Electronic Supplementary Information (ESI)

Self-Assembling Triazolophanes: From Croissants through Donuts to Spherical Vesicles

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I. Synthesis and characterization:

All solvents were distilled or dried from appropriate drying agents prior to use. Amino acid L-Leucine was purchased from SRL India. Progress of reactions was monitored by thin layer chromatography (TLC). Purification of compounds was done by silica gel (100-200 mesh) column chromatography. Silica gel G (Merck) was used for TLC. Melting points were recorded on a Fisher-Scientific melting point apparatus and were uncorrected. Optical rotations were measured using a Rudolph Research Analytical Autopol® V Polarimeter. Specific rotation was reported with concentrations in gram/100mL. IR spectra were recorded on a Nicolet, Protégé 460 spectrometer as KBr pellets. $^1$H NMR spectra were recorded on Brucker-DPX-300 spectrometer using tetramethylsilane ($^1$H) as an internal standard. Coupling constants are in Hz and the $^1$H NMR data are reported as s (singlet), d (doublet), br (broad), t (triplet) and m (multiplet), dd (double doublet). High Resolution mass spectra (HRMS) were recorded in Bruker MicrO-TOF-QII model using ESI technique.
Scheme S1: Scheme of synthesis (a) synthesis of macrocycles M1-M2 (b) Synthesis of macrocycle M3 incorporating L-leucine amino acid.
Synthesis of 2:

Propargyl amine (0.273 mL, 4.26 mmol) was dissolved in dry CH₂Cl₂ (10 mL), added triethylamine (NEt₃) (0.593 mL, 4.26 mmol); stirred for 5 min at 0°C and 5-t-butyl-isophthaloyl chloride 1 (0.5 g, 1.93 mmol) in dry CH₂Cl₂ (60 mL) was added dropwise. The reaction mixture was stirred for 12h at room temperature, diluted with CH₂Cl₂ (50 mL), washed sequentially with 2N H₂SO₄, NaHCO₃ and water. The organic layer was collected, dried over anhyd. Na₂SO₄ and evaporated to yield 490 mg of 2.

Yield: 85 %

Appearance: White solid

Mp: 156-158°C

¹H NMR (300 MHz, CDCl₃): 1.27 (s, 9H), 2.23 (t, J = 2.7Hz, 2H), 4.19 (d+d, J = 2.7Hz, 4H), 6.61 (br s, 2H), 7.90 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 29.7, 31.0, 34.9, 71.8, 79.4, 122.3, 127.8, 133.7, 152.5, 167.3.

IR (KBr): 3268, 3061, 2964, 2869, 2127, 1633, 1597, 1552, 1474, 1419, 1363, 1328, 1283, 1063 cm⁻¹.

HRMS: Calculated for C₁₈H₂₀N₂O₂Na m/z = 319.1417, found m/z = 319.1420.
**Synthesis of 3:**

To an ice-cooled and stirred solution of Boc-L-Leucine (450 mg, 1.948 mmol) in ~150 mL of dry CH$_2$Cl$_2$ was added N-hydroxysuccinimide (269 mg, 2.337 mmol), DCC (481 mg, 2.337 mmol) and stirred for 10 min. To the reaction mixture was added dry NEt$_3$ (0.32 mL, 2.337 mmol) followed by propargyl amine (0.15 mL, 2.337 mmol) and stirred for 24h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated, added ~250 mL of ethyl acetate, washed sequentially with 0.2 N H$_2$SO$_4$, saturated NaHCO$_3$ solution and with brine solution. The organic layer was dried over anhyd. Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was chromatographed on a column of silica gel using ethyl acetate-hexane as eluent to afford yield 430 mg of 3.

Yield: 82 %

Appearance: White solid

$[\alpha]_D^{34}$: -29 (c = 0.1, CH$_3$OH)

Mp: 124-126˚C

$^1$H NMR (300 MHz, CDCl$_3$): 0.90 (br d, 6H), 1.41 (s, 9H), 1.59 (m, 3H) 2.18 (s, 1H), 3.99 (s, 2H), 4.18 (br s, 1H), 5.25 (br s, 1H), 7.13 (br s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 21.8, 22.8, 24.5, 28.2, 28.8, 41.4, 52.7, 71.2, 79.5, 155.8, 173.0.

