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Supporting Information

Self-Assembling of the Porphyrin-Linked Acyclic Penta- and Heptapeptide in Aqueous Trifluoroethanol

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General Procedure for the Synthesis. The analytical HPLC was carried out using a C4 column (4.6×150 mm) eluted with a linear gradient of 5-95% CH₃CN/0.1% TFA over 30 min (*R_f*/min) at the 1.0 mL min⁻¹ flow rate. The preparative HPLC was carried out with a C5 column (1.0×25 cm) at the 3.0 mL min⁻¹ flow rate. MALDI-TOF-MS spectra were obtained using α-cyano-4-hydroxycinnamic acid as the matrix. The amino acid analyses were carried out at the Peptide Institute (Osaka, Japan).

Preparations

5-(4-Nitrophenyl)-10,15,20-tritolyldiporphyrin (1).^{S1} A mixture of distilled pyrrole (6.9 mL, 0.10 mol), *p*-tolualdehyde (8.8 mL, 75 mmol), *o*-nitrobenzaldehyde (3.8 g, 25 mmol), and BF₃OEt₂ (3.8 mL, 30 mmol) in CH₂Cl₂ (0.50 L) were stirred overnight under Ar. Tetrachloro-*p*-benzoquinone (18 g, 75 mmol) was added and the mixture was refluxed for 4 h. After evaporation, the residue was repeatedly chromatographed over silica gel (CHCl₃-benzene=5:3, v/v, then 1:1) to yield **1** (0.70 g, 4.0%): TLC *R_f* (CHCl₃-hexane=5:3, v/v) 0.63; FAB-MS (3-nitrobenzylalcohol) *m/z* 702 (M⁺). ¹H NMR spectrum was the same as reported.^{S1c}

5-(2-Nitrophenyl)-10,15,20-tritolyldiporphyrin (2). Compound **2** was synthesized in a manner similar to **1** in 5.0% yield (0.88 g): TLC (CHCl₃-hexane=5:3, v/v) *R_f* 0.51; FAB-MS (3-nitrobenzylalcohol) *m/z* 702 (M⁺), 656 (M-NO₂)⁺. ¹H NMR spectrum was the same as reported.^{S1c}

5-(4-Aminophenyl)-10,15,20-tritolyldiporphyrin (3). To a suspension of **1** (1.0 g, 1.4 mmol) in concentrated HCl aq (0.20 L), SnCl₂ 2H₂O (1.9 g, 8.5 mmol) was mixed and stirred overnight.^{S2} After neutralization with aq NH₃, the red precipitate was filtrated, which was washed (H₂O), dried, and extracted with CHCl₃. The obtained crude porphyrin was chromatographed over silica gel (benzene) to yield **3** (0.85 g, 89%): TLC (CH₂Cl₂-hexane=5:3, v/v) *R_f* 0.16, (CHCl₃-MeOH=40:1, v/v) *R_f* 0.80; FAB-MS (3-nitrobenzylalcohol) *m/z* 672 (M+H)⁺, 656 (M-CH₃)⁺. ¹H NMR spectrum was the same as reported.^{S1c}

5-(2-Aminophenyl)-10,15,20-tritolyldiporphyrin (4). Compound **4** was synthesized in a manner similar to **3** in 85% yield: TLC (CHCl₃-MeOH=40:1, v/v) *R_f* 0.90; FAB-MS (3-nitrobenzylalcohol) *m/z* 672 (M+H)⁺, 580 (M-C₆H₄NH₂+H)⁺. ¹H NMR spectrum was the same as reported.^{S1c}

5-(4-Bromoacetamidophenyl)-10,15,20-tritolyldiporphyrin (5).^{S3} To a CHCl₃ (1.5 mL) solution of bromoacetic acid (85 mg, 0.61 mmol), EDC HCl (58 mg, 0.30 mmol) was added at 0 °C and the chilled mixture was stirred for 1 h. Then, a CHCl₃ (7.0 mL) solution of **3** (0.10 g, 0.15 mmol) was added and the resultant green solution was stirred at rt in the absence of light. After 12 h, EDC HCl (30 mg, 0.15 mmol) was further added and stirred for another 3 h. The solution was diluted with

