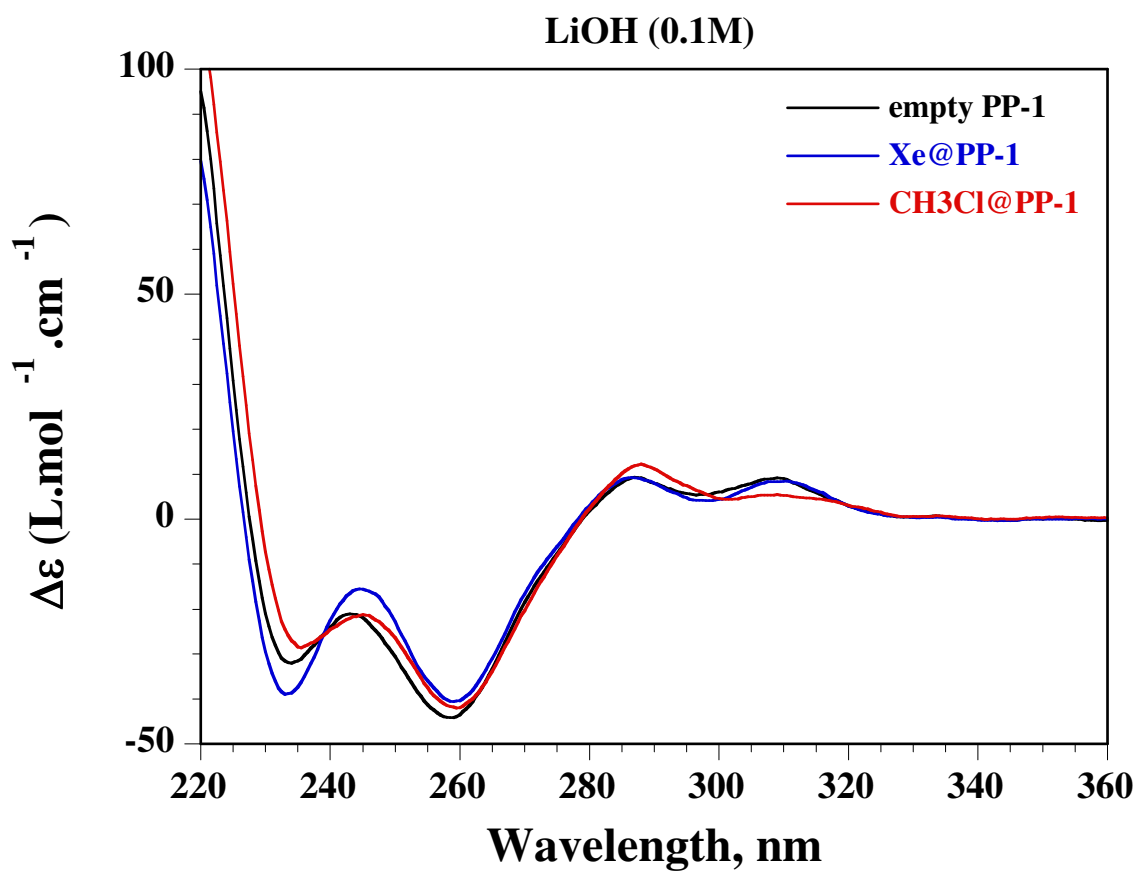


Figure S10 : ECD spectra of empty *PP-1* as well as *PP-1* in presence of Xe and CH₃Cl in H₂O/LiOH solution (0.1M).

