### **Supplementary Information**

# Bisthioxanthylidene biscrown ethers as potential stereodivergent chiral ligands

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**General:** Melting points (uncorrected) were determined on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-200 (200 MHz), a Varian VXR-300 (300 MHz), 400 (400 MHz), or a Varian Unity Plus Varian-500 (500 MHz). <sup>13</sup>C NMR spectra were recorded on a Varian Gemini-200 (50 MHz), a Varian VXR-300 (75 MHz), or a Varian Unity Plus Varian-500 (125 MHz). Chemical shifts are denoted in  $\delta$ -unit (ppm) relative to CDCl<sub>3</sub> (7.24), DMSO-*d*<sub>6</sub> (2.56), acetone-*d*<sub>6</sub> (2.19), benzene-*d*<sub>6</sub> (7.15), toluene-*d*<sub>8</sub> (2.09). The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). UV spectra were recorded on a Hewlett Packard HP 8453 UV-VIS spectrophotometer. CD spectra were recorded on a JASCO J-715 spectropolarimeter. MS spectra were obtained with a Jeol JMS-600 spectrometer by the electron ionization (EI) procedure. Column chromatography was performed on silica gel (Aldrich 60, 230-400 mesh) or on Al<sub>2</sub>O<sub>3</sub> (neutral). The solvents were distilled and dried, if necessary, by standard methods. Reagents and starting materials were used as obtained from Aldrich.

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15,18,21,24,27,30-Hexaoxa-9,36dithiaheptacyclo[30.10.2.210,13. 02,11.03,8.035,43.037,42]hexatetraconta-1,3,5,7,10(46),11,13(45),32, 34,37,39,41,43-tridecaene **5** 



14,17,20,23-Tetraoxa-9,28-dithiaheptacyclo[22.10.2.210,13.02,11. 03,8.027,35.029,34] octatriaconta-1,3,5,7,10(38),11,13(37),24,26,29, 31,33,35-tridecaene  ${\bf 6}$ 

Figure 1,ESI Atom numbering schemes of compounds 5 and 6.



Cyclohexyl 7-(2-{2-[2-({7-[(cyclohexyloxy)carbonyl]-9-oxo-9H-thioxanthen-2-yl}oxy)-ethoxy]-ethoxy]ethoxy)-9-oxo-9H-thioxanthene-2-carboxylate **24** 



5,32-Bis(chloromethyl)-14,17,20,23-tetraoxa-9,28-dithiaheptacyclo[22.10.2.2<sup>10,13</sup>.0<sup>2,11</sup>.0<sup>3,8</sup>.0<sup>27,35</sup>.0<sup>29,34</sup>]octatriaconta-1,3,5,7, 10(38),11,13(37),24,26,29,31,33,35-tridecaene **32** 



 $\begin{array}{l} \mbox{Dicyclohexyl 14,17,20,23-tetraoxa-9,28-dithiaheptacyclo} \\ \mbox{[22.10.2.2^{10.13}.0^{2.11}.0^{3.8}.0^{27.35}.0^{29.34}] octa-triaconta-1,3,5,7,10(38), \\ \mbox{11,13(37),24,26,29,31,33,35-tridecaene-5,32-dicarboxylate $\mathbf{28}$ \end{array}$ 



8,11,14,17,30,33,36,39,42,45-Decaoxa-52,54-dithiaoctacyclo-[45.3.1.1<sup>3,7</sup>,1<sup>4,50</sup>,1<sup>18,22</sup>,1<sup>21,25</sup>,1<sup>24,28</sup>,0<sup>2,23</sup>]-hexapentaconta-1(51), 2(23),3(56),4,6,18,20,22(55),24(53),25,27,47,49-tridecaene **9** 

Figure 2,ESI Atom numbering schemes of compounds 24, 28, 32, and 9.