IR (KBr): 3321, 3057, 2958, 2872, 1686, 1519, 1368, 1244, 1167, 1126, 1074 cm$^{-1}$.

HRMS: Calculated for C$_{14}$H$_{24}$N$_2$O$_3$Na m/z = 291.1679, found m/z = 291.1681.
Synthesis of 4:

Compound 3 (730 mg, 2.72 mmol) was dissolved in dry CH₂Cl₂ (~4 mL), and added TFA (4.1 mL, 54.47 mmol), and stirred for 4h at 0°C. It was subjected to vacuum and the amine obtained was dissolved in dry CH₂Cl₂ (~50 mL) and added triethylamine (0.2 mL, 2.04 mmol), stirred for 5 minutes, and slowly added 5-t-butyl-isophthaloyl chloride(240 mg, 0.93 mmol) as a solution in dry CH₂Cl₂ (~50 mL). The reaction mixture was stirred for 12h at 0°C, diluted with CH₂Cl₂ (50 mL), washed sequentially with 2N H₂SO₄, NaHCO₃ and water. The organic layer was collected, dried over anhyd. Na₂SO₄ and evaporated to yield 400 mg of 4.

Yield: 83 %

Appearance: White solid

Mp: 136-138 °C

[α]D⁰₄: -4.0 (c = 0.1, CH₃OH)

¹H NMR (300 MHz, CDCl₃): δ 0.94 (br d, 12H), 1.20-1.45 (s+m, 11H), 1.75 (br m, 4H), 2.20 (s, 2H), 3.85-4.12 (m, 4H), 4.72 (m, 2H), 7.24 (br m, 2H), 7.75 (d, J= 7.2 Hz, 2H), 7.97 (s, 2H), 8.06 (s, 1H).

¹³C NMR (75 MHz, CDCl₃): δ 24.8, 25.0, 29.2, 31.0, 33.8, 40.7, 52.6, 71.6, 79.4, 123.2, 127.9, 133.6, 152.1, 167.5 173.0.

IR (KBr): 3306, 3073, 2960, 2872, 1698, 2606, 2124, 1636, 1535, 1468, 1364, 1342, 1245, 1163 1085 cm⁻¹.

HRMS: Calcd for C₃₀H₃₄N₄O₄Na m/z =545.3098, found m/z = 545.3077.
Synthesis of M1:

To an ice cooled solution of 1 (250 mg, 0.844 mmol) in dry acetonitrile was added diisopropyl ethylamine (0.174 mL, 1.01 mmol) followed by m-xylylenediazide (158.73 mg, 0.844 mmol) under argon atmosphere and then CuI (15 mg, 0.0844 mmol) was added and stirred for ~24 h under argon. Filtered the reaction mixture, 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 anhyd. Na₂SO₄ and evaporated to give 160 mg of the crude M1. The crude M1 obtained was purified by silica gel column chromatography using CHCl₃/CH₃OH to yield 100 mg of M1.

Yield: 41 %

Mp: Above 300 °C

¹H NMR (300 MHz, DMSO-d₆): δ 1.32 (s, 9H), 4.57 (br d, 4H), 5.56 (s, 4H), 7.46 (br s, 3H), 7.53 (s, 1H), 7.93 (s, 3H), 8.05 (s, 2H), 8.47 (br s, 2H).

¹³C NMR (75 MHz, DMSO-d₆): 29.4, 33.1, 33.5, 51.6, 121.1, 124.6, 125.6, 126.7, 127.6, 132.6, 134.2, 137.1, 144.1, 149.9, 165.1.

IR (KBr): 3425, 3276, 3135, 2961, 2926, 2857, 1653, 1538, 1449, 1328, 1297, 1259, 1228, 1124, 1060, 1029 cm⁻¹.