CH₂Cl₂, washed with 5% aq NaHCO₃, and evaporated. The obtained crude porphyrin was chromatographed over silica gel (CH₂Cl₂-hexane=7:3, v/v, then CH₂Cl₂) to yield **5** (95 mg, 80%): TLC (CHCl₃-hexane=11:1, v/v) *R_f* 0.38; HPLC *R_t* 25.90; HIMS (3-nitrobenzylalcohol) *m/z* 791.2221 (C₄₉H₃₈BrN₅O requires 791.2260); λ_{max} (CH₂Cl₂) 419 (ε/M⁻¹ cm⁻¹ 438000), 516 (20200), 552 (12200), 592 (7490), 648 (6380). ¹H-NMR and MS spectra were the same as reported.^{S3}

5-(2-Bromoacetamidophenyl)-10,15,20-tritolylporphyrin (6). Compound **6** was synthesized in a manner similar to **5** and chromatographed with CH₂Cl₂-hexane (11:1, v/v) in 68% yield: TLC (CHCl₃-hexane=11:1, v/v) *R_f* 0.51; HPLC *R_t* 26.60; δ_H (500 MHz; CDCl₃); -2.75 (br, 2 H, pyrrole-NH), 2.69 (s, 9 H, tolyl-Me), 3.18 (s, 2 H, BrCH₂CO), 7.54 (overlap, 7 H, tolyl-CH and NHC₆H₄-CH), 7.82 (t, 1 H, J=8 Hz, NHC₆H₄-CH), 7.98 (m, 1 H, NHC₆H₄-CH), 8.06 (overlap, 7 H, tolyl-CH and NHC₆H₄-CH), 8.70 (overlap, 3 H, pyrrole-βH and NHC₆H₄-NH), 8.85 (s, 6 H, pyrrole-βH); FAB-MS (3-nitrobenzylalcohol) *m/z* 793 (M⁺), 713 (M-Br)⁺, 698 (M-CH₃Br)⁺, 670 (M-HCOCH₂Br)⁺; HIMS, *m/z* 791.2228 (C₄₉H₃₈BrN₅O requires 791.2260).

Ac-Cys-Lys-Val-Lys-Val-NH₂ (7). In a reaction tube with a glass filter and a suction outlet, 1.9 g of Fmoc-Rink amide resin^{S4} (100-200 mesh, 0.95 mmol Fmoc group) was swelled with DMF. After filtration, the resin was treated with 20% (v/v) piperidine in DMF for 30 min to remove Fmoc, which was confirmed by Kaiser's ninhydrin test.^{S5} After filtration and washing with DMF, a mixture of Fmoc-Val-OH (1.0 g, 3.0 mmol), PyBOP (1.6 g, 3.0 mmol),^{S6} HOBt H₂O (0.46 g, 3.0 mmol), and *N,N*-diisopropylethylamine (0.53 mL, 3.0 mmol) in 40 mL of DMF was added and the mixture was gently stirred for 1 h. The resin was filtered and washed with DMF, at which time a Kaiser's test showed the disappearance of the free amino group. The cycles of Fmoc removal/Fmoc-amino acid coupling were continued for Fmoc-Lys(Boc)-OH, again Fmoc-Val-OH, again Fmoc-Lys(Boc)-OH, and Fmoc-Cys(Tr)-OH. Each deprotection and coupling reaction was completed in 60 and 30 min, respectively, which were checked by Kaiser's tests. After the final coupling of Fmoc-Cys(Tr)-OH and the successive removal of Fmoc, the resin was treated with a DMF (40 mL) solution of Ac₂O (1.1 mL, 12 mmol) and *N,N*-diisopropylethylamine (2.1 mL, 12 mmol) for 1 h to acetylate the N-terminal. After filtration, the resin was successively washed with DMF, 25% AcOH in CH₂Cl₂, CH₂Cl₂, MeOH, and then dried.