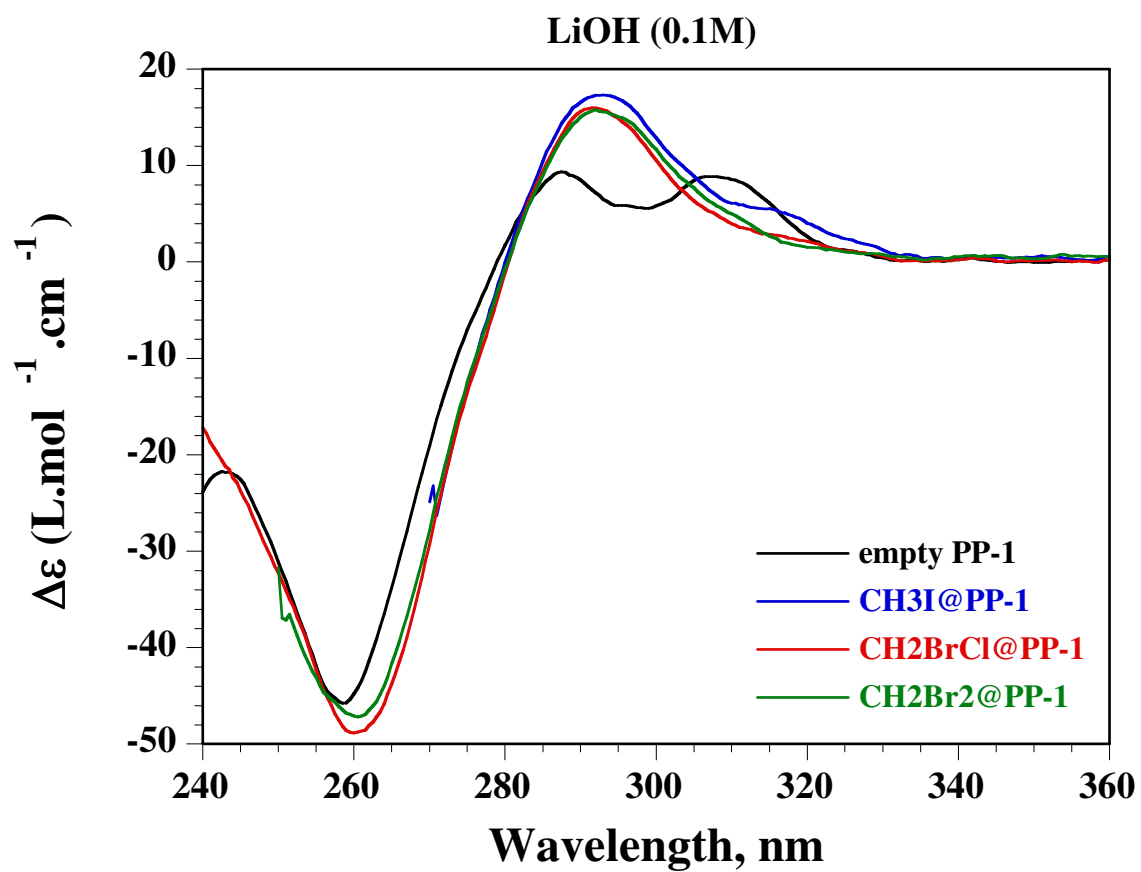


Figure S11 : ECD spectra of empty *PP-1* as well as *PP-1* in presence of CH₃I, CH₂BrCl and CH₂Br₂ in H₂O/LiOH solution (0.1M).

