Electronic Supplementary Information

Hierarchical organization from self-assembling disulfide macrocycles

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Preparation of 3 and 4

To an ice cold solution of 1 (510 mg, 0.993 mmol) in dry acetonitrile was added diisopropyl ethylamine (0.34 mL, 1.99 mmol), followed by compound 2 (186.54 mg, 0.993 mmol) under N₂ atmosphere. N₂ gas was bubbled for 15 minutes and then CuI (18.9 mg, 0.099 mmol) was added into it and stirred it for ~24 h under N₂ atmosphere. Filtered the reaction mixture and the residue obtained was washed with saturated solution of NH₄Cl: NH₄OH (9:1), 2N H₂SO₄, saturated solution of NaHCO₃, water and finally with acetone. The residue was then dried to yield 300 mg of compound 3 and 4.

Filtrate was evaporated and re dissolved in chloroform and washed with saturated solution of NH₄Cl: NH₄OH (9:1), 2N H₂SO₄, saturated solution of NaHCO₃ and water. The organic layer was dried over Na₂SO₄ and then evaporated to give 223 mg of the compound. The crude products were purified by silica gel column chromatography using CHCl₃/CH₃OH.

Data of 3

Yield 45 %

Mp: 226-228 °C

¹H NMR (CDCl₃, 300 MHz) δ 1.37 (s, 18H), 2.86 (m, 4H), 4.10 (d, J = 13.2 Hz, 2H), 4.69 (m, 2H), 5.01 (m, 2H), 5.25 (d, J = 14.7 Hz, 2H), 5.42 (d, J = 9.9 Hz, 2H), 5.69 (d, J = 14.7 Hz, 2H), 7.31 (s, 4H), 8.09 (br d, J = 7.5 Hz, 2H).
\[ ^{13} \text{C NMR (CDCl}_3, 75 \text{ MHz)} \delta 28.3, 35.3, 47.4, 53.9, 54.6, 80.6, 121.2, 129.6, 135.3, 146.4, 156.0, 170.2. \]

IR (KBr): 3332, 2929, 2852, 1664, 1627, 1575, 1524, 1437, 1374, 1315, 1242, 1171 cm\(^{-1}\).

HRMS: Calcd for C\(_{30}H_{42}N\(_{10}\)O\(_6\)S\(_2\)Na m/z = 725.2628, found m/z = 725.2631.

Data of 4
Yield: 12 %
Mp: 158-162 °C. (pls. check it in day time again).

\[ ^1 \text{H NMR (CDCl}_3+\text{CD}_3\text{OD, 300 MHz)} \delta 1.39 \text{ (s+s, 36H)}, 2.96 \text{ (m, 8H)}, 3.68 \text{ (s, 8H)}, 4.44 \text{ (m, 4H)}, 5.46 \text{ (s, 8H)}, 6.19 \text{ (br d, 4H)}, 7.20 \text{ (s, 8H)}, 7.67 \text{ (s, 4H)}, 8.36 \text{ (br d, 4H)}. \]

\[ ^1 \text{H NMR (DMSO-}d_6, 300 \text{ MHz)} \delta 1.34 \text{ (s, 36H)}, 2.80 \text{ (m, 4H)}, 3.01 \text{ (m, 4H)}, 4.17 \text{ (br s, 4H)}, 4.28 \text{ (s, 8H)}, 5.51 \text{ (s, 8H)}, 7.05 \text{ (br d, J = 7.8 Hz, 4H)}, 7.26 \text{ (s, 8H)}, 7.87 \text{ (s, 4H)}, 8.46 \text{ (br s, 4H)}. \]

\[ ^{13} \text{C NMR (CDCl}_3, 75 \text{ MHz)} \delta 28.6, 34.9, 52.5, 53.9, 78.9, 123.3, 128.8, 136.4, 145.6, 155.8, 170.9. \]

IR (KBr): 3361, 2976, 2927, 1667, 1520, 1369, 1323, 1176, 1052 cm\(^{-1}\).

HRMS: Calcd for C\(_{60}H_{84}N\(_{20}\)O\(_{12}\)S\(_4\)Na m/z = 1427.5358, found m/z = 1427.5329.