The obtained Ac-Cys(Tr)-Lys(Boc)-Val-Lys(Boc)-Val-Rink amide resin was treated in a flask with 15 mL of TFA (with 2.5% 1,2-ethanedithiol and 2.5% H₂O, v/v) at 0 °C for 4 h.^{S7} The red solution containing the free peptide was filtered and the orange resin was washed with cold diethyl ether. The combined solution was evaporated and the resultant oil was treated with cold diethyl ether (20 mL). The precipitate was then collected, treated with 1.0 mL of DMF and 10 mL of diethyl ether. The pale yellow solid was collected as the crude **7** (0.68 g).

The obtained crude **7** (0.68 g) was dissolved in 0.20 mL of H₂O and filtered using a cellulose acetate 0.45 μ m filter. Each 1.5 mL of this solution was applied to the preparative HPLC with a linear gradient of 14-68% CH₃CN/1% TFA over 20 min. The fractions containing only **7** were collected and lyophilized to yield pure **7** (0.45 g, 0.39 mmol as 53% free peptide content (see Ellman's determination below), yield 41%): HPLC R_t 10.80; δ_H (500 MHz; DMSO- d_6) 0.81 (t, 6 H, $J=7$ Hz, Val- γ), 0.83 (d, 6 H, $J=7$ Hz, Val- γ), 1.29 (m, 4 H, Lys- γ), 1.51 (m, 6 H, Lys- β and δ), 1.65 (m, 2 H, Lys- β'),⁵⁸ 1.86 (s, 3 H, Ac), 1.93 (m, 2 H, Val- β), 2.35 (t, 1 H, $J=9$ Hz, Cys-SH), 2.67 (m, 1 H, Cys- β), 2.74 (m, 5 H, Lys- ϵ CH and Cys- β'), 4.08 (dd, 1 H, $J=9$ and 7 Hz, Val-C α), 4.19 (dd, 1 H, $J=9$ and 15 Hz, Val-C α), 4.25 (m, 2 H, Lys-C α), 4.36 (q, 1 H, $J=7$ Hz, Cys-C α), 7.01 (s, 1 H, C-terminal NH), 7.36 (s, 1 H, C-terminal NH'), 7.61 (m, 8 H, Val-NH and Lys- ϵ NH₃⁺), 8.04 (d, 1 H, $J=8$ Hz, Lys- α NH), 8.09 (d, 1 H, $J=8$ Hz, Cys-NH), 8.18 (d, 1 H, $J=8$ Hz, Lys- α NH); FAB-MS (magic bullet) m/z 617 (M+H)⁺; HIMS m/z 617.3826 (C₂₇H₅₃N₈O₆S (M+H) requires 617.3808); Amino acid analysis Lys (2), Val (2.2), 1/2 (Cys)₂ (0.51), NH₃ (1.3).

The peptide content of **7** thus obtained was determined by Ellman's reagent (4,4'-dithiopyridine).⁵⁹ A solution of the sample of **7** (1.036 mg) in 10 mL pH 7.0 buffer solution was reacted with excess 4,4'-dithiopyridine. UV determination of 4-thiopyridone ($\epsilon_{324}=19800$)⁵⁹ showed that the content of the free peptide was 53.3%.

Attempted oxidation of 7 (SS dimer of 7). Air was blown into a stirred solution¹ of **7** (2.9 mg, 2.5 μ mol) in 5.0 mL of pH 9.0 buffer solution-50% TFE (v/v). After 8 h, the signal of **7** (R_t 10.80) decreased to 30% and correspondingly a new signal appeared at R_t 12.74. *Threo*-2,3-dihydroxybutane-1,4-dithiol (1.2 μ mol) in H₂O (0.10 mL) was added to the solution, and then the HPLC analysis of the mixture showed the disappearance of the peak at R_t 12.74 and the complete recovery of **7**. Thus, the SS dimer of **7** seemed to elute at R_t 12.74.

