Thickness Control of 2D Nanosheets

**Thicknes Control of 2D Nanosheets Assembled from Precise Side-Chain Giant Molecules**

Fengfeng Feng,1 Dong Guo,5 Yu Shao,2 Xiang Yan,4 Kan Yue,3 Zhipeng Pan,1 Xiangqian Li,1 Dongcheng Xiao,1 Liang Jin,1 Wen-Bin Zhang,2 and Hao Liu*,1

1State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Center for Advanced Low-Dimension Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China.

2Key Laboratory of Polymer Chemistry & Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.

3South China Advanced Institute of Soft Matter Science and Technology, School of Molecular Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China.

4School of Materials Science and Engineering, Baise University, Baise 533000, P. R. China.

5Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, Ohio 44325, United States.

*To whom correspondence should be addressed. E-mail: liuh@dhu.edu.cn
Contents

1. Chemicals and Solvents.
2. Instrumentation and Characterization.
3. Synthetic details.
4. 2D Nanosheets Preparation.
5. Formula Deduction.
6. Supplementary Schemes, Tables and Figures.
7. Scheme S1. Synthesis route of Mal-XPOSS-ST monomer. X represents B or V.
8. Scheme S2. Synthesis route of Mal-CONHS.
9. Scheme S3. Synthesis route of intermediate products BX. X represents B or V.
10. Scheme S4. Transformation of the intermediate products B_nV into the final products B_nA (n = 1~5).
11. Fig. S1. ^1^H NMR spectra and peak assignments of Fmoc-BPOSS-ST, NH_2-BPOSS-ST, and Mal-BPOSS-ST.
12. Fig. S2. ^1^H NMR spectra and peak assignments of intermediate giant molecules BV, B_3V, and B_5V.
13. Fig. S3. ^1^H NMR spectra of side-chain giant molecules B_nA (n = 1~5).
14. Fig. S4. ^1^H NMR spectra of giant molecules B_nV_2 and B_nA_2 (n= 2~4).
15. Fig. S5. GPC traces of giant molecules B_nV and B_nV_2 (n = 2~4).
16. Fig. S6. 2D WAXD pattern of APOSS.
17. Fig. S7. (a) [010] zone view and (b) [100] zone view of the crystal lattice model of T8 BPOSS with the corresponding simulated ED patterns.
18. Fig. S8. SAED patterns of 2D nanosheets assembled from (a) BA, (b) B_2A, (c) B_4A_2, (b) B_3A_2 and B_2A_2. Color inversion was conducted on the original SAED data for a better contrast.
19. Fig. S9. WAXD patterns of side-chain giant molecules B_nA (n = 1~5) and B_nA_2 (n = 2~4).
20. Fig. S10. (a) GPC traces of B, BV and BVV. (b) ^1^H NMR spectra of B, BV, BVV and BA_2. (c), (d) and (e) are BF TEM images of BA_2 evaporated from its THF/DMF(1/2) solution.
21. Table S1. Giant molecules self-assembly solution composition and concentrations.
1. Chemicals and Solvents.

Octavinyl polyhedral oligomeric silsesquioxane (V8T8, 98%, Shanghai Gileader Chemical Co., Ltd), isobutyltrisilanol-POSS, 2-mercaptoethanol (>98%, TCI America), 1-octanethiol (98%, Adamas), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma-Aldrich), β-Alanine (99%+, Adamas), 4-dimethylaminopyridine (DMAP, 98%, Adamas), N,N'-diisopropylcarbodiimide (DIPC, 98%+, Adamas), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%, Adamas), fmoc-S-trityl-L-cysteine (98%, Aladdin), triethylsilane (TES, 99%, Adamas), triethylamine (TEA, 99.5%, J&K Chemicals), N-hydroxymaleimide (98%, Adamas), 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone (>98%, TCI America), trifluoroacetic acid (TFA, 99%+, Maclin), maleic anhydride (99%+, Adamas), anhydrous sodium sulfate (Na₂SO₄, Adamas, 98%), mercapto acetic acid (98%, J&k Chemicals), anhydrous calcium chloride (CaCl₂, Adamas, 98%) were used as received. Dichloromethane (DCM), ethyl acetate (EA), petroleum ether (PE), tetrahydrofuran (THF), N,N-dimethylformamide (DMF, anhydrous 99.8%), chloroform, acetonitrile (ACN), toluene, methanol were used as received unless otherwise stated.

2. Instrumentation and Characterization.

Nuclear Magnetic Resonance (NMR). All ¹H NMR and ¹³C NMR spectra were acquired in CDCl₃ using a Bruker 400 MHz NMR spectrometer. ¹H NMR spectra were referenced to the residual solvent peak in CDCl₃ at δ 7.27 ppm, and ¹³C NMR spectra were referenced to the residual peak in CDCl₃ at δ 77.0 ppm.

Gel Permeation Chromatography (GPC). GPC was measured at 45 °C on the ACQUITY APC instrument equipped with four ACQUITY APC XT columns (XT-45, XT-125, XT-200, XT-450 in series), a double flow type RI detector, and an ACQUITY APC TUV detector, using THF as eluent. The flow-rate was 0.6 mL/min. Data acquisition was performed using the Empower software, and molecular weights and molecular weight distributions were calibrated with polystyrene standards. Fig. 1b was carried out with XT-45 and XT-125 columns in a tandem manner. Fig. S5 was recorded with all four columns.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF). MALDI-TOF mass spectra were acquired on an UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonics) equipped with a 1 KHz smart beam-Ⅱ laser. Trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Sigma-Aldrich, >98%) was used as matrix and prepared in CHCl₃ at a concentration of 20 mg/mL. The cationizing agent, sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in CHCl₃ at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, target plate was inserted
Thickness Control of 2D Nanosheets into the MALDI-TOF mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and maximize the sensitivity.

**Transmission Electron Microscopy (TEM).** TEM measurements were conducted on a Thermo Scientific Talos F200S equipment with an accelerating voltage of 200 kV to record the bright field images and SAED patterns. BF images were taken on a digital CCD camera and processed with the accessory digital imaging software. SAED patterns were obtained by using a tilting stage. The \( d \)-spacings were calibrated using an Al standard.