HRMS: Calcd for C₂₆H₂₈N₈O₂Na m/z = 507.2227, found m/z = 507.2239.
Synthesis of M2:

To an ice cold solution of 1 (250 mg, 0.84 mmol) in dry acetonitrile was added diisopropyl ethylamine (0.174 mL, 1.01 mmol) followed by p-xylylenediazide (158.73 mg, 0.84 mmol) under argon atmosphere. Argon gas was bubbled for 15 minutes and then CuI (15 mg, 0.084 mmol) was added and stirred for ~24 h under argon atmosphere. Filtered the reaction mixture, the filtrate was evaporated, 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 anhyd. Na₂SO₄ and then evaporated to give 150 mg of the crude M2. The crude M2 obtained was purified by silica gel column chromatography using CHCl₃/CH₃OH to yield 80 mg of M2.

Yield: 39 %
Mp: Above 300 °C

¹H NMR (300 MHz, DMSO-d₆): δ 1.31 (s, 9H), 4.49 (s, 4H), 5.57 (s, 4H), 7.35 (s, 4H), 7.55 (s, 1H), 7.73 (s, 2H), 7.86 (s, 2H), 8.66 (br s, 2H).

¹³C NMR (75 MHz, DMSO-d₆): δ 30.9, 34.6, 34.8, 52.7, 122.4, 122.9, 126.6, 129.0, 134.5, 135.8, 145.5, 151.3, 166.5.

IR (KBr): 3440, 3280, 2925, 2855, 1642, 1590, 1547, 1464, 1429, 1366, 1328, 1287, 1260, 1224, 1119, 1055 cm⁻¹.

HRMS: Calcd for C₂₆H₂₈N₈O₂Na m/z = 507.2227, found m/z = 507.2281.
Synthesis of macrocycle M3:

To an ice-cooled solution of 1 (100 mg, 0.844 mmol) in dry acetonitrile was added diisopropyl ethylamine (0.174 mL, 1.01 mmol) followed by m-xylylenediazide (158.73 mg, 0.844 mmol) under argon atmosphere. Argon gas was bubbled for 15 minutes and then CuI (15 mg, 0.0844 mmol) was added into it and stirred for ~24 h under argon atmosphere. Filtered the reaction mixture, and the filtrate was evaporated, re-dissolved in chloroform, 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 anhyd. Na$_2$SO$_4$, evaporated to give 100 mg of the crude M3. The crude product M3 was purified by silica gel column chromatography using CHCl$_3$/CH$_3$OH to yield 40 mg of M3.

Yield: 30 %

Mp: 226-228 °C

$[\alpha]_D^{34}$: +34 (c = 0.1, CH$_3$OH)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.91 (d+d, J = 5.7Hz, 12H), 1.34 (s, 9H), 1.42-2.03 (m, 6H), 4.20 (d, J = 3.6Hz, 1H), 4.24 (d, J = 15Hz, 1H), 4.45 (br d, 2H), 4.61-4.85 (m, 4H), 5.18-5.52 (m, 4H), 6.87 (s, 1H), 7.08-7.26 (m, 3H), 7.47 (d, J =7.8Hz, 2H), 7.57 (s, 2H), 8.03 (s, 2H), 8.19 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 21.9, 22.9, 24.9, 25.5, 33.8, 35.0, 49.2, 52.5, 122.9, 127.3, 128.0, 128.2, 129.6, 133.8, 135.5, 145.4, 152.6, 157.5, 167.5, 173.1.

IR (KBr): 3307, 2959, 2871, 1648, 1595, 1533, 1463, 1387, 1336, 1253, 1127, 1054 cm$^{-1}$.