Ac-Cys-Lys-Val-Ser-Val-Lys-Val-NH₂ (8). Compound **8** was synthesized in the similar manner as **7** from 1.0 g (0.56 mmol) of Fmoc-Rink amide resin. Fmoc-Ser(Bu')-OH was used as the fourth amino acid. For the coupling of Fmoc-Cys(Tr)-OH, *N*-methylpyrrolidone was used instead of DMF, otherwise the coupling did not complete. The obtained Ac-Cys(Tr)-Lys(Boc)-Val-Ser(Bu')-Val-Lys(Boc)-Val-Rink amide resin was treated with TFA (2.5 % ethanedithiol and 2.5 % H₂O, v/v) at 0 °C for 2 h. The red solution containing the peptide and CH₂Cl₂ washings were combined, evaporated, and the resultant thick oil was treated with cold diethyl ether (30 mL). The precipitate was washed with diethyl ether (three times) to afford crude **8** as a pale yellow solid (0.54 g).

The obtained crude **8** (0.54 g) was dissolved in 50 mL of TFE and each 0.15 mL of this solution was applied to the preparative HPLC with a linear gradient of 0-32% CH₃CN/1% TFA over 30 min. The fractions containing only **8** were collected and lyophilized to yield pure **8** (0.32 g).

Ellman's determination of this sample showed a 50.0% free peptide content, i.e., 0.32 g of product was 0.20 mmol, yield 35%: HPLC R_t 12.54; δ_H (500 MHz; DMSO- d_6) 0.83 (m, 18 H, Val- γ), 1.30 (m, 4 H, Lys- γ), 1.51 (m, 6 H, Lys- β and δ), 1.66 (m, 2 H, Lys- β'), 1.87 (s, 3 H, Ac), 1.94 (m, 3 H, Val- β), 2.36 (t, 1 H, $J=9$ Hz, Cys-SH), 2.66 (m, 1 H, Cys- β), 2.74 (m, 5 H, Lys- ϵ CH and Cys- β'), 3.55 (m, 2 H, Ser- β), 4.09 (t, 1 H, $J=8$ Hz, Val-C α), 4.20 (m, 2 H, Val-C α), 4.26 (m, 2 H, Lys-C α), 4.37 (m, 2 H, Cys-C α and Ser-C α), 4.96 (m, 1 H, Ser-OH), 7.03 (s, 1 H, C-terminal NH), 7.37 (s, 1 H, C-terminal NH'), 7.60 (m, 3 H, Val-NH), 7.68 (m, 6 H, Lys- ϵ NH $_3^+$), 8.03 (d, 1 H, $J=8$ Hz, Lys- α NH), 8.09 (m, 2 H, $J=8$ Hz, Cys-NH and Ser-NH), 8.18 (d, 1 H, $J=9$ Hz, Lys- α NH); FAB-MS (magic bullet) m/z 804 (M+H) $^+$, 826 (M+Na) $^+$; HIMS m/z 803.4788 (C $_{35}$ H $_{67}$ N $_{10}$ O $_9$ S (M+H) requires 803.4813); Amino acid analysis Lys (2), Val (3.1), Ser (0.91), 1/2 (Cys) $_2$ (0.56), NH $_3$ (1.2).

Attempted oxidation of 8 (SS dimer of 8). The air oxidation of 8 was done in a manner similar to that of 7. The HPLC signal of 8 (R_t 12.54) decreased and a new signal appeared at R_t 15.13, which disappeared with the addition of *threo*-2,3-dihydroxybutane-1,4-dithiol. Thus, the SS dimer of 8 seemed to elute at R_t 15.13.