**Atomic Force Microscopy (AFM).** AFM experiments were performed on an Oxford Instruments MFP-3D-BIO microscope to examine the 2D nanocrystals grown on the carbon-coated mica substrate by slow evaporation from its solution with a concentration of 0.2 mg/mL. The images were taken in the tapping mode. The cantilever force was light enough to avoid any damage to the sample, yet strong enough so that the height features could be accurately explored. The scanning rate was 1.0 Hz for low-magnification images at a resolution of 512 × 512 pixels per image.

**Grazing incidence Wide-Angle Scattering (GIWAXD).** GIWAXD data was collected on Sector 8-ID-E at the Advanced Photon Source, Argonne National Laboratory. Beamline 8-ID-E operates at an energy of 7.35 keV, and the scattered intensity was collected by a Pilatus 1M-F area detector. GIWAXD data were analyzed using the GIXSGUI package, and corrected for X-ray polarization, detector sensitivity, geometrical solid-angle, etc. The beam size is 100 \( \mu \text{m} \) (h) × 20 \( \mu \text{m} \) (v).

**Small angle X-ray scattering (SAXS).** SAXS experiments were performed on Shanghai Synchrotron Radiation (SSRF), beamline BL16B1. The incident X-ray photon energy was 10 keV; the wavelength of the X-ray was 0.124 nm; the photo flux was \( 1 \times 10^{11} \text{ phs/s} \). The beam size is around 0.4 × 0.5 mm². Scattered X-rays were captured on a two-dimensional Pilatus detector. The instrument was calibrated with diffraction patterns from silver behenate. Some of the SAXS data was also recorded at Beamline 1W2A of the Beijing Synchrotron Radiation Facility (RSRF) with a wavelength of 1.54 Å. All the samples were vacuum dried for more than 24h and then tested at room temperature.

**Wide angle X-ray diffraction (WAXD).** WAXD data were recorded at Beamline 1W2A of the Beijing Synchrotron Radiation Facility (BSRF) with a wavelength of 1.54 Å. All the samples were vacuum dried for more than 24h and then tested at room temperature.
3. Synthesis

3.1 Monomer synthesis

**BPOSS-OH.** To a test tube, BPOSS-vinyl (1 g, 1.19 mmol) dissolved in THF were added followed by adding 2-mercaptopethanol (185 mg, 2.4 mmol), and then to the resulting solution a catalytic amount of DMPA was added. Irradiation of the solution under a 365 nm UV lamp at room temperature for 30 minutes was to make sure no vinyl groups existed. Four test tubes filled with equal amount could be operated at the same time. The residue was finally purified by flash column chromatography silica gel with the mixture of DCM/petroleum ether (v/v = 1:1 to 3:1) as the eluent to afford the product as white solid. Yield: 82%. 

\[
\begin{align*}
\text{1H NMR (CDCl}_3, 400 MHz, ppm, } & \delta: 0.95 (42H, -\text{CH}_2-\text{CH-(CH}_3)_2), 0.88 (2H, -\text{Si-CH}_2-\text{CH}_2-), 0.62 (14H, -\text{CH}_2-\text{-CH}-(\text{CH}_3)_2), 1.85 (7H, -\text{CH}_2-\text{-CH}-(\text{CH}_3)_2), 2.5 (2H, -\text{Si-CH}_2-\text{-CH}_2-), 2.6 (2H, -\text{-S-CH}_2-\text{-CH}_2-), 3.9 (2H, -\text{-S-CH}_2-\text{-CH}_2-). \\
\text{13C NMR (CDCl}_3, 125 MHz, ppm): } & \delta 12.1, 16.5, 23.1, 25.2, 30.1, 35.4, 64.8 (\text{Scheme S1}).
\end{align*}
\]

**Fmoc-BPOSS-ST.** To a 100 mL round-bottomed flask equipped with a magnetic stirrer were added BPOSS-OH (2 g, 2.17 mmol), Fmoc-S-trityl-L-cysteine (1.27 g, 2.17 mmol) and DMAP (56.8 mg, 0.47 mmol), followed by the addition of 20 mL of freshly distilled DCM. The resulting solution was in ice bath conditions for 10 min. After that, DIPC (410 mg, 3.25 mmol, 504 µL) was added dropwise via a syringe with further stirring for 18 h at room temperature. The mixture was filtered and dried under vacuum. After being dissolved in a small amount of petroleum, the crude product was further purified by silica gel chromatography with the mixture of petroleum ether/ethyl acetate (v/v = 13:1 to 8:1) as the eluent to afford the product as white solid. Yield: 73%. 

\[
\begin{align*}
\text{1H NMR (CDCl}_3, 400 MHz, ppm, } & \delta: 0.94 (42H, -\text{CH}_2-\text{-CH-(CH}_3)_2), 0.62 (14H, -\text{-CH}_2-\text{-CH}-(\text{CH}_3)_2), 1.84 (7H, -\text{-CH}_2-\text{-CH}-(\text{CH}_3)_2), 0.88 (2H, -\text{Si-CH}_2-\text{-CH}_2-), 2.4 (2H, -\text{-Si-CH}_2-\text{-CH}_2-), 2.62 (2H, -\text{-S-CH}_2-\text{-CH}_2-), 4.17 (2H, -\text{-S-CH}_2-\text{-CH}_2-), 4.35 (1H, -\text{-S-CH}_2-C(-\text{C}=-\text{O})\text{H}- and 2H, -\text{CH}_2-\text{-O-CONH}-). \\
\text{13C NMR (CDCl}_3, 125 MHz, ppm): } & \delta 12.2, 16.5, 23.2, 25.2, 30.1, 35.4, 64.7 (\text{Scheme S1}).
\end{align*}
\]