HRMS: Calcd for C$_{38}$H$_{50}$N$_{10}$O$_4$Na m/z =733.3909, found m/z =733.3920.
II. Spectral data:

$^1$H NMR (300 MHz, CDCl$_3$) spectrum of 2

$^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of 2
Mass spectrum of 2

$\text{H NMR (300 MHz, CDCl}_3\text{)}$ spectrum of 3
$^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of 3

Mass spectrum of 3
$\text{H NMR (300 MHz, CDCl}_3\text{) spectrum of 4}$

$\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{) spectrum of 4}$
$\text{H NMR (300 MHz, DMSO-$d_6$) spectrum of M1}$

$\text{^{13}C NMR (75 MHz, DMSO-$d_6$) spectrum of M1}$
Mass spectrum of M1

H2O

DMSO

(300 MHz, DMSO-\textit{d}_6) spectrum of M2
$^{13}$C NMR (75 MHz, DMSO-$d_6$) spectrum of M2

Mass spectrum of M2
$^1$H NMR (300 MHz, CDCl$_3$) spectrum of M3

$^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of M3

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\[ (\text{M+Na})^+ \]

\[ 733.3920 \]

\[ 1251.6022 \]
III. Microscopic studies:

(a) Scanning Electron Microscopy (SEM)

A 10 μl solution of the compound was put on a fresh piece of glass, which is attached to a stub via carbon tape. The sample was allowed to evaporate at room temperature and coated with ~10nm of gold. All the samples were analyzed using ZEISS EVO 50 SEM.

(b) Field Emission-Scanning Electron Microscopy (FE-SEM)
A 10 μl aliquot of the sample solution was put on a fresh piece of glass, which is attached to a stub via carbon tape. The sample after drying at room temperature was coated with ~10 nm of gold. All the samples were analyzed using FEI Quanta 3D FEG Dual Beam system having High Resolution Field Emission Scanning Electron Microscope (FE-SEM). This dual beam instrument is equipped with Gallium ion column and electron column. The instrument permits the ablation of selected area on the sample followed by imaging. The focused ion beam (FIB) is used for milling the selected area on the sample. This dual beam instrument uses FIB to take cross section of sample and then capture the image using SEM.

A variety of conditions were tested before optimizing the FIB milling conditions. FIB energy of 20 keV was used for milling the selected area from toroid and vesicle.

(c) Atomic Force Microscopy (AFM)

Bruker Dimension Icon atomic force microscope was used for imaging the samples. About 10 μl aliquot of the sample solution was placed on the freshly cleaved mica and allowed to dry. It was then imaged using tapping mode AFM.

(d) High Resolution-Transmission Electron Microscopy (HR-TEM)

