## Supporting Information

## Enantioselective complexation of chiral propylene oxide by an enantiopure water-soluble cryptophane

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S1 : ECD spectra of $M M-1$ and $P P-1$ in presence of $r a c-\operatorname{PrO},(S)-\operatorname{PrO}$ and $(R)-\operatorname{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{NaOH}$ solution $(0.1 \mathrm{M})$ at 293 K .
S2 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $P P-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of (R)-PrO.

S3: ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $P P-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of (S)-PrO.

S4: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of (R)-PrO.

S5: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of (S)-PrO.

S6 : ECD spectra of $M M-1$ and $P P-1$ in presence of $r a c-\operatorname{PrO},(S)-\operatorname{PrO}$ and $(R)-\operatorname{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{LiOH}$ solution $(0.1 \mathrm{M})$ at 293 K .
S7: ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $P P-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (R)-PrO.

S8 : ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $P P-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (S) PrO .

S9: ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (R)-PrO.

S10 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (S)-PrO.

S11 : ECD spectra of $M M-1$ and $P P-1$ in presence of rac- $\mathrm{PrO},(S)-\mathrm{PrO}$ and $(R)-\mathrm{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{KOH}$ solution ( 0.1 M ) at 278 K .
S12 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{KOD}$ recorded at 275 K in presence of (R)-PrO.

S13: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{KOD}$ recorded at 275 K in presence of (S)-PrO.

S14: ECD spectra of empty $M M-\mathbf{1}$ and $P P-\mathbf{1}$ as well as $M M-\mathbf{1}$ and $P P-\mathbf{1}$ in presence of $(R)-$ PrO and $(S)-\mathrm{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{CsOH}$ solution ( 0.1 M ) at 293 K .
S15: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{KOD}$ recorded at 275 K in presence of (S)-PrO.

S16 : Dihedral angles of the three linkers during the 2 ns of the dynamics. These values have been extracted from the MD calculations for the phenolate form of $(R)-\operatorname{PrO} @ P P-1$ and $(S)-$ $\operatorname{PrO} @ P P-1$ complexes starting from the $T T T$ conformations of the linkers.
S17: Calculation of the potential energy difference from MD results.
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Figure S1: ECD spectra of $M M-\mathbf{1}$ and $P P-\mathbf{1}$ in presence of $(S)-\operatorname{PrO}$ and $(R)-\operatorname{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{NaOH}$ solution $(0.1 \mathrm{M})$ at 293 K .
${ }^{1} \mathrm{H}$ NMR spectrum of $P P-1$ in $\mathrm{NaOD}(\mathrm{pH}=13.2)$ in presence of ( R )-PrO
Temperature: 275 K


$$
\begin{gathered}
\mathrm{m}=4.17 \mathrm{mg} \text { of } P P-1 \text { in } 0.4 \mathrm{~mL} \text { of } \mathrm{NaOD}(\mathrm{pH}=13.2) \\
\text { CHost(total) }=12.15 \mathrm{mM} ; C \text { Host(empty guest })=0.95 \mathrm{mM} \\
C \text { (free guest) }=42.4 \mathrm{mM} ; C \text { Host }(\text { complex })=11.3 \mathrm{mM}
\end{gathered}
$$

Figure S2: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $P P-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of $(R)$-PrO.
${ }^{1} \mathrm{H}$ NMR spectrum of $P P-1$ in $\mathrm{NaOD}(\mathrm{pH}=13.2)$ in presence of $(\mathrm{S})-\mathrm{PrO}$
Temperature: 275 K


$$
\begin{gathered}
\mathrm{m}=4.19 \mathrm{mg} \text { of } P P-1 \text { in } 0.4 \mathrm{~mL} \text { of } \mathrm{NaOD}(\mathrm{pH}=13.2) \\
\text { CHost }(\text { total })=13.2 \mathrm{mM} ; \text { CHost }(\text { empty guest })=1.75 \mathrm{mM} \\
C \text { (free guest) })=49.7 \mathrm{mM} ; \text { CHost }(\text { complex })=11.4 \mathrm{mM}
\end{gathered}
$$

Figure S3: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $P P-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of $(S)$ - PrO .
${ }^{1} \mathrm{H}$ NMR spectrum of $M M-1$ in $\mathrm{NaOD}(\mathrm{pH}=13.2)$ in presence of $(\mathrm{R})-\mathrm{PrO}$
Temperature: 275 K

$\mathrm{m}=4.44 \mathrm{mg}$ of $M M-1$ in 0.4 mL of NaOD ( $\mathrm{pH}=13.2$ )
CHost(total) $=13.9 \mathrm{mM} ;$ CHost(empty guest) $=3.1 \mathrm{mM}$
$C$ (free guest $)=24.1 \mathrm{mM} ; C$ Host $($ complex $)=10.9 \mathrm{mM}$

Figure S4: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of $(R)$ - PrO .