Preparation of macrocycles 6 and 7

To an ice cold solution of 1 (510 mg, 0.993 mmol) in dry acetonitrile was added diisopropyl ethylamine (0.34 mL, 1.99 mmol), followed by compound 5 (186.54 mg, 0.993 mmol) under N\(_2\) atmosphere. N\(_2\) gas was bubbled for 15 minutes and then CuI (18.9 mg, 0.099 mmol) was added into it and stirred it for ~24 h under N\(_2\) atmosphere. Filtered the reaction mixture and the residue obtained was washed with saturated solution of NH\(_4\)Cl: NH\(_4\)OH (9:1), 2N H\(_2\)SO\(_4\), saturated solution of NaHCO\(_3\), water and finally with acetone. The residue was then dried to yield 300 mg of compound.

Filtrate was evaporated and re dissolved in chloroform and washed with saturated solution of NH\(_4\)Cl: NH\(_4\)OH (9:1), 2N H\(_2\)SO\(_4\), saturated solution of NaHCO\(_3\) and water. The organic layer was dried over Na\(_2\)SO\(_4\) and then evaporated to give 223 mg of the compound. The crude mixture was purified by column chromatography using CHCl\(_3\)/CH\(_3\)OH to afford pure 6 and 7.

Data for 6
Yield: 49 %
Mp: 169-170 °C.
$^1$H NMR (CDCl$_3$, 300 MHz) δ 1.33 (s, 18H), 2.94 (br s, 4H), 4.19 (d, J = 14.7 Hz, 2H),
4.67 (m, 2H), 5.00 (m, 2H), 5.37 (m, 4H), 5.59 (d, J = 14.7 Hz, 2H), 7.10 (s, 1H), 7.24 (s, 3H), 7.37 (br s, 3H), 8.24 (br s, 2H).
$^{13}$C NMR (CDCl$_3$+DMSO-$d_6$, 75 MHz) δ 28.2, 35.1, 42.8, 53.3, 54.4, 79.8, 122.0, 126.5, 128.2, 129.5, 135.9, 145.9, 155.7, 170.8.
IR (KBr): 3546, 3361, 2977, 2930, 1673, 1517, 1451, 1377, 1284, 1170, 1054 cm$^{-1}$.
HRMS: Calcd for C$_{30}$H$_{42}$N$_{10}$O$_6$S$_2$Na m/z = 725.2628, found m/z = 725.2602.

Data of compound 7
Yield: 13 %
Mp: 193-197 °C.
$^1$H NMR (CDCl$_3$+CD$_3$OD, 300 MHz) δ 1.39 (s+s, 36H), 2.98 (m, 8H), 3.79 (s, 8H), 4.45
(br m, 4H), 5.46 (d, J = 4.2 Hz, 8H), 6.31 (br s, 4H), 7.08 (s, 2H), 7.26 (br s, 4H), 7.33 (m, 2H), 7.69 (s, 4H), 8.39 (br d, J = 13.8 Hz, 4H).
$^{13}$C NMR (DMSO-$d_6$, 75 MHz) δ 33.3, 39.7, 57.7, 58.6, 58.8, 83.5, 83.62, 128.2, 132.7, 132.9, 134.4, 141.7, 150.3, 160.5, 175.5, 175.6.
$^1$H NMR (DMSO-$d_6$, 300 MHz) δ 1.49 (s, 36H), 3.00 (m, 4H), 3.18 (m, 4H), 4.33 (br s, 4H), 4.44 (s, 8H), 5.67 (s, 8H), 7.21 (d, J = 7.5 Hz, 3H), 7.34 (m, 4H), 7.46 (m, 4H), 8.04 (s, 2H), 8.64 (br s, 4H).
IR (KBr): 3331, 2977, 2930, 1691, 1662, 1526, 1456, 1369, 1316, 1245, 1169, 1053 cm$^{-1}$.
HRMS: Calcd for C$_{60}$H$_{85}$N$_{20}$O$_{12}$S$_4$ m/z = 1405.5539, found m/z = 1405.5536.
Spectral data

$^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 3

$^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound 3
COSY spectrum of compound 3

ROESY spectrum of compound 3

1 = b, c  
2 = c, d'  
3 = a, b  
4 = d, d'  
5 = f, f'
$^1$H NMR (300 MHz, CDCl$_3$+CD$_3$OD) spectrum of compound 4

$^1$H NMR (300 MHz, DMSO-$d_6$) spectrum of compound 4
$^{13}$C NMR (75 MHz, DMSO-$d_6$) spectrum of compound 4

$^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 6
$^{13}$C NMR (75 MHz, CDCl$_3$+DMSO-$d_6$) spectrum of compound 6

$^1$H NMR (300 MHz, CDCl$_3$+CD$_3$OD) spectrum of compound 7
$^1$H NMR (300 MHz, DMSO-$d_6$) spectrum of compound 7

$^{13}$C NMR (75 MHz, DMSO-$d_6$) spectrum of compound 7
1. Microscopy Methods

Scanning Electron Microscopy (SEM)
The gels were made in appropriate solvent systems. These samples were dried at room temperature on a piece of cleaved mica, attached to a stub via carbon tape and coated with ~10 nm of gold. Samples were analyzed using ZEISS EVO 50 SEM.