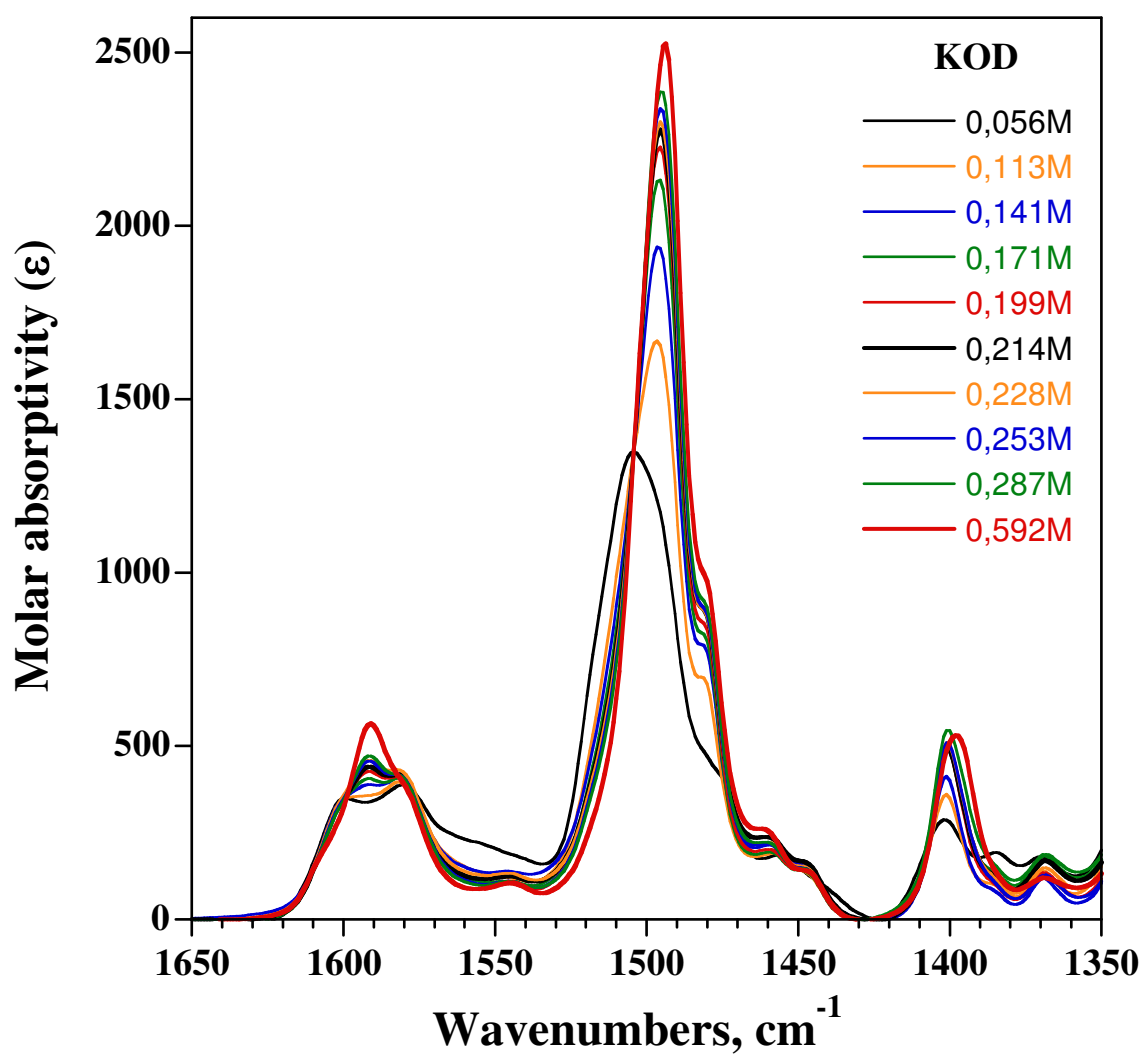


Figure S12 : IR spectra of *rac-1* in D₂O/KOD solution at different concentrations. The concentration of host **1** was 0.030 M.

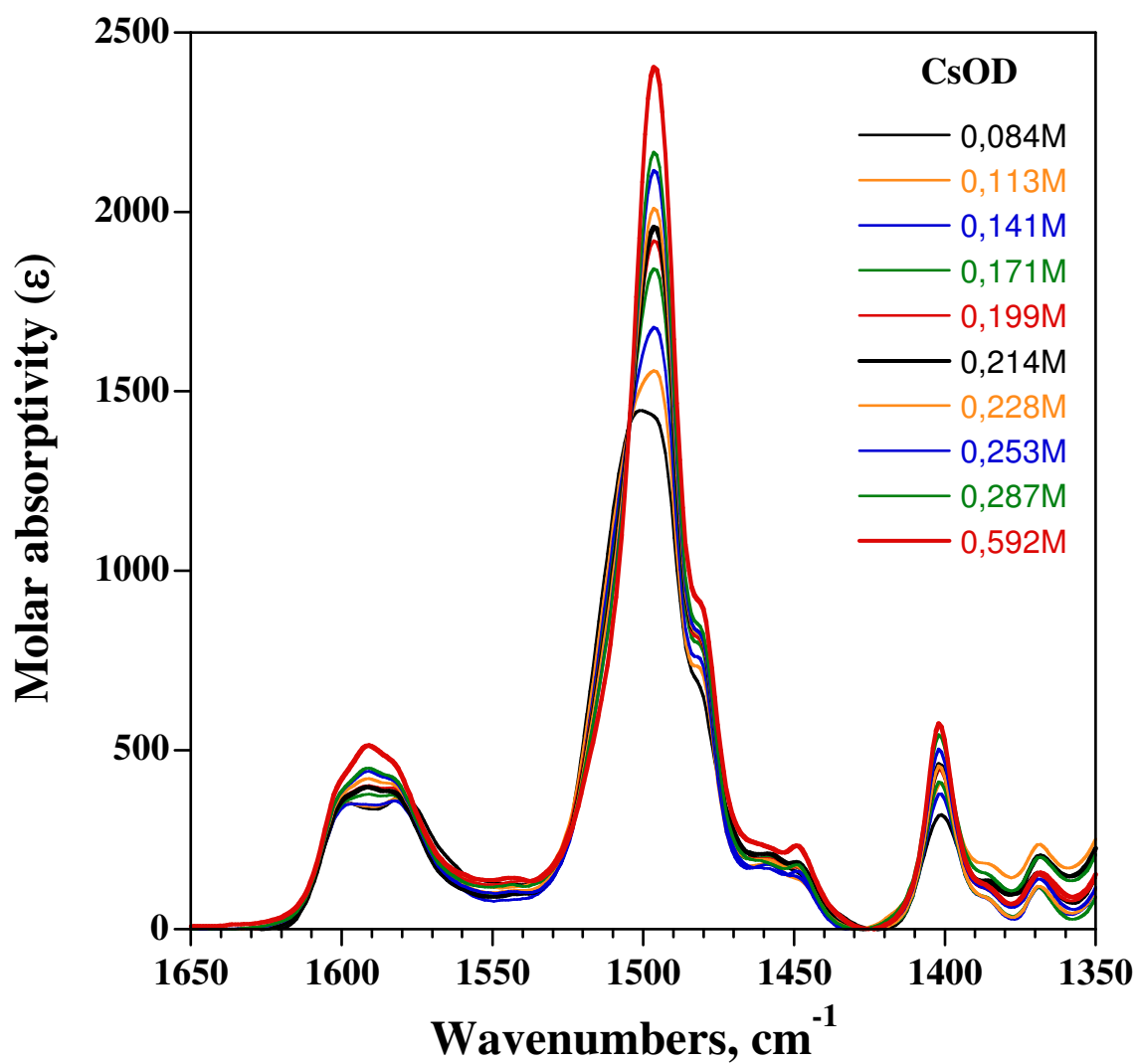


Figure S13 : IR spectra of *rac-1* in D₂O/CsOD solution at different concentrations. The concentration of host **1** was 0.030 M.

