

## Supporting Information

### Formation of a Macrobicyclic Tris(disulfide) by Molecular Self-Assembly

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#### General Procedure

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were obtained on a General Electric QE-300 300 MHz spectrometer. Equilibrium studies were performed on a Varian Unity Plus 500 MHz spectrometer. Chemical shift values are reported in ppm using known chemical shift values of solvent peaks as reference. High resolution mass spectrometric data were determined by the University of California, Riverside Mass Spectrometry Facility.

#### Tris(disulfide) (1)

$^1\text{H}$ -NMR (DMSO- $d_6$ ):  $\delta$  1.08 (t, 18H,  $\text{CH}_2\text{CH}_3$ ), 2.67 (q, 12H,  $\text{CH}_2\text{CH}_3$ ), 3.58 (d, 12H,  $\text{CH}_2\text{S}$ ), 4.29 (d, 12H,  $\text{ArCH}_2\text{NH}$ ), 7.82 (s, 6H  $\text{NH}$ );  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  1.19 (t, 18H,  $\text{CH}_2\text{CH}_3$ ), 2.58 (q, 12H,  $\text{CH}_2\text{CH}_3$ ), 3.53 (s, 12H,  $\text{CH}_2\text{S}$ ), 4.44 (d, 12H,  $\text{ArCH}_2\text{NH}$ ), 6.22 (s, 6H,  $\text{NH}$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  166.35, 144.42, 132.20, 41.55, 38.69, 23.26, 16.58; HRMS-FAB [ $\text{MH}^+$ ] calcd for  $\text{C}_{42}\text{H}_{61}\text{N}_6\text{O}_6\text{S}_6$  m/z 937.227, found m/z 937.2973

#### 2,4,6-Triethyl-1,3,5-tri((2-mercaptoacetamido)methyl)benzene (2)

$^1\text{H}$ -NMR (DMSO- $d_6$ ):  $\delta$  1.08 (t, 9H,  $\text{CH}_2\text{CH}_3$ ), 2.66 (q, 6H,  $\text{CH}_2\text{CH}_3$ ), 2.75 (t, 3H,  $\text{SH}$ ), 3.10 (d, 6H,  $\text{CH}_2\text{SH}$ ), 4.30 (d, 6H,  $\text{ArCH}_2\text{NH}$ ), 8.02 (s, 3H,  $\text{NH}$ );  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  1.23 (t, 9H,  $\text{CH}_2\text{CH}_3$ ), 1.86 (t, 3H,  $\text{SH}$ ), 2.71 (q, 6H,  $\text{CH}_2\text{CH}_3$ ), 3.29 (d, 6H,  $\text{CH}_2\text{SH}$ ), 4.52 (d, 6H,  $\text{ArCH}_2\text{NH}$ ), 6.51 (s, 3H,  $\text{NH}$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  168.88, 144.44, 131.93, 38.46, 27.99, 23.01, 16.41; HRMS-FAB [ $\text{MH}^+$ ] calcd for  $\text{C}_{21}\text{H}_{34}\text{N}_3\text{O}_3\text{S}_3$  m/z 472.1762, found m/z 472.1751.

### Oligomer (3)

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ 1.07 (broad, 18H, CH<sub>2</sub>CH<sub>3</sub>), 2.74 (broad, 12H, CH<sub>2</sub>CH<sub>3</sub>), 3.60 (broad, 12H, CH<sub>2</sub>S), 4.40 (broad, 12H, ArCH<sub>2</sub>NH), 8.10 (broad, 6H, NH).

### Equilibration of trithiol 2 with 2-hydroxyethyl disulfide (ME<sup>ox</sup>)

A 2 mM solution of ME<sup>ox</sup> in DMSO-d<sub>6</sub> was prepared and purged with Ar<sub>(g)</sub> for 30 minutes. In a 5 mm NMR tube was placed 0.5 ml of a 2 mM solution of trithiol 2 in DMSO-d<sub>6</sub>. This solution was purged with Ar<sub>(g)</sub> for 30 minutes followed by placing the NMR tube in a CO<sub>2(s)</sub>/acetone bath. On top of the solid trithiol solution was layered 0.5 ml of the 2 mM ME<sup>ox</sup> solution followed by flame sealing the NMR tube. The solidified solutions were allowed to thaw and mix to give 1 ml of a solution 1mM in each component. The reaction was then monitored periodically by <sup>1</sup>H-NMR.

This procedure was repeated to give solutions containing 1.5 and 3 mM of ME<sup>ox</sup>.

### Equilibration of tris(disulfide) 1 with 2-mercaptoethanol (ME)

A DMSO-d<sub>6</sub> solution 1 mM in tris(disulfide) 1 and 1 mM in ME was prepared and monitored by <sup>1</sup>H-NMR as above.

### Equilibration of oligomer 3 with 2-mercaptoethanol (ME)

A DMSO-d<sub>6</sub> solution 0.5 mM in oligomer 3 and 1 mM in ME was prepared and monitored by <sup>1</sup>H-NMR as above.