Ac-Cys(4-(10,15,20-tritolyldiporphyrin-5-yl)phenylcarbamoylethyl)-Lys-Val-Lys-Val-NH $_2$ (9). To a solution of 5 (9.6 mg, 12 μ mol) in DMF (2.0 mL), the solution of 7 (33 mg, 29 μ mol supposing the 53 % purity) in DMF (3.0 mL) and the solution of Et $_3$ N (16 μ mol) in DMF (0.10 mL) were added under Ar. The HPLC analysis showed the reaction was complete after 4 h when the solution contained some purple gels. After evaporation, the residue dissolved in MeOH (10 mL) was filtered using a PTFE 0.50 μ m filter. Each 0.50 mL of this solution was applied to the preparative HPLC eluted with 46% CH $_3$ CN/1% TFA. The fractions containing only 9 were collected and lyophilized to yield pure 9 (14 mg). UV determination of this sample showed a 77.4% content, i.e., 14 mg of product was 8.2 μ mol, yield 68%: HPLC R_t 20.80; δ_H (500 MHz; DMSO- d_6) -2.93 (br, 2 H, pyrrole-NH), 0.80 (t, 6 H, $J=6$ Hz, Val- γ), 0.84 (t, 6 H, $J=6$ Hz, Val- γ), 1.31 (m, 4 H, Lys- γ), 1.52 (m, 8 H, Lys- β and δ), 1.90 (s, 3 H, Ac), 1.99 (m, 2 H, Val- β), 2.66 (s, 9 H, tolyl-Me), 2.72 (m, 4 H, Lys- ϵ CH), 2.92 (m, 1 H, Cys- β), 3.09 (m, 1 H, Cys- β'), ~3.5 (overlapped with H $_2$ O, SCH $_2$ CO), 4.07 (t, 1 H, $J=8$ Hz, Val-C α), 4.20 (t, 1 H, $J=7$ Hz, Val-C α), 4.29 (m, 2 H, Lys-C α), 4.57 (m, 1 H, Cys-C α), 7.03 (s, 1 H, C-terminal NH), 7.37 (s, 1 H, C-terminal NH'), 7.63 (overlap, 14 H, tolyl-CH, Val-NH, and Lys- ϵ NH $_3^+$), 8.05 (d, 2 H, $J=8$ Hz, HNC $_6$ H $_4$ -CH), 8.08 (overlap, 7 H, tolyl-CH and Lys- α NH), 8.15 (d, 2 H, $J=8$ Hz, HNC $_6$ H $_4$ -CH), 8.29 (d, 1 H, $J=7$ Hz, Lys- α NH), 8.33 (d, 1 H, $J=8$ Hz, Cys-NH), 8.83 (s, 8H, pyrrole- β H), 10.55 (s, 1 H, HNC $_6$ H $_4$ -NH); δ_H (CD $_3$ OD) 0.95-1.00 (m, 12 H, Val- γ), 1.45-1.83 (m, 12 H, Lys- β , γ and δ), 2.04 (m, 1 H, Val- β), 2.08 (s, 3 H, Ac), 2.14 (m, 1 H, Val- β), 2.77 (s, 9 H, tolyl-Me), 2.94 (m, 4 H, Lys- ϵ CH), 3.11-3.23 (m, 2 H, Cys- β), 3.69 (m, 2 H, SCH $_2$ CO), 4.21 (m, 2 H, Val-C α), 4.44 (m, 2 H, Lys-C α), 4.66 (m, 1 H, Cys-C α), 7.82 (d, 6 H, tolyl-CH), 8.25 (d, 2 H, HNC $_6$ H $_4$ -CH),

8.35 (d, 6 H, tolyl-CH), 8.45 (d, 2 H, HNC₆H₄-CH), 8.86 (s, 8 H, pyrrole-βH); FAB-MS (3-nitrobenzylalcohol) *m/z* 1329 (M⁺), 1313 (M-CH₄)⁺, 1286 (M-CH₃CO)⁺, 1057 [M-(COLysValNH₂)]⁺, 875 [M-(CH(C₄H₈NH₂))COValLysValNH₂]⁺, 698 [M-(AcCH(CH₂SCH₃))COLysValLysValNH₂]⁺; HIMS *m/z* 1328.6813 (C₇₆H₉₀N₁₃O₇S (M+H) requires 1328.6806); MALDI-TOF-MS *m/z* 1330 (M+H)⁺, 2691 (calcd for (2M+Na)⁺, 2680), 4021 (calcd for (3M+Na)⁺, 4009); λ_{max} (TFE-1% Et₃N (v/v)) 413 (ε/M⁻¹ cm⁻¹ 443000), 516 (14100), 554 (8130), 584 (5420), 639 (4340); Amino acid analysis Lys (2), Val (1.9), NH₃ (1.2).

Ac-Cys(2-(10,15,20-tritolylporphyrin-5-yl)phenylcarbamoymethyl)-Lys-Val-Lys-Val-NH₂ (10). Compound **10** was synthesized in a manner similar to **9** from **6** (9.8 mg, 12 μmol), **7** (32 mg, 27 μmol supposing the 53% purity), and Et₃N (18 μmol) in 5.1 mL of DMF (overnight under Ar). After evaporation of the mixture containing some purple gels, the residue was dissolved in 8.0 mL of MeOH, filtered, and each 0.50 mL of the solution was applied to the preparative HPLC eluted with a linear gradient of 48-59% CH₃CN/1% TFA over 20 min. The fractions containing only **10** were collected and lyophilized to yield pure **10** (20 mg). UV determination of this sample showed an 81.3% content, i.e., 20 mg of product was 12 μmol, yield 91%. HPLC *R_t* 21.28; δ_H (500 MHz; DMSO-*d*₆) -2.87 (br, 2 H, pyrrole-NH), 0.67 (dd, 6 H, *J*=7 and 20 Hz, Val-γ), 0.77 (dd, 6 H, *J*=7 and 17 Hz, Val-γ), 1.24 (m, 4 H, Lys-γ), 1.48 (m, 6 H, Lys-β and δ), 1.57 (s, 3 H, Ac), 1.59 (m, 2 H, Lys-β'), 1.88 (m, 2 H, Val-β), 2.11 (m, 1 H, Cys-β), 2.39 (m, 1 H, Cys-β'), 2.59 (s, 2 H, SCH₂CO), 2.67 (overlap, 13 H, tolyl-Me and Lys-εCH), 4.07 (m, 3 H, Val-Cα and Cys-Cα), 4.20 (m, 2 H, Lys-Cα), 7.01 (s, 1 H, C-terminal NH), 7.36 (s, 1 H, C-terminal NH'), 7.53 (t, 2 H, *J*=9 Hz, Val-NH), 7.59 (t, 1 H, *J*=8 Hz, HNC₆H₄-CH), 7.64 (overlap, 12 H, tolyl-CH and Lys-εNH₃⁺), 7.84 (overlap, 2 H, HNC₆H₄-CH and Cys-NH), 7.90 (d, 1 H, *J*=9 Hz, Lys-αNH), 7.96 (d, 1 H, *J*=9 Hz, Lys-αNH), 8.00 (d, 1 H, *J*=7 Hz, HNC₆H₄-CH), 8.08 (m, 6 H, *J*=7 Hz, tolyl-CH), 8.27 (t, 1 H, *J*=8 Hz, HNC₆H₄-CH), 8.71 (br, 2 H, pyrrole-βH), 8.83 (br, 6 H, pyrrole-βH), 9.02 (s, 1 H, HNC₆H₄-NH); FAB-MS (3-nitrobenzylalcohol) *m/z* 1329 (M⁺), 1286 (M-CH₃CO)⁺, 746 [M-(AcNHCH(CH₂))COLysValLysValNH₂)+H]⁺; HIMS *m/z* 1328.6836 (C₇₆H₉₀N₁₃O₇S (M+H) requires, 1328.6806); λ_{max} (TFE-1% Et₃N) 414 (ε/M⁻¹ cm⁻¹ 411000), 515 (15000), 552 (7210), 585 (5700), 639 (4140); Amino acid analysis Lys (2), Val (2.1), NH₃ (1.4).

Ac-Cys(4-(10,15,20-tritolylporphyrin-5-yl)phenylcarbamoymethyl)-Lys-Val-Ser-Val-Lys-Val-NH₂ (11). Compound **8** (15 mg, 9.6 μmol supposing the 50 % purity) was dissolved in 4.0 mL of DMF with the aid of sonication, to which the solution of **5** (7.8 mg, 9.8 μmol) in DMF (1.8 mL) and *N,N*-diisopropylethylamine (0.83 mL, 4.8 μmol) were quickly added under Ar. The HPLC analysis showed that the reaction was complete after 17 h when the solution contained some purple precipitates. After evaporation, the residue was washed with water, and taken up in DMF (30 mL). The DMF solution was filtered, concentrated to half volume and each 0.30 mL of this solution was