$\mathrm{m}=3.95 \mathrm{mg}$ of $M M-1$ in 0.4 mL of $\mathrm{NaOD}(\mathrm{pH}=13.2)$
CHost(total) $=12.4 \mathrm{mM} ;$ CHost $($ empty guest $)=2.23 \mathrm{mM}$
$C($ free guest $)=14.8 \mathrm{mM} ;$ CHost $($ complex $)=10.19 \mathrm{mM}$

Figure $55:{ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{NaOD}$ recorded at 275 K in presence of $(S)$ - $\operatorname{PrO}$.


Figure S6: ECD spectra of $M M-\mathbf{1}$ and $P P-\mathbf{1}$ in presence of $r a c-\operatorname{PrO},(S)-\operatorname{PrO}$ and $(R)-\operatorname{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{LiOH}$ solution ( 0.1 M ) at 293 K .
${ }^{1} \mathrm{H}$ NMR spectrum of $P P-1$ in LiOD $(\mathrm{pH}=12.4)$ in presence of $(\mathrm{R})-\mathrm{PrO}$ Temperature: 275 K


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\begin{gathered}
\mathrm{m}=3.58 \mathrm{mg} \text { of } P P-1 \text { in } 0.4 \mathrm{~mL} \text { of } \mathrm{LiOD}(\mathrm{pH}=12.4) \\
C \text { Host }(\text { total })=11.3 \mathrm{mM} ; \text { CHost }(\text { empty guest })=1.55 \mathrm{mM} \\
C \text { (free guest })=32.4 \mathrm{mM} ; C \text { Host }(\text { complex })=9.7 \mathrm{mM}
\end{gathered}
$$

S7: ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $P P-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (R)-PrO.
${ }^{1} \mathrm{H}$ NMR spectrum of $P P-1$ in LiOD ( $\mathrm{pH}=12.4$ ) in presence of $(\mathrm{S})$ - PrO Temperature: 275 K


$$
\begin{gathered}
\mathrm{m}=3.44 \mathrm{mg} \text { of } P P-1 \text { in } 0.4 \mathrm{~mL} \text { of LiOD }(\mathrm{pH}=12.4) \\
C \text { (Host(total) }=13.36 \mathrm{mM} ; C \text { Host(empty guest })=2.24 \mathrm{mM} \\
C(\text { free guest })=51.9 \mathrm{mM} ; C \text { Host(complex })=11.1 \mathrm{mM}
\end{gathered}
$$

S8 : ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $P P-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (S) PrO .
${ }^{1} \mathrm{H}$ NMR spectrum of $M M-1$ in LiOD ( $\mathrm{pH}=12.4$ ) in presence of ( R )-PrO
Temperature: 275 K


$$
\begin{gathered}
\mathrm{m}=3.70 \mathrm{mg} \text { of } M M-1 \text { in } 0.4 \mathrm{~mL} \text { of LiOD }(\mathrm{pH}=12.4) \\
C \text { Host(total })=12.6 \mathrm{mM} ; \text { CHost(empty guest })=4.1 \mathrm{mM} \\
C(\text { free guest })=19.2 \mathrm{mM} ; \text { CHost }(\text { complex })=8.5 \mathrm{mM}
\end{gathered}
$$

S9: ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz})$ spectrum of $M M-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (R)-PrO.
${ }^{1} \mathrm{H}$ NMR spectrum of $M M-1$ in LiOD ( $\mathrm{pH}=12.4$ ) in presence of (S)-PrO
Temperature: 275 K


$$
\mathrm{m}=5.32 \mathrm{mg} \text { of } M M-1 \text { in } 0.4 \mathrm{~mL} \text { of } \mathrm{LiOD}(\mathrm{pH}=12.4)
$$

CHost(total) $=16.73 \mathrm{mM} ;$ CHost $($ empty guest $)=1.87 \mathrm{mM}$ $C($ free guest $)=32.9 \mathrm{mM} ;$ CHost $($ complex $)=14.86 \mathrm{mM}$

S10 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{LiOD}$ recorded at 275 K in presence of (S)-PrO.


S11: ECD spectra of $M M-1$ and $P P-1$ in presence of rac- $\mathrm{PrO},(S)-\mathrm{PrO}$ and $(R)-\mathrm{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{KOH}$ solution ( 0.1 M ) at 278 K .
${ }^{1} \mathrm{H}$ NMR spectrum of $M M-1$ in $\mathrm{KOD}(\mathrm{pH}=13.6)$ in presence of $(\mathrm{R})$-PrO
Temperature: 275 K


S12 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-1$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{KOD}$ recorded at 275 K in presence of (R)-PrO.
${ }^{1} \mathrm{H}$ NMR spectrum of $M M-1$ in $\mathrm{KOD}(\mathrm{pH}=13.6)$ in presence of $(\mathrm{S})-\mathrm{PrO}$ Temperature: 275 K


$$
\begin{gathered}
\mathrm{m}=4.01 \mathrm{mg} \text { of } M M-1 \text { in } 0.4 \mathrm{~mL} \text { of KOD }(\mathrm{pH}=13.6) \\
C \text { Host(total) }=12.6 \mathrm{mM} ; C \text { Host(empty guest })=8.0 \mathrm{mM} \\
C(\text { free guest })=33.6 \mathrm{mM} ; C \text { Host }(\text { complex })=4.6 \mathrm{mM}
\end{gathered}
$$

S13 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $M M-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{KOD}$ recorded at 275 K in presence of (S)-PrO.


S14 : ECD spectra of empty $M M-1$ and $P P-\mathbf{1}$ as well as $M M-\mathbf{1}$ and $P P-1$ in presence of $(R)$ PrO and $(S)-\mathrm{PrO}$ in $\mathrm{H}_{2} \mathrm{O} / \mathrm{CsOH}$ solution $(0.1 \mathrm{M})$ at 293 K .

# ${ }^{1} \mathrm{H}$ NMR spectrum of rac-1 in CsOD $(\mathrm{pH}=13.5)$ in presence of $(\mathrm{rac})-\mathrm{PrO}$ 

Temperature: 275 K


S15 : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz ) spectrum of $\mathrm{rac}-\mathbf{1}$ in $\mathrm{D}_{2} \mathrm{O} / \mathrm{CsOD}$ recorded at 275 K in presence of (rac)-PrO.


S16: Dihedral angles of the three linkers during the 2 ns of the dynamics. These values have been extracted from the MD calculations for the phenolate form of $(R)-\operatorname{PrO} @ P P-1$ and $(S)$ PrO@ $@ P-1$ complexes starting from the $T T T$ conformations of the linkers.

To determine the relative stability of the two complexes $(R)-\operatorname{PrO} @ P P-\mathbf{1}$ and $(S)-\operatorname{PrO} @ P P-\mathbf{1}$ for the phenol form, we optimized several points along the MD trajectories (OPLS ForceField). For the last ns, we optimized one frame every 2 ps ( 500 geometries). The energy of the host-guest system being hidden by the fluctuation of energy of the water molecules of the box, we had to suppress them during the optimization. The energy converged to $132.3 \pm 0.3$ $\mathrm{kcal} / \mathrm{mol}$ and $133.4 \pm 0.3 \mathrm{kcal} / \mathrm{mol}$ for the $(R)-\mathrm{PrO} @ P P-\mathbf{1}$ and $(S)-\mathrm{PrO} @ P P-\mathbf{1}$ complexes, respectively. The potential energy difference $(1.1 \mathrm{kcal} / \mathrm{mol})$ is in reasonable agreement with the experimental value.

|  | $(R)$-PrO@PP-1 |  | $(S)$-PrO@ $P P-\mathbf{1}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | AVG | STDEV | AVG | STDEV |
| Energy <br> $(\mathrm{kcal} / \mathrm{mol})$ | 132.3 | 0.3 | 133.4 | 0.3 |
| Bond Stretching | 5.4 | 0.2 | 5.4 | 0.2 |
| Angle Bending | 145.1 | 0.4 | 145.3 | 0.4 |
| Improper <br> Torsion | 0.2 | 0.1 | 0.2 | 0.1 |
| Torsional Angle | 21.6 | 0.5 | 21.8 | 0.5 |
| Van Der Waals | 15.4 | 0.4 | 15.8 | 0.4 |
| Charge-Charge | -55.4 | 0.3 | -55.1 | 0.3 |

S17 : Calculation of the potential energy difference from MD results.

Full list of authors of reference [16]

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