5,35-Bis(chloromethyl)-14,17,20,23,26-pentaoxa-9,31-dithiaheptacyclo[25.10.2.2<sup>10,13</sup>.0<sup>2,11</sup>.0<sup>3,8</sup>.0<sup>30,38</sup>.0<sup>32,37</sup>]hentetraconta-1,3, 5,7,10(41),11,13(40),27,29,32,34,36,38-tridecaene **33** 



Dicyclohexyl 14,17,20,23,26-pentaoxa-9,31-dithiaheptacyclo [25.10.2.2<sup>10,13</sup>.0<sup>2,11</sup>.0<sup>3,8</sup>.0<sup>30,38</sup>.0<sup>32,37</sup>]hentetraconta-1,3,5,7,10(41), 11,13(40),27,29,32,34,36,38-tridecaene-5,35-dicarboxylate **29** 



8,11,14,17,20,33,36,39,42,45,48-Undecaoxa-55,57-dithiaoctacyclo[48.3.1.1<sup>3,7</sup>,1<sup>4,53</sup>,1<sup>21,25</sup>,1<sup>24,28</sup>,1<sup>27,31</sup>,0<sup>2,26</sup>]nonapentaconta-1(54),2(26),3(59),4,6,21,23,25(58),27(56),28,30,50,52-tridecaene **10** 

Figure 3,ESI Atom numbering schemes of compounds 25, 29, 33, and 10.

Chiroptical data 7:

 $\lambda_{\text{max}}$  (*n*-hexane)/nm 213 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 56300), 236 (28700), 269 (16200), 366 (6400); Chiral HPLC analysis; Daical AD column, *n*-hexane/*i*-propanol 120/1, retention times: 64 (*P*) and 72 min (*M*); CD: (*M*)-7:  $\lambda_{\text{max}}$  (*n*-hexane)/nm 227 ( $\epsilon$ /1000 cm<sup>2</sup> mol<sup>-1</sup> +20.3), 247 (+23.5), 268 (-6.8), 287 (+28.0), 308 (-12.4).

Chiroptical data 8:

 $\lambda_{max}$  (*n*-hexane)/nm 212 ( $\epsilon/dm^3 mol^{-1} cm^{-1} 62500$ ), 235 (30400), 269 (16600), 366 (7100); Chiral HPLC analysis; Daical AD column, *n*-hexane/*i*-propanol 60/1, retention times: 44 (*M*) and 56 min (*P*): CD: (*P*)-7:  $\lambda_{max}$  (*n*-hexane)/nm 218 ( $\epsilon/1000 cm^2 mol^{-1} + 22.3$ ), 228 (-18.4), 248 (-23.7), 268 (+9.5), 287 (-40.0), 310 (+21.8).

#### X-Ray Analysis of bisthioxanthylidene biscrown ether (M)-9.



Figure 4,ESI PLUTO (left) and ORTEP (right) drawing of bisthioxanthylidene biscrown ether (M)-9. All atoms are represented by their displacement vibrational ellipsoids drawn to encompass 50% of the electron density (ORTEP).

Recrystallization from acetone yielded crystals of **9** suitable for X-ray analysis (Figure 4,ESI). The folded structure of the central bisthioxanthylidene moiety is clearly visible and folding angles between 48.8° and 54.7° for the two thioxanthylidene halves were found. Slight deviations from planarity were observed for the central double bond and folding angles amounting to  $6.4^{\circ}$  were established. The 'small' crown ether moiety with four oxygen atoms is visible at the right side of the drawing while the 'large' crown ether moiety with six oxygen atoms is present at the left side. Refinement of the structure was complicated (frustrated) by a disorder problem. From the solution it was clear that the 'large' crown ether moiety (C27 – C38) was highly disordered. The electron density of these atoms appeared to be spread out indicating conformational disorder. Refinements on these site occupancy factors did not converge, so ultimately bond restraints were used in the refinement which resulted in unrealistic displacement parameters for these positions. This fact suggests the major problem with the structure is related to several possible conformations of the 'large' crown ether ring (see ORTEP drawing). Largest shift/error ratio observed was found to be 0.714 for parameter U12 of atom C32 (most disordered position, see ORTEP drawing).