**NH2-BPOSS-ST.** To a 100 mL three-neck round-bottomed flask equipped with a magnetic stirrer were added 5 mL of dried CH2Cl2 solvent and Fmoc-BPOSS-ST (1 g, 0.67 mmol) white solid under N2 atmosphere followed by addition of 1-Octanethiol (1.113 g, 7.6 mmol, 1320 µL) and DBU (47 mg, 0.31 mmol, 46 µL). The mixture was kept at the room temperature and further stirred for 45 min to complete the reaction. The residue was purified by flash column chromatography on silica gel with the mixture of ethyl acetate/DCM (v/v = 1:10) as the eluent to afford the protected product as a white powder. Yield: 71%. 

\[
\begin{align*}
\text{1H NMR (CDCl}_3, 400 MHz, ppm, } & \delta: 0.93 (42H, -\text{-CH}_2-\text{-CH-(CH}_3)_2), 0.6 (14H, -\text{-CH}_3-\text{-CH-(CH}_3)_2), 1.84 (7H, -\text{-CH}_2-\text{-CH-(CH}_3)_2),
\end{align*}
\]
Thickness Control of 2D Nanosheets  

0.86 (2H, -Si-CH$_2$-CH$_2$-), 2.49 (2H, -Si-CH$_2$-CH$_2$-), 2.58 (2H, -S-CH$_2$-CH$_2$-), 4.18 (2H, -S-CH$_2$-CH$_2$-), 3.18 (2H, -S-CH$_2$-(-C=O)H-). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 12.1, 16.5, 30.3, 25.4, 32.6, 59.3, 128.7, 171.8 (Scheme S1).

**Mal-CONHS.** Maleic anhydride (1 g, 10.2 mmol) and $\beta$-alanine (908 mg, 10.2 mmol) dissolved in 30 mL DMF were added to a 100 mL round-bottomed flask while vigorously stirring under 60 °C in an oil bath. Two hours later, to the resulting solution placed in a 0~5 °C ice bath was added N-hydroxymaleimide (1.46 g, 12.68 mmol) followed by the stepwise addition of DIPC (1.93 g, 15.3 mmol, 2.41 mL). After that, the mixture was stirred for 18 h at room temperature and filtered by vacuum filtration. Precipitation of the concentrated filtrate into water afforded Mal-CONHS as a white powder which was collected by vacuum filtration and dried in oven. Yield: 85%.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 2.73 (4H, -CO-CH$_2$-CH$_2$-), 6.94 (2H, -CO-CH=CH-CO-), 3.75 (2H, -NH-CH$_2$-CH$_2$-), 2.49 (2H, -NH-CH$_2$-CH$_2$-).

$^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 22.7, 29.4, 35.6, 136.4, 164.2, 168.5 (Scheme S2).

**Mal-BPOSS-ST.** NH$_2$-BPOSS-ST (1 g, 0.79 mmol) and Mal-CONHS (420 mg, 1.58 mmol) were added into a reaction flask filled with 5 mL freshly dried DCM and equipped with a magnetic stirrer. To the resulting solution was added three drops of TEA in a single portion, and then the product was stirred at normal temperature for 16 h. The crude product was purified by flash column chromatography on silica gel with the mixture of petroleum ether/ethyl acetate (v/v = 3:1) as the eluent to afford the product as a white solid. Yield: 69%.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 0.95 (42H, -CH$_2$-CH-(CH$_3$)$_2$), 0.61 (14H, -CH$_2$-CH-(CH$_3$)$_2$), 1.85 (7H, -CH$_2$-CH-(CH$_3$)$_2$), 0.86 (2H, -Si-CH$_2$-CH$_2$-), 2.48 (2H, -Si-CH$_2$-CH$_2$-), 2.59 (2H, -S-CH$_2$-CH$_2$-), 4.2 (2H, -S-CH$_2$-CH$_2$-), 4.52 (1H, -S-CH$_2$-(C=O)H-), 2.48 (2H, -CH$_2$-CH$_2$-CONH-), 3.81 (2H, -CH$_2$-CH$_2$-CONH-).

$^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 11.9, 23.2, 25.3, 30.2, 32.9, 59.3, 68.6, 129, 136.5, 164.5 (Scheme S1).

**VPOSS-OH.** Octavinyl-POSS (1 g, 1.57 mmol) was dissolved in a test tube filled with THF, and then 2-mercaptoethanol (123 mg, 1.57 mmol) was added dropwise via a syringe followed by adding a catalytic amount of DMPA. Four test tubes filled with equal amount could be operated at the same time. Irradiated under a 365 nm UV lamp at usual temperature for 30 min, the crude product was purified by flash column chromatography on silica gel with the mixture of petroleum ether/DCM (v/v = 3:1) as the eluent to afford the product as a white solid. Yield: 21%.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 5.3 (21H, -CH=CH$_3$), 2.5 (2H, -CH$_2$-CH$_2$-S-), 0.95 (2H, -CH$_2$-CH$_2$-S-), 2.63 (2H, -S-CH$_2$-CH$_2$-), 3.9 (2H, -S-CH$_2$-CH$_2$-). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 16.7, 23.6, 35.7, 64.8 (Scheme S1).

**Fmoc-VPOSS-ST.** VPOSS-OH (1 g, 1.41 mmol), DMAP (37 mg, 0.3 mmol) and Fmoc-S-trityl-L-cysteine...
Thickness Control of 2D Nanosheets

(1.27 g, 2.17 mmol) were added into a reaction flask equipped with a magnetic stirrer followed by adding 20 mL of dried DCM to dissolve all the reactants. To the solution, DIPC (265 mg, 2.1 mmol, 650 µL) was added dropwise via a syringe after the mixture was cooled to 0 °C for 10 minutes. The reaction was kept at room temperature with stirring for 18 hours. The residue was filtered and purified by silica gel column with petroleum ether/ethyl acetate (v/v = 3:1 to 1:1) as the eluent to give the product as a white solid. Yield: 72%.