Samples for HR-TEM were prepared by dissolving the compound in 1:1 methanol and chloroform mixture. A 2 μl aliquot of the sample solution was placed on a 200 mesh copper grid allowed to dry at room temperature and samples were viewed using a TECHNAI G2 (20S-TWIN) electron microscope.
Figure S1: (I) HR-TEM images of (a) M1 at 0.25 mM showing formation of toroids (b) M1 at 0.5 mM showing formation of toroids (c) M1 at 1 mM showing vesicles. (II) HR-TEM images of (d) M2 at 0.1 mM showing hemi-toroids and toroids (e) M2 at 0.25 mM showing hemi-toroids and mostly toroids (f) M2 at 1 mM showing vesicles. Cartoon representations of (f) toroids and (g) vesicles based on the dimensions estimated by SEM, TEM and AFM.
Figure S2: AFM images of (a) M1 at 0.25 mM showing hemi-toroids and toroids (b) M1 at 1 mM showing vesicles (c) Cross-section along the line in (b). (d) AFM image of M2 at 0.25 mM showing hemi-toroids and toroids (e) Cartoon representation of toroid at 0.25 mM with dimensions estimated by SEM, TEM and AFM. (f) Cross section along the line in (d), (g) M2 at 1 mM showing vesicles. (h) Cross-section along the line in (g).
Figure S3: SEM images of (a) M1 at 0.1 mM showing mostly hemi-toroids and toroids (b) M1 at 0.25 mM showing mostly toroids (c) M1 at 1 mM showing vesicles. Histogram generated from various measurements (d) diameter of toroids of M1 and (e) diameter of vesicles of M1.
Figure S4: SEM images of (a) M2 at 0.25 mM showing mostly toroids (b) M2 at 0.5 mM showing toroids with decreasing internal cavity and vesicles; FE-SEM images of (c) M2 at 0.5 mM showing toroids with decreased internal cavity and vesicles (d) M2 at 1 mM showing vesicles. Histogram generated from various measurements (e) diameter of toroids of M2 and (f) diameter of vesicles of M2.
Figure S5: (I) TEM images of (a) M3 at 0.25 mM showing formation of toroids. Inset shows a single magnified hemi-toroid (b) M3 at 0.5 mM showing toroids. Inset shows a single magnified toroid (c) M3 at 1 mM showing vesicles. (II) HR-TEM images of (d-e) M3 at 1 mM showing vesicles. Cartoon representations of (f) toroids and (g) vesicles based on the dimensions estimated by SEM, TEM and AFM.
**Figure S6**: AFM images of (a) M3 at 0.1 mM showing hemi-toroids (b) M3 at 0.25 mM showing toroids. Inset shows a single magnified toroid (c) M3 at 1 mM showing vesicles (d) Cross-section along the line in (c).
Figure S7: FE-SEM images of (a-b) M3 at 0.1 mM showing hemi-toroids and toroids (c) M3 at 0.25 mM showing hemi-toroids and mostly toroids (d) M3 at 0.5 mM showing toroids with decreased internal cavity and vesicles (e) M3 at 1 mM showing vesicles (f) SEM of M3 at 1 mM showing vesicles.
Figure S8: DLS of (a) M2 at different concentrations in 1:1 MeOH/CHCl₃ (b) M3 at different concentrations in 1:1 MeOH/CHCl₃. Malvern Zetasizer NanoS operating at 25 °C is used for the measurement.
Figure S9: FE-SEM images of (a-d) M1 after FIB milling (e-f) M3 after FIB milling. The selected part of the vesicles was excised out by focused ion beam. The hollow interior is clear from the images of the vesicles after FIB milling a-f. The wall (layer) of the vesicle is relatively thick as seen in the cross-section of the vesicle.
IV. X-ray crystal structure:

Single crystals of $\text{C}_{26}\text{H}_{28}\text{N}_8\text{O}_2$ (M2) were obtained by (the slow evaporation of its solution in chloroform:methanol (1:1) and few drops of acetonitrile). A suitable crystal was mounted on a Nylon loop and placed on an Agilent Gemini, EOS, single crystal X-ray diffractometer. The crystal was kept at 173(2) K during data collection. Using the Olex2 software package$^{[1]}$, the structure was solved with the Superflip$^{[2]}$ using Charge Flipping and refined with the ShelXL$^{[3]}$ refinement package using Least Squares minimization.
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**Figure S10:** Crystal structure of M2 with atom numbering. Two molecules are present in the unit cell. These molecules differ in the arrangement of triazole rings. In one, triazole units are in *syn* and in the other triazole units are in the *anti*-arrangement.
Figure S11: (a) Stacking of syn molecules along $a$ axis (b) Stacking of syn molecules along $c$ axis (c) Stacking of anti molecules along $a$ axis (d) Stacking of anti molecules along $c$ axis.
Figure S12: X-ray crystal structure of M2: (a) the hydrogen bonded tetrad arrangement with atom labels (b) Chemical structure representation of tetrad assembly. Blue colored structures represent syn conformer and red colored structures represent anti conformer. Dashed lines indicate hydrogen bonds between anti and syn conformers of M2.
Figure S13: X-ray crystal structure of M2, (a-b) the hydrogen bonded arrangement between stacks (c) Packing diagram of M2 in the solid state.
**Table S2**: Hydrogen bonds and weak intermolecular interactions for M2

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V. Mechanism of self-assembly

Figure S14: (a) Schematic representation of the mechanism of self-assembly of M2 (b) A toroid showing poloidal and toroidal components.
REFERENCES:

