

## Electronic supplementary information for:

### **p-Tolyl glycerol ether: is it possible to find more simple molecular organogelator with pronounced chirality driven properties?**

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### Literature cited

## Experimental section

### Instrumentation

The NMR spectra (600 MHz for  $^1\text{H}$  and 150.864 MHz for  $^{13}\text{C}$ ) were recorded on a Bruker Avance-600 spectrometer in  $\text{CDCl}_3$  with TMS or the signals of the solvent as the internal standard. The IR spectra of the polycrystalline samples in KBr pellets were recorded on a Bruker IFS-66v Fourier-transform spectrometer.

The X-ray diffraction data for two compounds were collected on a Bruker AXS Apex II diffractometers equipped with a monochromator in the  $\text{Mo K}_\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) for *rac*-7 and  $\text{Cu K}_\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) for (*S*)-7 incident beam,  $T = 296(2) \text{ K}$ . The CCD data were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELXTL V6.14.

Optical rotations were measured on a Perkin-Elmer model 341 polarimeter. Throughout the text the value of specific rotation is given in  $\text{deg mL g}^{-1} \text{ dm}^{-1}$ , and the concentration of solutions  $c$  appears in  $\text{g (100 ml)}^{-1}$ . Circular dichroism spectra were recorded on a JASCO 500A spectropolarimeter.

Enantiomeric purity was checked by HPLC analysis performed on a Shimadzu LC-20AD system controller, and UV monitor 275 nm was used as a detector. The column used, from Daicel, Inc., was Chiralcel OD-RH (0.46 x 15 cm).

### Chemicals

The following chemicals were purchased and used as received: racemic epichlorohydrin (99%) from Alfa Aesar ®; *n*-hexane (99%) and cyclohexane (99%) from Labscan Limited; *rac*-3-chloropropane-1,2-diol (99+%) from Acros Organics ®; *p*-cresol (99%), *n*-heptane (99%), *n*-octane (98+%), *n*-nonan (99%), and *n*-decane (99%) from Lancaster.

(-)-(*R*)-3-chloropropane-1,2-diol  $\{[\alpha]_{\text{D}}^{20} - 6.4 (c 5, \text{H}_2\text{O})\}$ , and (+)-(*S*)-3-chloropropane-1,2-diol  $\{[\alpha]_{\text{D}}^{20} + 6.1 (c 4.8, \text{H}_2\text{O})\}$  were prepared through Jacobsen kinetic hydrolytic resolution of *rac*-epichlorohydrin without modifications.<sup>1</sup>

### Synthesis and characterizations of *p*-tolyl glycerol ethers

Racemic and enantiopure diols 7 were synthesized by analogy with a published procedure<sup>2</sup> from *p*-cresol and racemic or scalemic 3-chloropropane-1,2-diols.

**General procedure:** To the solution of *p*-cresol (10 mmol) in ethanol (6 ml) a solution of NaOH (0.5 g, 12.5 mmol) in water (2 ml) was added and the resulting mixture was stirred and heated under reflux for 30 min. Then a solution of 3-chloropropane-1,2-diol (1.3 g, 12 mmol) in ethanol (1 ml) was added, and the mixture was further stirred and heated at reflux for 3 h. After cooling, the mixture was concentrated under reduced pressure followed by addition of water (6 ml) and extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 ml). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. The crude diols **7** were purified by recrystallization; (*S*)-**7** was obtained from (+)-(*S*)-3-chloropropane-1,2-diol, and (*R*)-**7** was obtained from (-)-(*R*)-3-chloropropane-1,2-diol.