1H NMR (CDCl3, 400 MHz, ppm, δ): 5.3 (21H, -CH=CH2), 2.5 (2H, -CH2-CH2-S-), 0.95 (2H, -CH3-CH2-S-), 2.72 (2H, -S-CH2-CH2-), 4.45 (2H, -S-CH2-CH2-), 4.7 (3H, -CH2-C(-C=O)H-CONH- and -CH2-O-CO-). 13C NMR (CDCl3, 125 MHz, ppm): δ 16.4, 23.6, 32.4, 59.4, 68.7, 126, 126.5, 129, 143 (Scheme S1).

NH2-VPOSS-ST. To the solution of Fmoc-VPOSS-ST (1.7 g, 1.33 mmol) in a three-neck reaction flask equipped with a stirring bar were added 5 mL freshly distilled DCM, 1-Octanethiol (2.2 g, 15 mmol, 2610 µL) and DBU (93 mg, 0.6 mmol, 91 µL), successively. The product was stirred at room temperature for 45 min, and further purified by silica gel chromatography with the mixture of petroleum ether/ethyl acetate (v/v = 3:1 to 1:1) as the eluent to afford the product as a white solid. Yield: 65%. 1H NMR (CDCl3, 400 MHz, ppm, δ): 5.3 (21H, -CH=CH2), 2.5 (2H, -CH2-CH2-S-), 0.95 (2H, -CH3-CH2-S-), 2.72 (2H, -S-CH2-CH2-), 3.05 (2H, -S-CH2-C(-C=O)H-). 13C NMR (CDCl3, 125 MHz, ppm): δ 16.2, 23.5, 32.1, 60.8, 68.5, 126, 128.8, 142.7 (Scheme S1).

Mal-VPOSS-ST. NH2-VPOSS-ST (1 g, 0.95 mmol) and Mal-CONHS (504 mg, 1.89 mmol) were dissolved in 5 mL anhydrous CH2Cl2 with vigorously stirring, followed by the addition of three drops of TEA. The mixture was stirred at room temperature for 16 h and further purified by silica gel column with the mixture of petroleum ether/ethyl acetate (v/v = 3:1) as the eluent to afford the product as a white solid. Yield: 73%. 1H NMR (CDCl3, 400 MHz, ppm, δ): 5.3 (21H, -CH=CH2), 0.88 (2H, -Si-CH2-CH2-), 2.5 (2H, -Si-CH2-CH2-), 2.6 (2H, -S-CH2-CH2-), 4.2 (2H, -S-CH2-CH2-), 4.53 (1H, -S-CH2-CH(-C=O)-), 2.48 (2H, -CH2-CH2-CONH-), 3.81 (2H, -CH2-CH2-CO-). 13C NMR (CDCl3, 125 MHz, ppm): δ 16.2, 23.4, 32.3, 57.6, 128.4, 68.7, 126, 129, 136.6, 143, 164.5 (Scheme S1).

3.2 Side-chain Giant Molecule Synthesis

Fmoc-nBPOSS-ST. Taking Fmoc-2BPOSS-ST as an example. Fmoc-BPOSS-ST (388 mg, 0.26 mmol) and 2 mL freshly dried CH2Cl2 were added into a reaction flask equipped with a magnetic stirrer. To the resulting solution was added 500 µL of TFA. The solution became yellow immediately, and two minutes later the solvent became colorless followed by adding TES dropwise via a syringe. Precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering afford Fmoc-BPOSS-SH as a white powder. The product was then directly transferred into vacuum to remove the residual solvent.
Fmoc-BPOSS-SH (376 mg, 0.3 mmol) obtained from above reaction and Mal-BPOSS-ST (340 mg, 0.24 mmol) were dissolved in 2 mL of DCM followed by the addition of one drop of TEA and by vigorously stirring at room temperature for 6 h, and then Precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering gave product as a white powder with removal of solvent in vacuum. The further purification was performed by column chromatography silica with the mixture of DCM/Methanol (v/v = 79:1 to 59:1) as the eluent to afford the pure product as a white solid. Yield: 80.2%.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 0.96 (84H, -CH$_2$-CH-(CH$_3$)$_2$), 0.64 (28H, -CH$_2$-CH-(CH$_3$)$_2$), 1.87 (14H, -CH$_2$-CH-(CH$_3$)$_2$), 0.89 (4H, -Si-CH$_3$-CH$_2$-), 2.47 (4H, -Si-CH$_2$-CH$_2$-), 2.6 (4H, -S-CH$_2$-CH$_2$-), 4.2 (4H, -S-CH$_2$-CH$_2$-), 4.66 (4H, -CH$_3$-O-CONH-C(-C=O)H-), 3.67 (1H, -S-C(-C=O)H-CH$_2$-), 3.06 (4H, -CONH-C(-C=O)H-CH$_2$-S), 3.16 (2H, -C(-C=O)H-CH$_2$-CO-), 4.47 (1H, -C(-C=C-)H-CH$_2$-CO-).

$^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 12.2, 16.3, 25.2, 30.4, 32.1, 49.8, 58.6, 126, 126.7, 128.5, 143.2, 172. FT-IR (KBr) $\nu$ (cm$^{-1}$): 3429, 2953, 2360, 1707, 1622, 1463, 1382, 1226, 1108 (Si-O-Si asymmetric stretching), 831, 737, 698, 620 (Scheme S3).

Fmoc-3BPOSS-ST (270 mg, 80.5%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 0.95 (126H, -CH$_2$-CH-(CH$_3$)$_2$), 0.62 (42H, -CH$_2$-CH-(CH$_3$)$_2$), 1.85 (21H, -CH$_2$-CH-(CH$_3$)$_2$), 0.88 (6H, -Si-CH$_2$-CH$_2$-), 2.5 (6H, -Si-CH$_2$-CH$_2$-), 2.6 (6H, -S-CH$_2$-CH$_2$-), 4.2 (6H, -S-CH$_2$-CH$_2$-), 4.69 (5H, -CH$_3$-O-CONH-C(-C=O)H-), 3.05 (6H, -CONH-C(-C=O)H-CH$_2$-S), 3.69 (2H, -S-C(-C=O)H-CH$_2$-), 3.16 (4H, -C(-C=O)H-CH$_2$-CO-), 3.76 (4H, -CH$_2$-CH$_2$-CONH-), 2.51 (4H, -CH$_2$-CH$_2$-CONH-), 4.45 (1H, -C(-C=C-)H-CH$_2$-CO-). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 12.1, 16.4, 25.5, 30.4, 50.1, 58.8, 126, 126.5, 129, 143, 172. FT-IR (KBr) $\nu$ (cm$^{-1}$): 3430, 2952, 2362, 1708, 1623, 1463, 1382, 1226, 1106 (Si-O-Si asymmetric stretching), 831, 737, 698, 620 (Scheme S3).