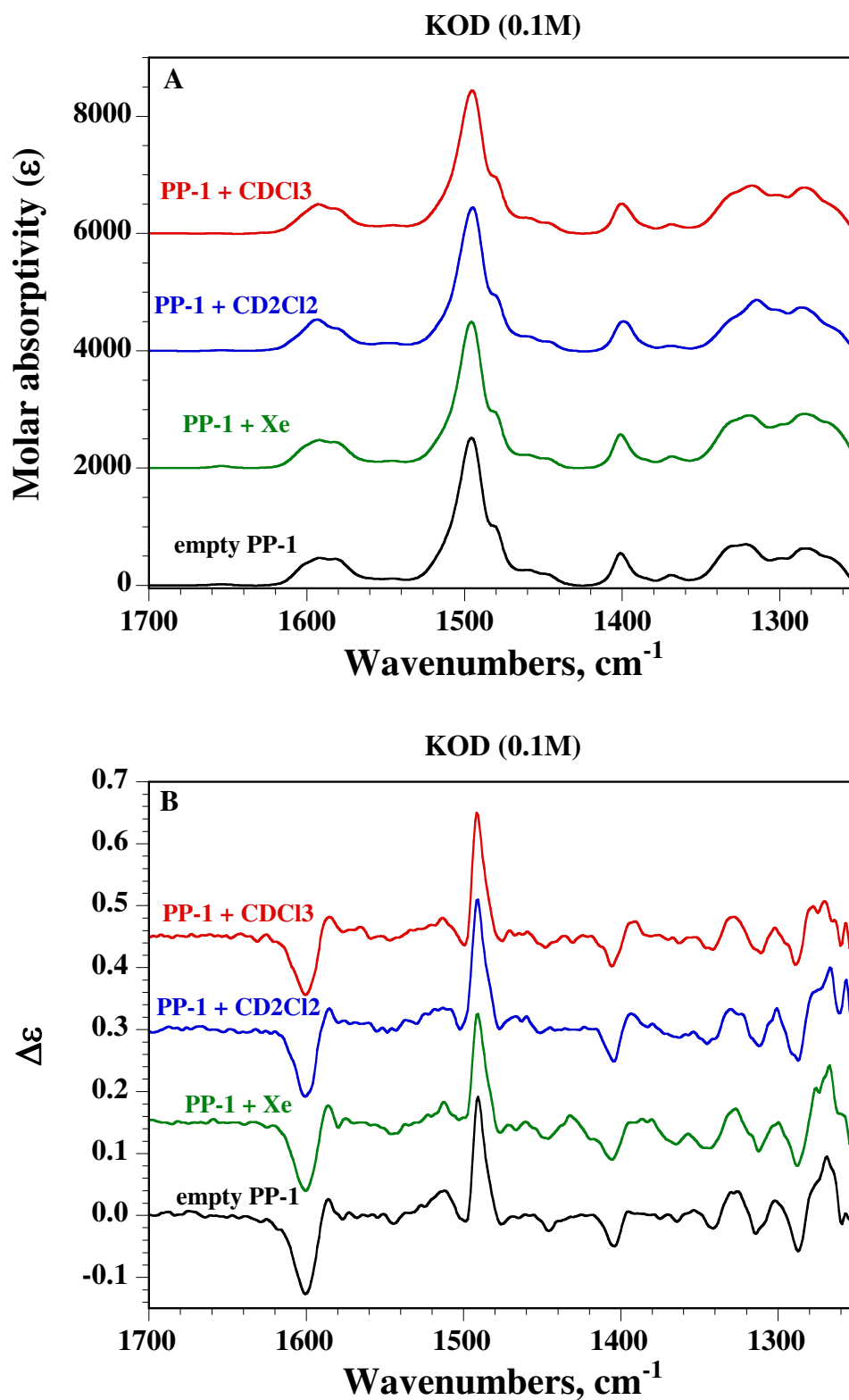


Figure S14 : (A) IR and (B) VCD spectra of empty *PP-1* as well as *PP-1* in presence of xenon, CD_2Cl_2 and CDCl_3 in D_2O using KOD solution (0.21 M). The concentration of host **1** was 0.030 M.