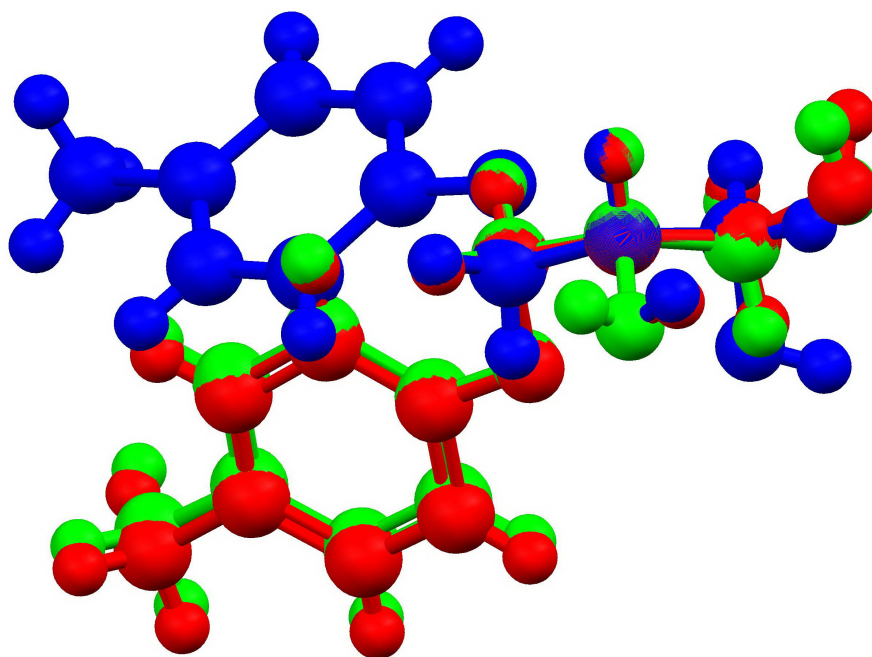
*rac*-3-(4-Methylphenoxy)-propane-1,2-diol, (*S*)-**7**. Mp 73-75 °C (CCl<sub>4</sub>). Lit.: mp 73-74 °C.<sup>3</sup>

(*S*)-3-(4-Methylphenoxy)-propane-1,2-diol, (*S*)-**7**. Mp 67-69 °C (CCl<sub>4</sub>); [α]<sub>D</sub><sup>20</sup> +9.0 (*c* = 0.8, EtOH); 96 % ee [HPLC; Daicel Chiralcel OD-RH (0.46 x 15 cm) column; 29 °C; eluent: water/isopropanol = 3/1; flow rate 0.4 ml/min; *t*<sub>R</sub> = 20.1 min]. Lit.: [α]<sub>D</sub><sup>20</sup> +7.5 (*c* = 1, EtOH); 71% ee.<sup>4</sup> <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ: 2.14 (t, *J* = 5.9 Hz, 1H, OH), 2.28 (s, 3H, CH<sub>3</sub>), 2.70 (d, *J* = 4.3 Hz, 1H, OH), 3.72-3.77 (m, 1H, 1CH<sub>2</sub>), 3.81-3.86 (m, 1H, 1CH<sub>2</sub>), 3.99-4.05 (m, 2H, CH<sub>2</sub>O), 4.06-4.09 (m, 1H, CH), 6.81 (d, *J* = 8.8 Hz, 2H, Ar), 7.08 (d, *J* = 8.8 Hz, 2H, Ar). <sup>13</sup>C-NMR (150.864 MHz, CDCl<sub>3</sub>) δ: 20.4, 63.7, 69.4, 70.4, 114.5, 130.0, 130.6, 156.3.

(*R*)-3-(4-Methylphenoxy)-propane-1,2-diol, (*R*)-**7**. Mp 64-66 °C; [α]<sub>D</sub><sup>20</sup> -8.4 (*c* = 1, EtOH); 92 % ee [HPLC; *t*<sub>R</sub> = 18.4 min]. Lit.: [α]<sub>D</sub><sup>20</sup> -9.2 (*c* = 1, EtOH), 97% ee.<sup>4</sup>

### Single crystals for X-ray diffraction studies preparation

The single crystals of *rac*- and (*S*)-**7** for X-ray experiments were prepared from the above-described material by liquid diffusion method.<sup>5</sup> Close to saturation CH<sub>2</sub>Cl<sub>2</sub> solutions (0.2 ml) were placed in the tube and 1 ml portions of hexane were layered carefully down the side of the tube on the solutions. The tubes were corked and left to stand for 24 hours at room temperature. The crystals precipitated (thin plates for *rac*-**7** and long needles for (*S*)-**7** were analyzed under microscope to choose the suitable ones.



**Fig. S1.** The superposition of two symmetry independent (*S*)-A (red) and (*S*)-B (green) molecules of *rac*-7 and the only symmetry independent (blue) molecule of (*S*)-7 as they packed in the crystals; the superposed parts are chiral C2 atom tetrahedrons of common configurations.

**Table S1.** Gelation properties of (*R*)- or (*S*)-**7** in some hydrocarbon solvents at 25 °C.

Solvent	<i>scal</i> - <b>7</b> /solvent (wt %)	solvent/ <i>scal</i> - <b>7</b> (mol/mol)
<i>n</i> -Hexane	0.15	1409
<i>n</i> -Heptane	0.14	1299
<i>n</i> -Octane	0.16	998
<i>n</i> -Nonan	0.10	1420
<i>n</i> -Decane	0.20	640
Cyclohexane	0.19	1139
Petroleum (70-100 °C)	0.14	-

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