Fmoc-4BPOSS-ST (360 mg, 73%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 0.96 (168H, -CH$_2$-CH-(CH$_3$)$_2$), 0.62 (56H, -CH$_2$-CH-(CH$_3$)$_2$), 1.87 (28H, -CH$_2$-CH-(CH$_3$)$_2$), 0.86 (8H, -Si-CH$_2$-CH$_2$-), 2.5 (8H, -Si-CH$_2$-CH$_2$-), 2.48 (8H, -S-CH$_2$-CH$_2$-), 4.2 (8H, -S-CH$_2$-CH$_2$-), 4.67 (6H, -CH$_3$-O-CONH-C(-C=O)H-), 3.7 (3H, -S-C(-C=O)H-CH$_2$-), 3.07 (6H, -CONH-C(-C=O)H-CH$_2$-S), 3.18 (6H, -C(-C=O)H-CH$_2$-CO-), 3.79 (6H, -CH$_2$-CH$_2$-CONH-), 2.51 (6H, -CH$_2$-CH$_2$-CONH-), 4.47 (1H, -C(-C=C-)H-CH$_2$-CO-). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 12.3, 16.6, 25.2, 30.4, 50.1, 58.8, 125.8, 126.8, 129, 143, 172.2. FT-IR (KBr) $\nu$ (cm$^{-1}$): 3429, 2949, 2364, 1710, 1623, 1465, 1382, 1228, 1108 (Si-O-Si asymmetric stretching), 830, 739, 696, 619.

Fmoc-5BPOSS-ST (185 mg, 65%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm, $\delta$): 0.95 (210H, -CH$_2$-CH-(CH$_3$)$_2$), 0.64 (70H, -CH$_2$-CH-(CH$_3$)$_2$), 1.83 (35H, -CH$_2$-CH-(CH$_3$)$_2$), 0.87 (10H, -Si-CH$_2$-CH$_2$-), 2.5 (10H, -Si-CH$_2$-CH$_2$-), 2.6 (10H, -S-CH$_2$-CH$_2$-), 4.19 (10H, -S-CH$_2$-CH$_2$-), 4.69 (7H, -CH$_3$-O-CONH-C(-C=O)H-), 3.67 (4H, -S-C(-C=O)H-CH$_2$-), 3.06 (10H, -CONH-C(-C=O)H-CH$_2$-S), 3.18 (8H, -C(-C=O)H-CH$_2$-CO-), 3.75 (8H, -
B₃V. Taking B₃V as an example. To the solution of Fmoc-3BP-ST (360 mg, 0.09 mmol) in 5 mL of freshly distilled dichloromethane in a reaction flask equipped with a stirring bar was added 500 μL of TFA making the solution become yellow immediately, and two minutes later the solvent became colorless followed by adding TES dropwise via a syringe. Precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering afford Fmoc-3BP-SH as a white powder. The product was then directly transferred into vacuum to remove the residual solvent. Fmoc-3BP-SH (350 mg, 0.1 mmol) obtained from above reaction and Mal-VP-ST (153 mg, 0.13 mmol) were added into a reaction flask equipped with a magnetic stirrer followed by adding 5 mL of waterless DCM and one drop of TEA. The device was vigorously stirred at room temperature for 6 h. Then precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering gave product as a white powder with removal of solvent in vacuum. The residue was finally purified by flash column chromatography silica gel with the mixture of DCM/Methanol (v/v = 59:1 to 39:1) as the eluent to afford the product as a white solid. Yield: 73%. 

1H NMR (CDCl₃, 400 MHz, ppm, δ): 0.97 (126H, -CH₂-CH-(CH₃)₂), 0.65 (42H, -CH₂=CH-(CH₃)₂), 1.75 (21H, -CH₂=CH-(CH₃)₂), 5.4 (21H, CH₂=CH-), 0.88 (8H, -Si-CH₂-CH₂-), 2.5 (8H, -Si-CH₂-CH₂-), 2.97 (8H, -S-CH₂-CH₂-), 3.08 (8H, -S-CH₂-CH₂-), 2.53 (6H, -CH₂-CH₂-CONH-), 3.53 (8H, -S-CH₂-CH₂-CONH-), 4.47 (1H, -C(-C=O)-H-CH₂-CO-). 13C NMR (CDCl₃, 125 MHz, ppm): δ 12.3, 16.4, 25.7, 50.3, 58.6, 126, 126.7, 129.2, 142.8, 172. FT-IR (KBr) υ (cm⁻¹): 3430, 2954, 2364, 1710, 1625, 1466, 1383, 1224, 1108 (Si-O-Si asymmetric stretching), 830, 740, 698, 621.

B₃V (350 mg, 75%). 1H NMR (CDCl₃, 400 MHz, ppm, δ): 0.96 (42H, -CH₂-CH-(CH₃)₂), 0.65 (14H, -CH₂-CH-(CH₃)₂), 1.87 (7H, -CH₂=CH-(CH₃)₂), 5.27 (21H, CH₂=CH-), 0.87 (4H, -Si-CH₂-CH₂-), 2.46 (4H, -Si-CH₂-CH₂-), 2.62 (4H, -S-CH₂-CH₂-), 4.18 (4H, -CH₂=CH-), 4.67 (4H, -CH₂-O-CONH-C(-C=O)H-), 3.71 (1H, -S-C(-C=O)-H-CH₂-), 3.08 (4H, -CONH-C(-C=O)-H-CH₂-CONH-), 3.16 (2H, -C(-C=O)-H-CH₂-CO-). 13C NMR (CDCl₃, 125 MHz, ppm): δ 12.3, 16.4, 25.7, 30.5, 32.2, 50.2, 58.9, 126.5, 128.8, 142.8, 172. FT-IR (KBr) υ (cm⁻¹): 3430, 2954, 2364, 1710, 1625, 1466, 1383, 1224, 1108 (Si-O-Si asymmetric stretching), 830, 740, 698, 621.

