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Supporting Information

Bionanosphere Lithography via Hierarchical Peptide Self-Assembly of Aromatic Triphenylalanine**

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NMR spectra were obtained on Bruker AVANCE 400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) and measured in $CDCl_3$ or DMSO-d_6. Chemical shifts were recorded in ppm relative to internal standard $CDCl_3$, and coupling constants were reported in Hz. The high resolution mass spectra were recorded on VG Autospec Ultima spectrometer. All reactions were carried out in oven-dried glassware under a N_2 atmosphere. All solvents were distilled from the indicated drying reagents right before use: CH_2Cl_2 (P_2O_5) and MeCN (CaH_2). The normal work-up included extraction, drying over Na_2SO_4 or $MgSO_4$ and evaporation of volatile materials *in vacuo*. Purifications by column chromatography were performed using Merck silica gel 60 (230 ~ 400 mesh). DMF = *N*, *N*-Dimethylformamide, HBTU = O-Benzotriazole-*N,N,N',N'*-tetramethyl-uronium-hexafluoro-phosphate, HOBt = Hydroxybenzotriazole, DIEA = Diisopropylethylamine.

Synthetic procedures for *N*-(*t*-Boc)-protected triphenylalanine.

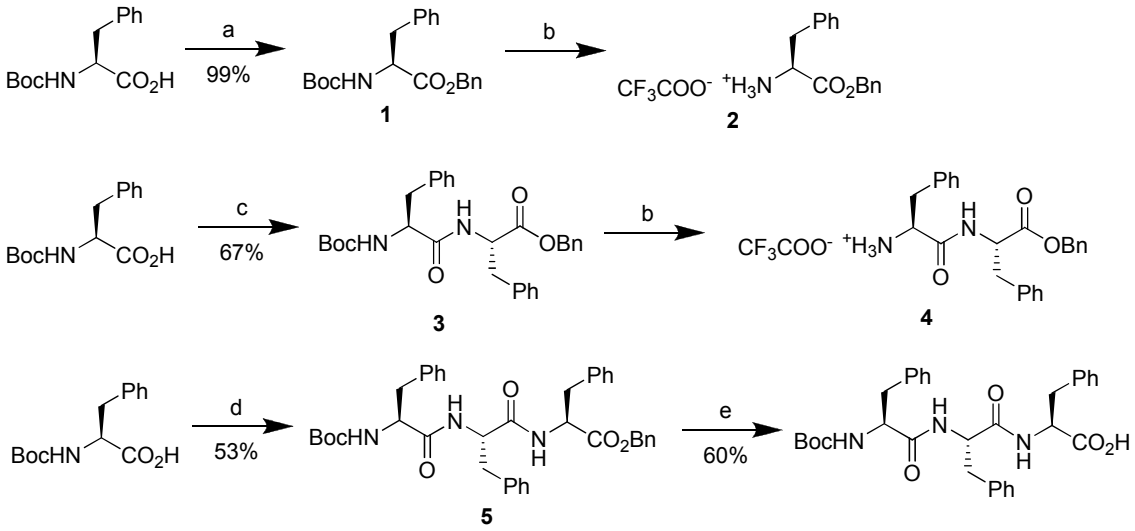
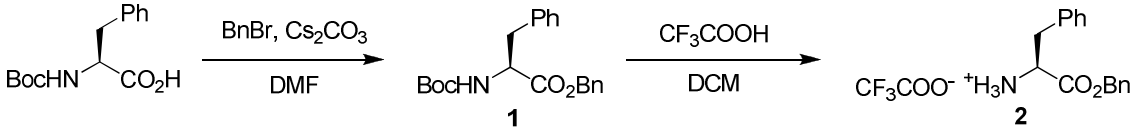


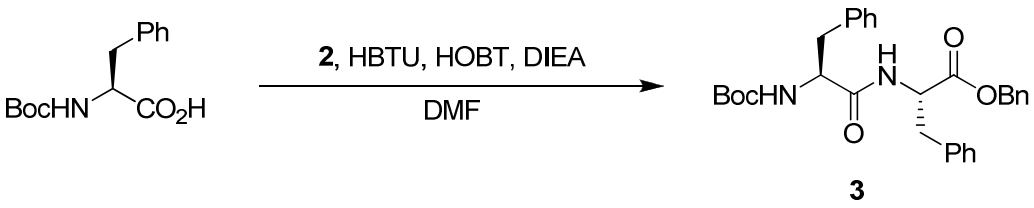
Figure S1. (a) BnBr, Cs_2CO_3, DMF, rt (b) CF_3COOH, DCM (c) **2**, HBTU, HOBT, DIEA, DMF, rt (d) **4**, HBTU, HOBT, DIEA, DMF, rt (e) 10% Pd/C, 10% MeOH/DCM.