Transmission Electron Microscopy and High-Resolution Transmission Electron Microscopy (TEM and HR-TEM)
Samples for TEM and HR-TEM were prepared by dissolving the compound in 4:1 methanol and chloroform mixture. A 2 µl aliquot of the sample solution was placed on a 200 mesh copper grid. After 3 min., the grid was stained with 2 % phosphotungstate in water for 2 min. and the excess fluid was removed. Samples were viewed using a TECHNAI G2 (20S-TWIN) electron microscope.

Confocal Microscope
Samples for confocal microscope were prepared by dissolving the macrocycle 4 in 4:1 methanol and chloroform mixture. To this was added 0.02 equivalent of Rhodamine B. A 10 µl aliquot of the sample solution was dried on a cover glass and covered with a cover slip. The samples were viewed by using OLYMPUS Fv 1000 confocal microscope.

Atomic Force Microscopy (AFM)
Sample images were acquired using a Park systems XE-70 atomic force microscope operating in non-contact mode in air. About 20 µl aliquot of the sample solution was transferred onto freshly cleaved mica and allowed to dry.

II. Powder XRD measurement
Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer using Ni-filtered CuKα radiation. Data were collected with a step size of 0.02° and a count time of 2s per step.
Figure S1: HR-TEM image of macrocycle 3

Figure S2: SEM image of gel formed from 3 in ethylacetate

Figure S3: (a) Tube-like morphology of insoluble aggregate of macrocycle 3 observed in SEM (b) careful analysis of the SEM image showed twisted morphology.
Figure S4: SEM image obtained from a concentrated solution 4

Figure S5: HR-TEM image of the macrocycle 4
Figure S6: AFM image of macrocycle 4. Measurement was made in non-contact mode.

Figure S7: Confocal image of 4, indicating leakage of the dye from the vesicles after reduction.
**Figure S8:** UV spectra (methanol and chloroform mixture (4:1)) of (i) Rhodamine B alone (violet), (ii) 30 min. after addition of 0.02 equivalents of 4 (blue), (iii) 3h after addition of 0.02 equivalents of 4 (green), (iv) 6h after addition of 0.02 equivalents of 4 (red)

**Figure S9:** UV spectrum of 3 (0.0002M) in methanol

**Figure S10:** A) CD spectrum of 3 (0.0002M) in methanol B) Temperature dependent CD spectra of 3: (a) at 10 °C, (b) at 45 °C, and (c) at 65 °C
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Critical gel concentration (g/ml)</th>
</tr>
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<tbody>
<tr>
<td>Chloroform</td>
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</tr>
<tr>
<td>Ethylacetate</td>
<td>0.0098</td>
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<tr>
<td>Methanol</td>
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</tr>
<tr>
<td>Acetonitrile</td>
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<tr>
<td>THF</td>
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<tr>
<td>Acetone</td>
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<tr>
<td>Dichloromethane</td>
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</tr>
<tr>
<td>Ethanol</td>
<td>0.009</td>
</tr>
<tr>
<td>Water</td>
<td>No gel</td>
</tr>
</tbody>
</table>

**Table S1:** Gelation studies of macrocycle 3 in various solvents
Figure S11: Macrocycle 3 (flask a) was dissolved in 1:4 chloroform:methanol (flask b). After keeping the solution for 2 days, insoluble material was observed (flask c). After decanting, the solid obtained (flask d) was analyzed by SEM and PXRD. See Figure S12 for PXRD and SEM of macrocycle. The insoluble aggregate (flask d) gave birefringence upon staining with congo red.
**Figure S12**: (a) PXRD of macrocycle 3 (flask a, figure S11) along with SEM image (b) PXRD of insoluble aggregate of macrocycle 3 (flask d, figure S11) along with SEM image. Green arrows inside the SEM image indicate twist in the morphology.
**Figure S13**: Dynamic light scattering study on macrocycle 4 in 1:4 chloroform:methanol. The concentration of 4 was 0.23 mM.

**Figure S14**: Photographs of gels formed from 3 in (a) chloroform (b) dioxane (c) ethylacetate (d) methanol