B₂V (300 mg, 70%). 1H NMR (CDCl₃, 400 MHz, ppm, δ): 0.94 (84H, -CH₂-CH-(CH₃)₂), 0.63 (28H, -CH₂-CH-(CH₃)₂), 1.87 (7H, -CH₂=CH-(CH₃)₂), 5.27 (21H, CH₂=CH-), 0.87 (4H, -Si-CH₂-CH₂-), 2.46 (4H, -Si-CH₂-CH₂-), 2.62 (4H, -S-CH₂-CH₂-), 4.18 (4H, -CH₂=CH-), 4.67 (4H, -CH₂-O-CONH-C(-C=O)H-), 3.71 (1H, -S-C(-C=O)-H-CH₂-), 3.08 (4H, -CONH-C(-C=O)-H-CH₂-CONH-), 3.16 (2H, -C(-C=O)-H-CH₂-CO-). 13C NMR (CDCl₃, 125 MHz, ppm): δ 12.3, 16.4, 25.7, 30.5, 32.2, 50.2, 58.9, 126.5, 128.8, 142.8, 172. FT-IR (KBr) υ (cm⁻¹): 3430, 2954, 2364, 1710, 1625, 1466, 1383, 1224, 1108 (Si-O-Si asymmetric stretching), 830, 740, 698, 621.
Thickness Control of 2D Nanosheets

Supporting Information

CH-(CH$_3$)$_2$, 1.86 (14H, -CH$_2$-CH-(CH$_3$)$_2$), 5.25 (21H, CH$_2$=CH-), 0.86 (6H, -Si-CH$_2$-CH$_2$), 2.48 (6H, -Si-CH$_2$-CH$_2$), 2.6 (6H, -S-CH$_2$-CH$_2$), 4.25 (6H, -S-CH$_2$-CH$_2$), 4.69 (5H, -CH$_2$O-CONH-C(-C=O)H-), 3.7 (2H, -S-(C=O)H-CH$_2$-), 3.08 (6H, -CONH-C(-C=O)H-CH$_2$S-), 3.19 (4H, -C(-C=O)H-CH$_2$CO-), 3.76 (4H, -CH$_2$-CH$_2$-CONH-), 2.47 (4H, -CH$_2$-CH$_2$-CONH-), 4.46 (1H, -C(-C=C-)H-CH$_2$CO-).

13C NMR (CDCl$_3$, 125 MHz, ppm): δ 12.2, 16.5, 25.3, 30.4, 32.4, 49.8, 58.8, 126, 126.5, 129.2, 143, 172.

FT-IR (KBr) $\nu$ (cm$^{-1}$): 3428, 2950, 2361, 1708, 1620, 1463, 1384, 1228, 1107 (Si-O-Si asymmetric stretching), 834, 740, 698, 617.

BV (250 mg, 71%). 1H NMR (CDCl$_3$, 400 MHz, ppm, δ): 0.97 (168H, -CH$_2$-CH-(CH$_3$)$_2$), 0.62 (56H, -CH$_2$-CH-(CH$_3$)$_2$), 1.85 (28H, -CH$_2$-CH-(CH$_3$)$_2$), 5.3 (21H, CH$_2$=CH-), 0.87(10H, -Si-CH$_2$-CH$_2$), 2.48 (10H, -Si-CH$_2$-CH$_2$), 2.58 (10H, -S-CH$_2$-CH$_2$), 4.2 (10H, -S-CH$_2$-CH$_2$), 4.7 (7H, -CH$_2$O-CONH-C(-C=O)H-), 3.66 (4H, -S-(C=O)H-CH$_2$-), 3.04 (10H, -CONH-C(-C=O)H-CH$_2$S-), 3.14 (8H, -C(-C=O)H-CH$_2$CO-), 3.73 (8H, -CH$_2$-CH$_2$-CONH-), 2.54 (8H, -CH$_2$-CH$_2$-CONH-), 4.46 (1H, -C(-C=-C-)H-CH$_2$CO-).

13C NMR (CDCl$_3$, 125 MHz, ppm): δ 12.4, 16.4, 25.2, 30.6, 32.7, 50.4, 59.1, 126.7, 129.3, 143, 172. FT-IR (KBr) $\nu$ (cm$^{-1}$): 3431, 2952, 2364, 1707, 1625, 1465, 1384, 1228, 1106 (Si-O-Si asymmetric stretching), 835, 740, 698, 617.

BV (317 mg, 68%). 1H NMR (CDCl$_3$, 400 MHz, ppm, δ): 0.95 (210H, -CH$_2$-CH-(CH$_3$)$_2$), 0.62 (70H, -CH$_2$-CH-(CH$_3$)$_2$), 1.87 (35H, -CH$_2$-CH-(CH$_3$)$_2$), 5.3 (21H, CH$_2$=CH-), 0.89 (12H, -Si-CH$_2$-CH$_2$), 2.5 (12H, -Si-CH$_2$-CH$_2$), 2.6 (12H, -S-CH$_2$-CH$_2$), 4.2 (12H, -S-CH$_2$-CH$_2$), 4.64 (8H, -CH$_2$O-CONH-C(-C=O)H-), 3.67 (5H, -S-(C=O)H-CH$_2$-), 3.06 (12H, -CONH-C(-C=O)H-CH$_2$S-), 3.18 (10H, -C(-C=O)H-CH$_2$CO-), 3.75 (10H, -CH$_2$-CH$_2$-CONH-), 2.53 (10H, -CH$_2$-CH$_2$-CONH-), 4.45 (1H, -C(-C=-C-)H-CH$_2$CO-).