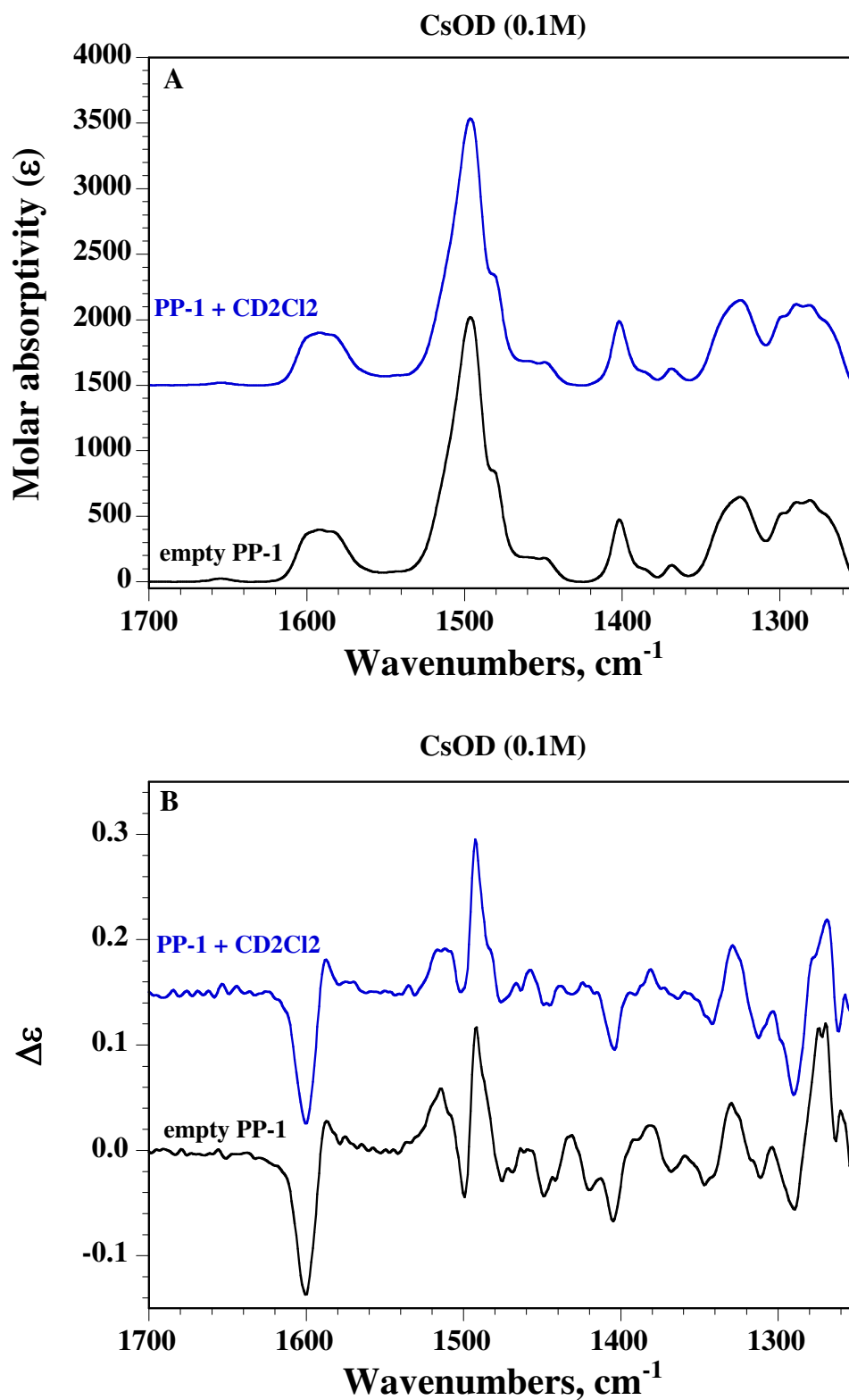
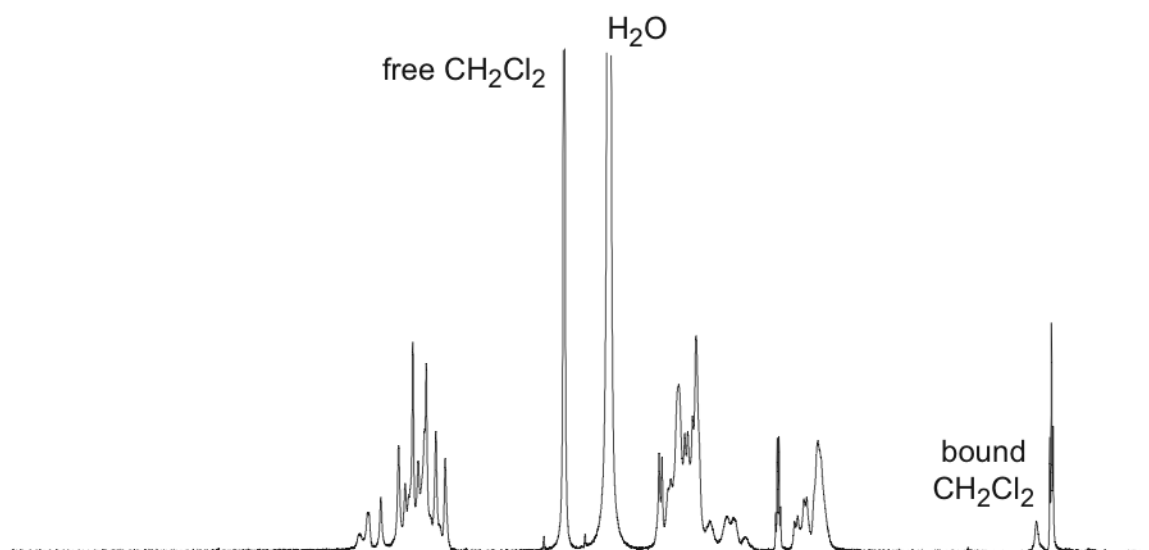
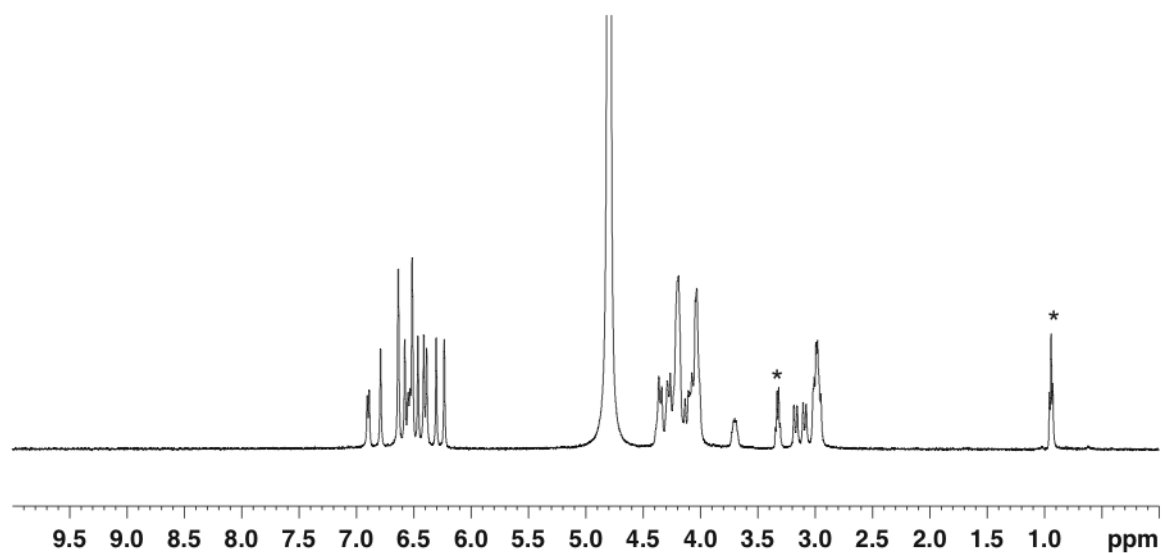


Figure S15 : (A) IR and (B) VCD spectra of empty *PP-1* as well as *PP-1* in presence of CD_2Cl_2 in D_2O using CsOD solution (0.21 M). The concentration of host **1** was 0.030 M.

rac-**1** in presence of CH₂Cl₂ at 278 K in KOD (0.1 M)



guest free *rac*-**1** at 278 K in KOD (0.1 M)



(* traces of diethyl ether)

Figure S16 : ¹H NMR (500 MHz) spectra of empty *rac*-**1** as well as *rac*-**1** in presence of CH₂Cl₂ recorded at 278 K in D₂O/KOD.

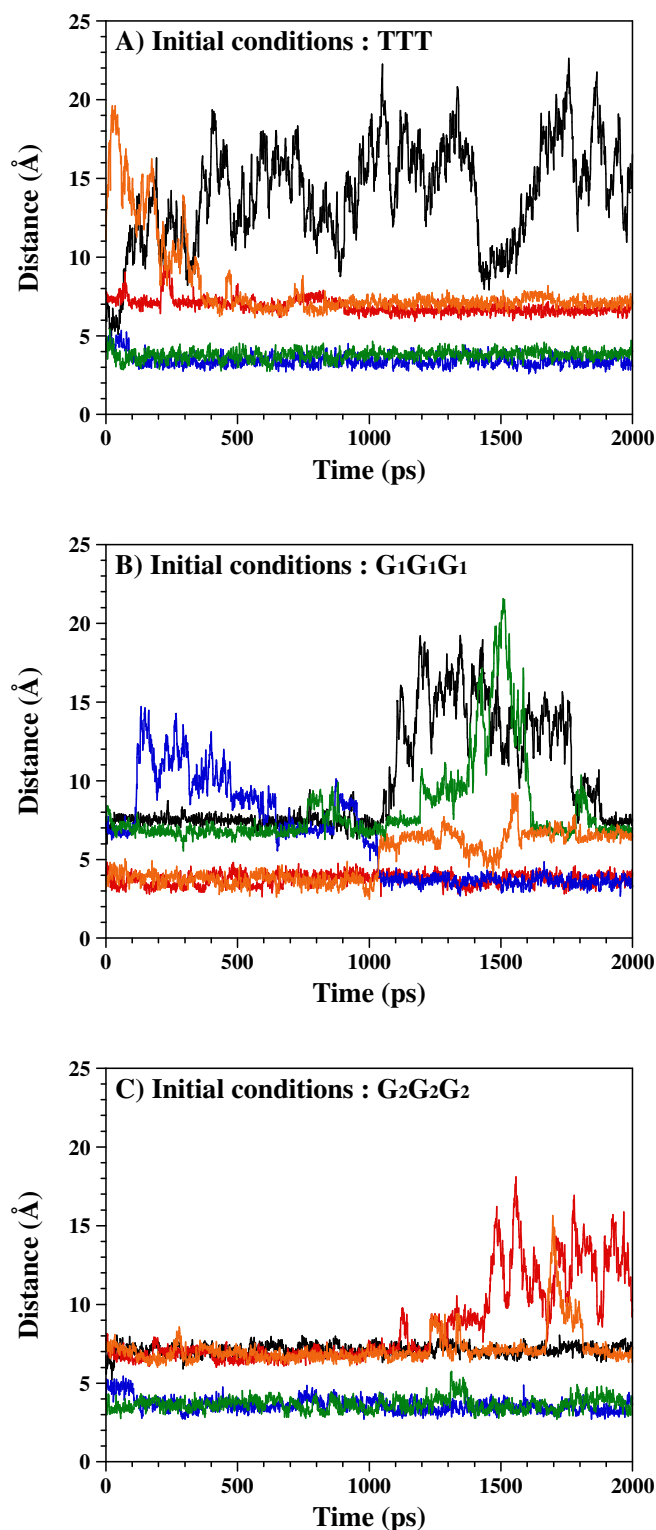


Figure S17 : Distance (in Angströms), between the center of the cavity and the sodium cations, extracted from MD calculations of empty *PP-1*, starting from the *TTT* (A), *G₁G₁G₁* (B), and *G₂G₂G₂* (C) conformations of the linkers. The five sodium cations were placed at a distance larger than 5 Å from the center of the cavity at $t=0$. Each color characterizes one of the five sodium atoms surrounding host **1**.

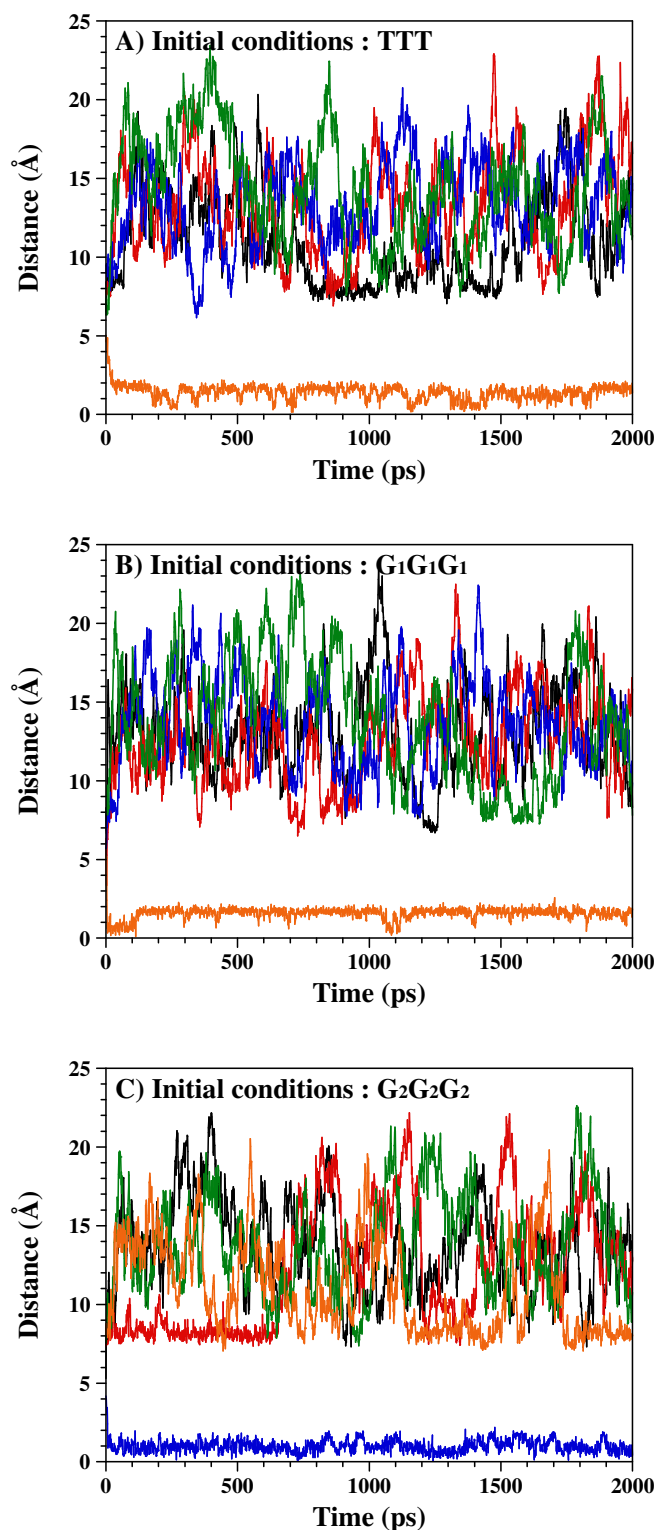


Figure S18 : Distance (in Angströms), between the center of the cavity and the cesium cations, extracted from MD calculations of empty *PP-1*, starting from the *TTT* (A), $G_1G_1G_1$ (B), and $G_2G_2G_2$ (C) conformations of the linkers. The five cesium cations were placed at a distance larger than 5 Å from the center of the cavity at $t=0$. Each color characterizes one of the five cesium atoms surrounding host **1**.

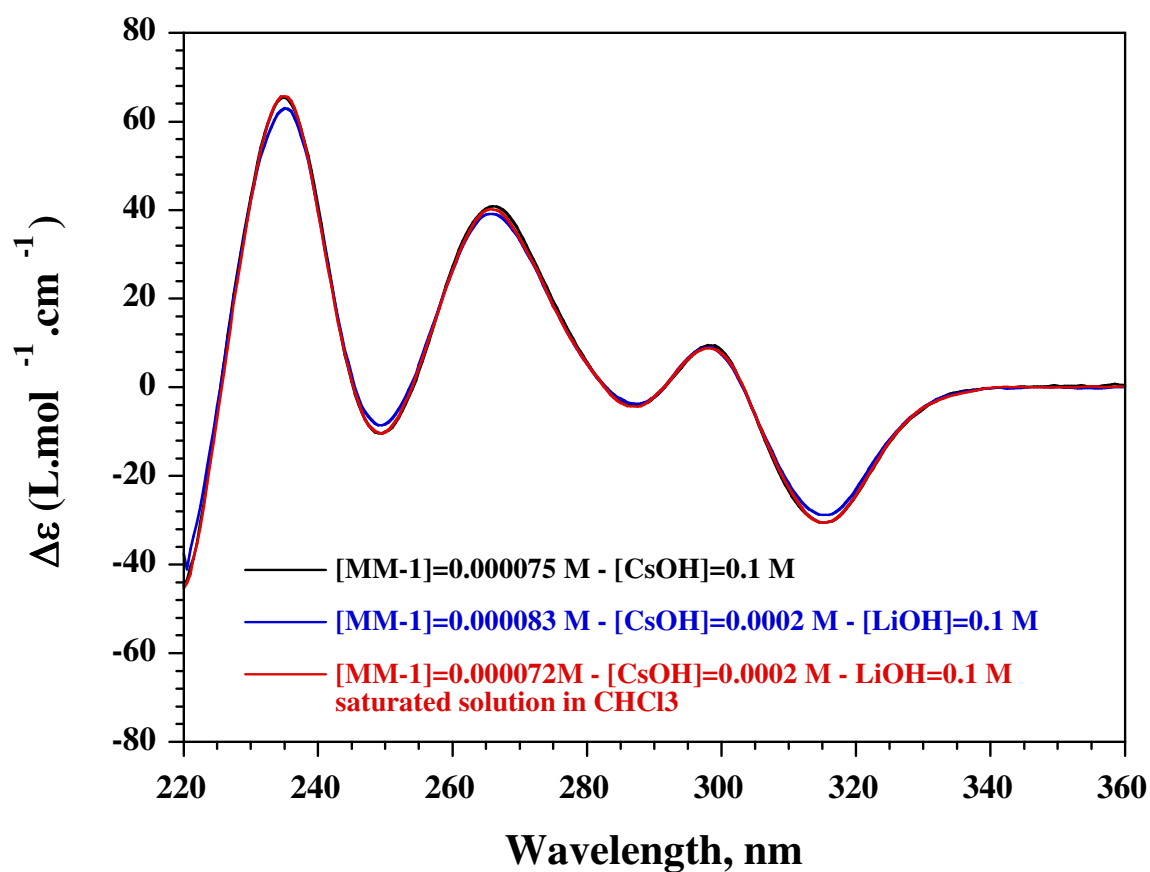


Figure S19 : ECD spectra of empty *MM-1* in H₂O/CsOH solution (0.1 M) as well as *MM-1* in H₂O/LiOH (0.1 M) + CsOH (2 10⁻⁴ M) solution in presence (saturated solution) or not of CHCl₃.

Full list of authors of reference [17]

Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatasuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Statmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P. Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, D.J.; Fox, T.; Keith, M.A.; Al-Laham, C.Y.; Peng, A.; Nanayakkara, M.; Challacombe, R.L.; Gill, P.M. W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A. *Gaussian 03*, revision B.04, Gaussian Inc., Pittsburgh, PA, **2003**.