Boc-Phe-Phe-Phe-OBn (1) : Boc-protected phenylalanine (2.00g, 7.54mmol), Cs_2CO_3 (3.19g, 9.79mmol), and benzyl bromide (1.34ml, 11.3mmol) was stirred in 50ml of DMF at room temperature for 1.5 h. The reaction was quenched with ammonium chloride saturated solution and the product was extracted with methylene chloride (×3) and was dried over anhydrous sodium sulfate. The residue was purified by silica gel column chromatography using 10% EtOAc/Hexane to afford **1** (2.54g, 99%) as a white solid.: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.34 (3H, m), 7.28 (2H, m), 7.21 (3H, m), 7.02 (2H, m), 5.12 (2H, q, J_{HH} = 12.3Hz), 4.95 (1H, m), 4.61 (m, 1H), 3.06 (2H, d, J_{HH} = 6.3Hz), 1.39 (9H, s).

TFA·H-Phe-OH (2): To a stirred solution of **1** (2.54g, 7.44mmol) in anhydrous methylene chloride (10ml) was added trifluoroacetic acid (10ml). The reaction mixture was stirred at

room temperature for 1 h. The reaction mixture was concentrated *in vacuo* to afford **2** as a crude product.



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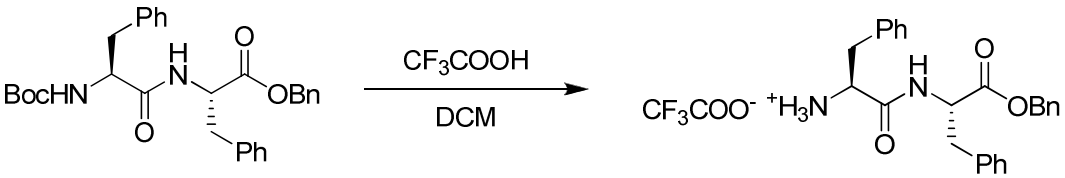
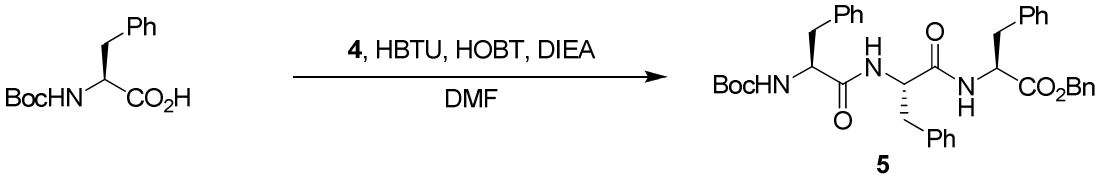
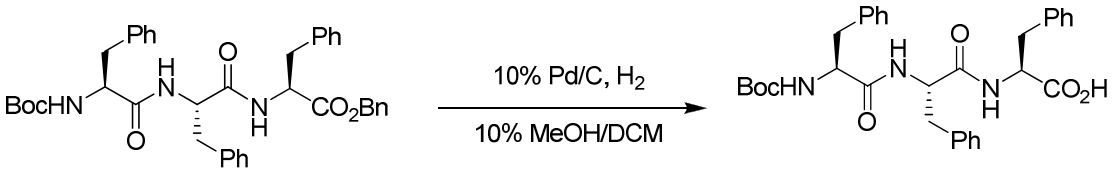