13C NMR (CDCl$_3$, 125 MHz, ppm): δ 12.1, 16.2, 25.6, 30.4, 32.4, 50.1, 58.9, 126.6, 129.3, 143, 172.2. FT-IR (KBr) $\nu$ (cm$^{-1}$): 3432, 2954, 2362, 1705, 1623, 1465, 1382, 1228, 1109 (Si-O-Si asymmetric stretching), 835, 738, 698, 619.

BV. BV (200 mg, 0.085mmol) were added into a reaction flask equipped with a magnetic stirrer followed by adding 10 mL of dried DCM to dissolve the reactants. To the resulting solution was added 500 µL of TFA making the solution become yellow immediately, and two minutes later the solvent became colorless followed by adding TES dropwise via a syringe. Precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering afford BV as a white powder. BV (190 mg, 0.09 mmol) obtained from above reaction and Mal-VPOSS-ST (231 mg, 0.18 mmol) were dissolved in 2 mL of DCM followed by the addition of three drop of TEA and by vigorously stirring at room temperature for 6 h, and then Precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering gave product as a white powder with removal of solvent in vacuum. The residue was finally purified by flash column
Thickness Control of 2D Nanosheets  

Supporting Information

chromatography silica gel with the mixture of petroleum ether/ethyl acetate (v/v = 3:1 to 1:1) as the eluent to afford the product as a white solid. Yield: 67%.  

$^1$H NMR (CDCl$_3$, 400 MHz, ppm, δ): 0.95 (42H, -CH$_2$-CH-(CH$_3$)$_2$), 0.65 (14H, -CH$_2$- CH-(CH$_3$)$_2$), 1.87 (7H, -CH$_2$-CH=-(CH$_3$)$_2$), 5.29 (42H, CH$_2$=CH-), 0.84 (6H, -Si-CH$_2$-CH$_2$-), 2.46 (6H, -Si- CH$_2$-CH$_2$-), 2.61 (6H, -S-CH$_2$-CH$_2$-), 4.23 (6H, -S-CH$_2$-CH$_2$-), 4.67 (5H, -CH$_2$-CONH-C(-C=O)H-), 3.72 (2 H, -S-C(-C=O)H-CH$_2$-), 3.09 (6H, -CONH-C(-C=O)H-CH$_2$-S-), 3.16 (4H, -C(-C=O)H-CH$_2$-CO-), 3.74 (4H, -CH$_2$-CH$_2$-CONH-), 2.46 (4H, -CH$_2$-CH$_2$-CONH-), 4.47 (1H, -C(-C=)-H-CH$_2$-CO-). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 12.2, 16.4, 25.6, 30.3, 32.3, 50.4, 58.8, 126.5, 128.9, 142.7, 172.1. FT-IR (KBr) υ (cm$^{-1}$): 3421, 2948, 2361, 1714, 1619, 1463, 1379, 1226, 1105 (Si-O-Si asymmetric stretching), 828, 736, 695, 619.

3.2 General procedure for synthesizing $B_nA$ (n = 1, 2, 3, 4, 5) and $B_nA_2$ (n =1, 2, 3, 4).

Taking $B_5A$ as an example. A catalytic amount of 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone were dissolved in a tube filled with THF, and then 51 μL mercapto acetic acid was added dropwise via a syringe. The mixed solution was illuminated under 362 nm UV light for 50 min. Then precipitation of 1 mL of the resulting concentrated solution into 50 mL methanol followed by vacuum filtering gave product as a white powder with removal of solvent in vacuum (Scheme S4).

4. 2D Nanosheets Preparation

Considering the solubility difference, side-chain giant molecules $B_nA$ (n = 1~5) and $B_nA_2$ (n = 2~4) were respectively dissolved in toluene or THF to give a clear solution with concentration of 1 mg/mL. Then, to a 2 mL glass vial filled with 200 μL of the giant molecule solution, DMF was dropwise injected until reaching particular contents (see details in Table S1). After completion of the injecting process, the glass vial was placed in a 25 °C oven. Powder samples for SAXS and WAXD measurements were collected after all the solvents were fully evaporated. Samples for TEM experiments were grown by dropping 20 μL of the mixture solution on a 1×1 cm$^2$ carbon-coated mica substrate. After the solvents were fully evaporated, carbon film was carefully departed from the mica substrate by diffusing water into the carbon-mica interface. The floating carbon film was then picked up by copper grids for TEM experiments. Samples for AFM measurements were prepared by dropping 20 μL of the mixture solution on a freshly exfoliated 1×1 cm$^2$ mica substrate and letting
5. Formula Deduction

Based on the models in Fig. 4, the overall volume of nanosheets is from three components: BPOSS crystalline bilayers, amorphous APOSS cages and backbone. Therefore, the total volume can be represented as follows:

\[ V = V_{BP} + V_{AP} + V_b \]  

(S1)

We can define \( r \) as the number ratio of BPOSS to APOSS. Assuming a single nanosheet that has \( n \) BPOSS cages, the number of APOSS and backbone monomers can be represented as \( n/r \) and \( n + n/r \), respectively. Then, the three volumes can be written as:

\[ V_{BP} = \frac{n \times M_{BP}}{N_A \rho_{BP}} \]  

(S2)

\[ V_{AP} = \frac{n \times r \times M_{AP}}{N_A \rho_{AP}} \]  

(S3)

\[ V_b = \frac{(n + n/r) \times M_b}{N_A \rho_b} \]  

(S4)

Where \( M_b, M_{AP} \) and \( M_{BP} \) are the molecular weights of the backbone monomer, APOSS and BPOSS, respectively; \( \rho_b, \rho_{AP}, \) and \( \rho_{BP} \) are densities of the backbone, APOSS and BPOSS, respectively. On the other hand, since the thickness contribution from crystalline BPOSS bilayers is identical for all samples, namely 2 nm, \( V_{BP} \) can be also written as:

\[ V_{BP} = S \times h_{BP} = S \times 2 \text{ nm} \]  

(S5)

Where \( S \) is the surface area of this nanosheet. Combining eq. S2 and eq. S5, we can obtain such an equation:

\[ V_{BP} = \frac{n \times M_{BP}}{N_A \rho_{BP}} = S \times 2 \text{ nm} \]  

(S6)

And the surface area can written as:

\[ S = \frac{1}{2 \text{ nm}} \times \frac{n \times M_{BP}}{N_A \rho_{BP}} \]  

(S7)

Now, let us go back to eq. S1 and divide both sides with \( S \). The following equations can be deduced:
where $h$ is the total thickness of the nanosheet. After clearing eq. S8, we can get eq. 1.
6. Supplementary Schemes, Tables and Figures.