applied to the preparative HPLC eluted with a linear gradient of 46-59% CH₃CN/1% TFA over 30 min. The fractions containing only **11** were collected and lyophilized to yield pure **11** (22 mg). UV determination of this sample showed a 53.0% content, i.e., 22 mg of product was 7.6 μ mol, yield 78%: HPLC *R*_t 21.50; δ_{H} (500 MHz; DMSO-*d*₆) -2.92 (br, 2 H, pyrrole-NH), 0.82 (m, 18 H, Val- γ), 1.31 (m, 4 H, Lys- γ), 1.5-1.7 (m, 8 H, Lys- β and δ), 1.93 (s, 3 H, Ac), 1.99 (m, 3 H, Val- β), 2.68 (s, 9 H, tolyl-Me), 2.75 (m, 4 H, Lys- ϵ CH), 2.93 (m, 1 H, Cys- β), 3.10 (m, 1 H, Cys- β'), ~3.5 (overlapped with H₂O, SCH₂CO and Ser- β), 4.07 (t, 1 H, *J*=8 Hz, Val-C α), 4.19 (t, 1 H, *J*=8 Hz, Val-C α), 4.27 (m, 2 H, Val-C α and Lys-C α), 4.35 (m, 1 H, Lys-C α), 4.40 (m, 1 H, Ser-C α), 4.60 (m, 1 H, Cys-C α), 4.95 (br, 1 H, Ser-OH), 7.01 (s, 1 H, C-terminal NH), 7.35 (s, 1 H, C-terminal NH'), 7.63 (overlap, 13 H, tolyl-CH, Val-NH, and Lys- ϵ NH₃⁺), 7.68 (d, 1 H, *J*=9 Hz, Val-NH), 7.74 (d, 1 H, *J*=9 Hz, Val-NH), 8.01 (d, 1 H, *J*=8 Hz, Lys- α NH), 8.10 (overlap, 9 H, HNC₆H₄-CH, tolyl-CH, and Ser- α NH), 8.15 (d, 2 H, *J*=8 Hz, HNC₆H₄-CH), 8.27 (d, 1 H, *J*=7 Hz, Lys- α NH), 8.32 (d, 1 H, *J*=8 Hz, Cys-NH), 8.84 (s, 8 H, pyrrole- β H), 10.53 (s, 1 H, HNC₆H₄-NH); FAB-MS (3-nitrobenzylalcohol) *m/z* 1538 (M+Na)⁺, 1516 (M+H)⁺, 746, 713; HIMS *m/z* 1513.7670 (C₈₄H₁₀₃N₁₅O₁₀S requires 1513.7732); MALDI-TOF-MS *m/z* 1515 (M+Na)⁺, 3062 (calcd for (2M+Na)⁺, 3053); λ_{max} (TFE-1% Et₃N) 413 (ϵ /M⁻¹ cm⁻¹ 376000), 517 (11500), 555 (7160), 582 (5570), 639 (4380); Amino acid analysis Lys (2), Val (3.1), Ser (0.89), NH₃ (1.5).

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Fig. S1 ^1H NMR spectrum of **6** in CDCl_3 .

S9

Fig. S2 ^1H NMR spectrum of 7 in $\text{DMSO}-d_6$.

Fig. S3 ^1H NMR spectrum of **8** in DMSO- d_6 .

S11

Fig. S4 ^1H NMR spectrum of **9** in $\text{DMSO}-d_6$.

S12

Fig. S5 ^1H NMR spectrum of 10 in $\text{DMSO}-d_6$.

S13

Fig. S6 ^1H NMR spectrum of 11 in $\text{DMSO-}d_6$.

Fig. S7 SEC profile of aggregated **9** eluted by tris buffer solution (5.0 mM, pH 8.0)-20% (v/v) CH₃CN.

Fig. S8 SEC profile of aggregated **11** eluted by tris buffer solution (5.0 mM, pH 8.0)-20% (v/v) CH₃CN.