4

Boc-Phe-Phe-OBn (3): Boc-protected phenylalanine (2.0g, 7.54mmol), HBTU (3.72g, 9.81mmol), HOBt (1.32g, 9.81mmol), and DIEA (6.23ml, 37.7mmol) was stirred at room temperature in anhydrous DMF (30ml). To the mixture was transferred **2** (7.44mmol) dissolved in anhydrous DMF (20ml) via cannular. The reaction mixture was stirred overnight. The reaction was quenched with ammonium chloride saturated solution and was extracted with methylene chloride (×3) and dried over anhydrous magnesium sulfate. All the solvents in the organic phase were removed under reduced pressure. The residue was purified by silica gel column chromatography using 20% EtOAc/Hexane to afford **3** (2.40g, 67%) as a white solid.: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.34 (3H, m), 7.23 (6H, m), 7.14 (4H, m), 6.87 (2H, m), 6.25 (1H, d, J_{HH} = 7.3Hz), 5.07 (2H, s), 4.90 (1H, bs), 4.79 (1H, q, J_{HH} = 6.8Hz), 4.29 (1H, bs), 3.02 (4H, m), 1.37 (9H, s).

TFA·H-Phe-Phe-OBn (4): To a stirred solution of **3** (2.40g, 4.78mmol) in anhydrous methylene chloride (7ml) was added trifluoroacetic acid (7ml). The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated *in vacuo* to afford **4** as a crude product.





Boc-Phe-Phe-Phe-OBn (5): Boc-protected phenylalanine (1.4g, 5.28mmol), HBTU (2.60g, 6.86mmol), HOBt (0.93g, 6.86mmol), and DIEA (4.36ml, 26.4mmol) was stirred at room temperature in anhydrous DMF (20ml). To the mixture was transferred **4** (4.78mmol) dissolved in anhydrous DMF (20ml) via cannular. The reaction mixture was stirred overnight. The reaction was quenched with ammonium chloride saturated solution and was extracted with methylene chloride (×3) and dried over anhydrous magnesium sulfate. All the solvents in the organic phase were removed under reduced pressure. The residue was purified by silica gel column chromatography using 1% MeOH/CH_2Cl_2 to afford **5** (1.64g, 53%) as a white solid.: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.34 (3H, m), 7.20 (13H, m), 7.12 (2H, m), 6.91 (2H, m), 6.40 (1H, d, J_{HH} = 7.5Hz), 6.18 (1H, bs), 5.07 (2H, s), 4.80 (1H, bs), 4.72 (1H, q, J_{HH} = 7.3Hz), 4.52 (1H, q, J_{HH} = 7.0Hz), 4.27 (1H, d, J_{HH} = 6.6Hz), 2.94 (6H, m), 1.36 (9H, s).

Boc-Phe-Phe-Phe-OH (Boc-FFF-OH) : Boc-FFF-OBn (5) (3.15g, 4.85mmol) and 10% Pd/C (300mg) was stirred at room temperature in MeOH/CH_2Cl_2 (1:9) (100ml) under hydrogen balloon. The mixture was filtered through a pad of celite, washed with CH_2Cl_2. The filtrate was concentrated *in vacuo* to afford a crude product which was recrystallized by CH_3CN with heating. After cooling, the solid product was filtered, washed with cold CH_3CN to afford **Boc-**

FFF-OH (1.64g, 60%) as a white powder.: ^{1}H NMR (400 MHz, DMSO-d6) δ12.76 (1H, bs), 8.36 (1H, d, J_{HH} = 7.7Hz), 7.89 (1H, d, J_{HH} = 8.4Hz), 7.24 (15H, m), 6.83 (1H, d, J_{HH} = 8.8Hz), 4.58 (1H, m), 4.46 (1H, q, J_{HH} = 5.3Hz), 4.08 (1H, m), 3.04 (2H, m), 2.99 (1H, m), 2.90 (1H, m), 2.49 (1H, t, J_{HH} = 1.7Hz), 1.26 (9H, s); ^{13}C NMR (100 MHz, DMSO-d6) δ172.6, 171.2, 170.9, 155.0, 138.1, 137.4, 137.3, 129.3, 129.1, 129.0, 128.2, 127.9, 127.9, 126.4, 126.2, 126.1, 78.0, 55.8, 53.4, 53.3, 37.8, 37.5, 36.7, 28.1; HRMS (EI) calcd. for $C_{32}H_{38}N_3O_6$ $[M+H]^+$: 560.2761, found: 560.2835.