Scheme S1. Synthesis route of Mal-XPOSS-ST monomer. X represents B or V.

Scheme S2. Synthesis route of Mal-CONHS.
Scheme S3. Synthesis route of intermediate products BX. X represents B or V.

Scheme S4. Transformation of the intermediate products BₙV into the final products BₙA(n = 1~5).
Fig. S1. $^1$H NMR spectra of Fmoc-BPOSS-ST, NH$_2$-BPOSS-ST, and Mal-BPOSS-ST.

Fig. S2. $^1$H NMR spectra of intermediate giant molecules BV, B$_3$V, and B$_5$V.
Fig. S3. $^1$H NMR spectra of side-chain giant molecules $B_nA$ ($n = 1$–5).

Fig. S4. $^1$H NMR spectra of giant molecules $B_nV_2$ and $B_nA_2$ ($n = 2$–4).
**Fig. S5.** GPC traces of giant molecules $B_nV$ and $B_nV_2$ ($n = 2 \sim 4$).

**Fig. S6.** 2D WAXD pattern of APOSS.
**Fig. S7.** (a) [010] zone view and (b) [100] zone view of the crystal lattice model of T8 BPOSS with the corresponding simulated ED patterns.

**Fig. S8.** SAED patterns of 2D nanosheets assembled from (a) BA, (b) B₂A, (c) B₄A₂, (b) B₃A₂ and B₂A₂. Color inversion was conducted on the original SAED data for a better contrast.
### Thickness Control of 2D Nanosheets

#### Supporting Information

**BA**

| No. | 2θ   | d'-spacing (nm) |
|-----|------|-----------------|
| 1   | 5.71 | 1.546           |
| 2   | 6.84 | 1.290           |
| 3   | 8.39 | 1.053           |
| 4   | 9.94 | 0.869           |
| 5   | 11.18| 0.790           |
| 6   | 12.31| 0.718           |
| 7   | 16.77| 0.528           |
| 8   | 17.92| 0.494           |
| 9   | 19.38| 0.457           |
| 10  | 25.25| 0.352           |

**B2A**

| No. | 2θ   | d'-spacing (nm) |
|-----|------|-----------------|
| 1   | 5.71 | 1.546           |
| 2   | 7.46 | 1.184           |
| 3   | 8.39 | 1.053           |
| 4   | 10.14| 0.871           |
| 5   | 11.17| 0.781           |
| 6   | 12.52| 0.706           |
| 7   | 16.77| 0.528           |
| 8   | 17.81| 0.497           |
| 9   | 19.48| 0.456           |
| 10  | 25.24| 0.352           |

**B3A**

| No. | 2θ   | d'-spacing (nm) |
|-----|------|-----------------|
| 1   | 5.72 | 1.543           |
| 2   | 6.23 | 1.417           |
| 3   | 8.39 | 1.053           |
| 4   | 10.25| 0.882           |
| 5   | 11.18| 0.790           |
| 6   | 12.42| 0.712           |
| 7   | 16.87| 0.531           |
| 8   | 17.92| 0.494           |
| 9   | 19.38| 0.457           |
| 10  | 25.14| 0.354           |

**B4A**

| No. | 2θ   | d'-spacing (nm) |
|-----|------|-----------------|
| 1   | 5.71 | 1.546           |
| 2   | 6.74 | 1.310           |
| 3   | 8.39 | 1.053           |
| 4   | 10.25| 0.862           |
| 5   | 11.18| 0.790           |
| 6   | 12.42| 0.712           |
| 7   | 16.77| 0.528           |
| 8   | 17.92| 0.494           |
| 9   | 19.48| 0.455           |
| 10  | 25.14| 0.354           |

**B5A**

| No. | 2θ   | d'-spacing (nm) |
|-----|------|-----------------|
| 1   | 5.81 | 1.519           |
| 2   | 6.74 | 1.310           |
| 3   | 8.39 | 1.053           |
| 4   | 10.14| 0.871           |
| 5   | 11.07| 0.796           |
| 6   | 12.41| 0.712           |
| 7   | 16.77| 0.528           |
| 8   | 18.02| 0.492           |
| 9   | 19.37| 0.456           |
| 10  | 25.04| 0.356           |

---

**Graphs:**

- BA
- B2A
- B3A
- B4A
- B5A

**Tables:**

- BA
- B2A
- B3A
- B4A
- B5A
**Fig. S9.** WAXD patterns of side-chain giant molecules $B_nA$ ($n = 1$–$5$) and $B_nA_2$ ($n = 2$–$4$).

**Fig. S10.** (a) GPC traces of B, BV and BVV. (b) $^1$H NMR spectra of B, BV, BVV and BA$_2$. (c), (d) and (e) are BF TEM images of BA$_2$ evaporated from its THF/DMF(1/2) solution.
Table S1. Giant molecules self-assembly solution composition and concentrations.

| Sample | Toluene:DMF | C (mg/mL) | Sample | THF:DMF | C (mg/mL) |
|--------|-------------|-----------|--------|---------|-----------|
| BA     | 0:1         | 0.1       | B₂A₂   | 1:2     | 0.2       |
| B₂A    | 1:2         | 0.2       | B₃A₂   | 2:1     | 0.2       |
| B₃A    | 2:1         | 0.2       | B₄A₂   | 2:1     | 0.2       |
| B₄A    | 2:1         | 0.2       |        |         |           |
| B₅A    | 2:1         | 0.2       |        |         |           |