## IUPAC-name: **8,11,14,17,30,33,36,39,42,45-Decaoxa-52,54-dithiaoctacyclo-**[**45.3.1.1**<sup>3,7</sup>.1<sup>4,50</sup>.1<sup>18,22</sup>.1<sup>21,25</sup>. 1<sup>24,28</sup>.0<sup>2,23</sup>]-hexapentaconta-1(51),2(23),3(56),4,6,18,20,22(55),24(53),25,27,47,49-tridecaene

C<sub>44</sub>H<sub>48</sub>O<sub>10</sub>S<sub>2</sub> M = 800.2688 Monoclinic  $P2_1/a, a = 20.617(1), b = 9.336(1), c = 20.742(2) Å$   $\beta = 95.882(6)^{\circ}$   $V = 3971.4(6) Å^3$  Z = 4  $D_x = 1.340 \text{ g cm}^{-3}$   $\lambda(\text{MoK}\alpha) = 0.71073 Å$   $\mu = 1.94 \text{ cm}^{-1}$   $F(000) = 1696, T = 130 \text{ K}, wR(F^2) 0.3425 \text{ for } 6952 \text{ reflections with } F_0^2 \ge 0 \text{ and } 506 \text{ parameters}$ 16 restraints and R(F) = 0.1148 for 4456 reflections obeying  $F_0 \ge 4.0 \sigma(F_0)$  criterion of observability GooF = 1.090 Residual electron density in final Fourier map,  $e/Å^3 = -0.90, 1.87(12)$ 

#### **Complexation experiments**<sup>1</sup>

<sup>1</sup>H NMR data of bisthioxanthylidene crown ethers 5, 9, and 10 in acetone- $d_6$ .

**15,18,21,24,27,30-Hexaoxa-9,36-dithiaheptacyclo**[**30,10,2.2**<sup>10,13</sup>.**0**<sup>2,11</sup>.**0**<sup>3,8</sup>.**0**<sup>35,43</sup>.**0**<sup>37,42</sup>]hexatetraconta -1,3,5,7,10(46),11,13(45),32,34,37,39,41,43-tridecaene (5) <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ , 25°C)  $\delta$  7.76 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H, H<sub>II</sub>), 7.40 (d, J = 7.7 Hz, 2H), 7.36 (dd, J = 7.7, 7.3 Hz, 2H, H<sub>IV</sub>), 7.12 (t, J = 7.7, 7.3 Hz, 2H), 6.93 (d, J = 7.7, 2H), 6.89 (s, 2H), 4.41 (AB,  $J_{AB} = 12.8$  Hz,  $\Delta v = 9.1$  Hz, 4H, H<sub>II(A)</sub>,H<sub>II(B)</sub>), 3.80 – 3.73 (m, 12H), 3.68 (AB part of ABXY system, apparent as ddd, J = 20.9, 10.1, 5.3 Hz, 4H, H<sub>I(AB)</sub>), 3.48 (XY part of ABXY system, apparent as ddd, J = 20.9, 10.1, 5.3 Hz, 4H, H<sub>I(XY)</sub>).

**8,11,14,17,30,33,36,39,42,45-Decaoxa-52,54-dithiaoctacyclo**[**45.3.1.1**<sup>3,7</sup>.**1**<sup>4,50</sup>.**1**<sup>18,22</sup>.**1**<sup>21,25</sup>.**1**<sup>24,28</sup>.**0**<sup>2,23</sup>] **hexapentaconta-1(51),2(23),3(56),4,6,18,20,22(55),24(53),25,27,47,49-tridecaene (9)** <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ , 25°C)  $\delta$  7.70 (d, J = 7.7 Hz, 2H, **H**<sub>III</sub>), 7.65 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.04 (dd, J = 8.8, 2.6 Hz, 2H, **H**<sub>IV</sub>), 6.84 (s, 2H), 6.56 (d, J = 2.6 Hz, 2H), 4.39 (AB,  $J_{AB}$  = 12.8 Hz,  $\Delta v$  = 12.6 Hz, 4H, **H**<sub>II(A)</sub>,**H**<sub>II(B)</sub>), 4.22 - 4.16 (m, 2H, **H**<sub>V</sub>), 3.90 - 3.72 (m, 22H), 3.67 (AB part of ABXY system, apparent as 2 × ddd, J = 11.0, 5.5, 4.0 Hz, 4H, **H**<sub>I(AB)</sub>), 3.45 (XY part of ABXY system, apparent as 2 × ddd, J = 11.0, 5.5, 4.0 Hz, 4H, **H**<sub>I(XY)</sub>).

**8,11,14,17,20,33,36,39,42,45,48-Undecaoxa-55,57-dithiaoctacyclo[48.3.1.1<sup>3,7</sup>.1<sup>4,53</sup>.1<sup>21,25</sup>.1<sup>24,28</sup>.1<sup>27,31</sup>. 0**<sup>2,26</sup>]**nonapentaconta-1(54),2(26),3(59),4,6,21,23,25(58),27(56),28,30,50,52-tridecaene (10)** <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ , 25°C)  $\delta$  7.71 (d, J = 7.7 Hz, 2H, **H**<sub>III</sub>), 7.66 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.04 (dd, J = 8.4, 2.6 Hz, 2H, **H**<sub>IV</sub>), 6.86 (s, 2H), 6.56 (d, J = 2.6 Hz, 2H), 4.40 (AB,  $J_{AB}$  = 12.8 Hz,  $\Delta v_{AB}$  = 10.9 Hz, 4H, **H**<sub>II(A)</sub>,**H**<sub>II(B)</sub>), 4.05 - 4.00 (ddd, J = 9.5, 5.0, 2.8 Hz 2H, **H**<sub>V</sub>), 3.79 - 3.70 (m, 26H), 3.66 (AB part of ABXY system, apparent as 2 × ddd, J = 10.5, 6.1, 4.1 Hz, 4H, **H**<sub>I(AB)</sub>), 3.46 (XY part of ABXY system, apparent as 2 × ddd, J = 10.5, 6.1, 4.1 Hz, 4H, **H**<sub>I(XY)</sub>).

**Complexation of biscrown ether 9 with KSCN.** A solution of **9** (38 mg,  $4.75 \times 10^{-2}$  mmol) in acetoned<sub>6</sub> (5.00 mL) was prepared which was stored under a nitrogen atmosphere. Nine oven-dried (100°C) NMR tubes were charged with 0.50 mL of this stock solution. Different portions of a solution of KSCN in acetone-d<sub>6</sub> (stored under a nitrogen atmosphere) were added in order to obtain samples with 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 equivalents of KSCN with respect to **9**. Acetone-d<sub>6</sub> was added to the samples till each NMR-tube was charged with 0.75 mL of acetone-d<sub>6</sub>. Concentration of **9** in each NMR-tube:  $6.33 \times 10^{-3}$  M.

**Complexation of biscrown ether 9 with NaSCN.** Complexation was measured with 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 equivalents of NaSCN with respect to **9**. Concentration of **9** in each NMR-tube:  $6.33 \times 10^{-3}$  M.

**Complexation of biscrown ether 10 with KSCN.** Complexation was measured with 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 equivalents of KSCN with respect to **10**. Concentration of **10** in each NMR-tube:  $6.32 \times 10^{-3}$  M.

**Complexation of biscrown ether 10 with NaSCN.** Complexation was measured with 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 equivalents of NaSCN with respect to **10**. Concentration of **10** in each NMR-tube:  $6.32 \times 10^{-3}$  M.

**Complexation of monocrown ether 5 with KSCN.** Complexation was measured with 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 equivalents of KSCN with respect to **5**. Concentration of **5** in each NMR-tube:  $6.33 \times 10^{-3}$  M.

**Complexation of monocrown ether 5 with NaSCN.** Complexation was measured with 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, and 5.00 equivalents of NaSCN with respect to **5**. Concentration of **5** in each NMR-tube:  $9.06 \times 10^{-3}$  M.

**Table 1** Protons  $H_I - H_V$  (Figure 5 in main text article) and their assignment according to IUPAC nomenclature (see Figures 1,ESI – 3,ESI of Suplementary information.

| proton                  |               | crown ether compounds |              |
|-------------------------|---------------|-----------------------|--------------|
| (Figure 5 in main text) | 5             | 9                     | 10           |
| H <sub>I(AB)</sub>      | 4Н, 17-, 28-Н | 4Н, 32-,43-Н          | 4Н, 35-,46-Н |
| $H_{I(XY)}$             | 4H, 16-, 29-H | 4H, 31-,44-H          | 4Н, 34-,47-Н |
| $H_{II(A)}, H_{II(B)}$  | 4H, 14-, 31-H | 4H, 29-,46-H          | 4Н, 32-,49-Н |
| H <sub>III</sub>        | 4H, 34-,46-H  | 4H, 26-,49-H          | 4Н, 29-,52-Н |
| H <sub>IV</sub>         | 4H, 6-,39-H   | 4Н, 6-,19-Н           | 4Н, 6-,22-Н  |
| $H_V$                   | -             | 2Н, 9-,16-Н           | 2Н, 9-,19-Н  |

Table 2 Changes in system, splitting pattern, coupling constants of protons  $H_I - H_V$  (Figure 5 in main text) of compounds 5, 9, and 10 upon addition of 5 equivalents of salt.<sup>b</sup>

|       |       |       | $H_{I(X)}, H_{I(Y)}$ |         | $H_{II(A)}, H_{II(B)}$ |        | $H_{I}$                   | $H_{III}$ |     | H <sub>IV</sub> | $H_V$    |         |               |
|-------|-------|-------|----------------------|---------|------------------------|--------|---------------------------|-----------|-----|-----------------|----------|---------|---------------|
| entry | crown | salt  | system               | pattern | $J(\mathrm{Hz})$       | system | $J_{AB}$ (Hz), $\Delta v$ | pattern   | J   | pattern         | J        | pattern | J             |
| 1     | 5     | -     | XY                   | $ddd^a$ | 20.9, 10.1, 5.3        | AB     | 12.8, 9.1                 | d         | 7.7 | dd              | 7.7, 7.3 | -       | -             |
| 2     | 5     | KSCN  | XY                   | m       | -                      | AM     | 13.2, 88.4                | d         | 8.1 | dd              | 7.7, 7.3 | -       | -             |
| 3     | 5     | NaSCN | XY                   | 2×ddd   | 13.6, 5.7, 3.1         | AM     | 12.5, 50.9                | d         | 8.1 | dd              | 7.7, 7.3 | -       | -             |
| 4     | 9     | -     | XY                   | 2×ddd   | 11.0, 5.5, 4.0         | AB     | 12.8, 12.6                | d         | 7.7 | dd              | 8.8, 2.6 | m       | -             |
| 5     | 9     | KSCN  | XY                   | m       | -                      | AM     | 12.8, 91.9                | d         | 8.1 | dd              | 8.4, 2.6 | m       | -             |
| 6     | 9     | NaSCN | XY                   | 2×ddd   | 13.7, 5.9, 3.1         | AM     | 12.5, 36.8                | d         | 8.1 | dd              | 8.4, 2.2 | m       | -             |
| 7     | 10    | -     | XY                   | 2×ddd   | 10.5, 6.1, 4.1         | AB     | 12.8, 10.9                | d         | 7.7 | dd              | 8.4, 2.6 | ddd     | 9.5, 5.0, 2.  |
| 8     | 10    | KSCN  | XY                   | 2×ddd   | 9.5, 7.7, 5.1          | AM     | 12.8, 87.3                | d         | 8.1 | dd              | 8.6, 2.8 | ddd     | 9.7, 4.6, 2.9 |
| 9     | 10    | NaSCN | XY                   | 2×ddd   | 13.9, 5.9, 3.0         | AM     | 12.6, 40.4                | d         | 8.1 | dd              | 8.6, 2.8 | ddd     | 9.6, 4.4, 2.  |















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