Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Effect of oscillation dynamics on long-range electron transfer in a helical peptide monolayer

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Materials and synthesis

All chemicals were purchased from commercial suppliers and used without further purification. Aib-Pro peptides were synthesized by a conventional liquid-phase method. All the intermediates were identified by ^{1}H NMR spectroscopy (Bruker DPX-400) and further confirmed by FAB mass spectrometry (JEOL JMS-HX110A), ESI mass spectrometry (Thermo Fischer Scientific Exactive Plus spectrometer), and MALDI mass spectrometry (Bruker ultraflexIII-KE). The purity of the intermediates was checked by thin-layer chromatography and that of the final compounds was checked by HPLC (TOSOH System 8020).

NMR: spectroscopy: hydrogen nuclear magnetic resonance spectroscopy

FAB: mass spectrometry: fast atom bombardment mass spectrometry

ESI: mass spectrometry: electrospray ionization mass spectrometry

MALDI: mass spectrometry: matrix assisted laser desorption Ionization mass spectrometry

HPLC: high-performance liquid chromatography

HATU: 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate

HOAt:1-hydroxy-7-azabenzotriazole

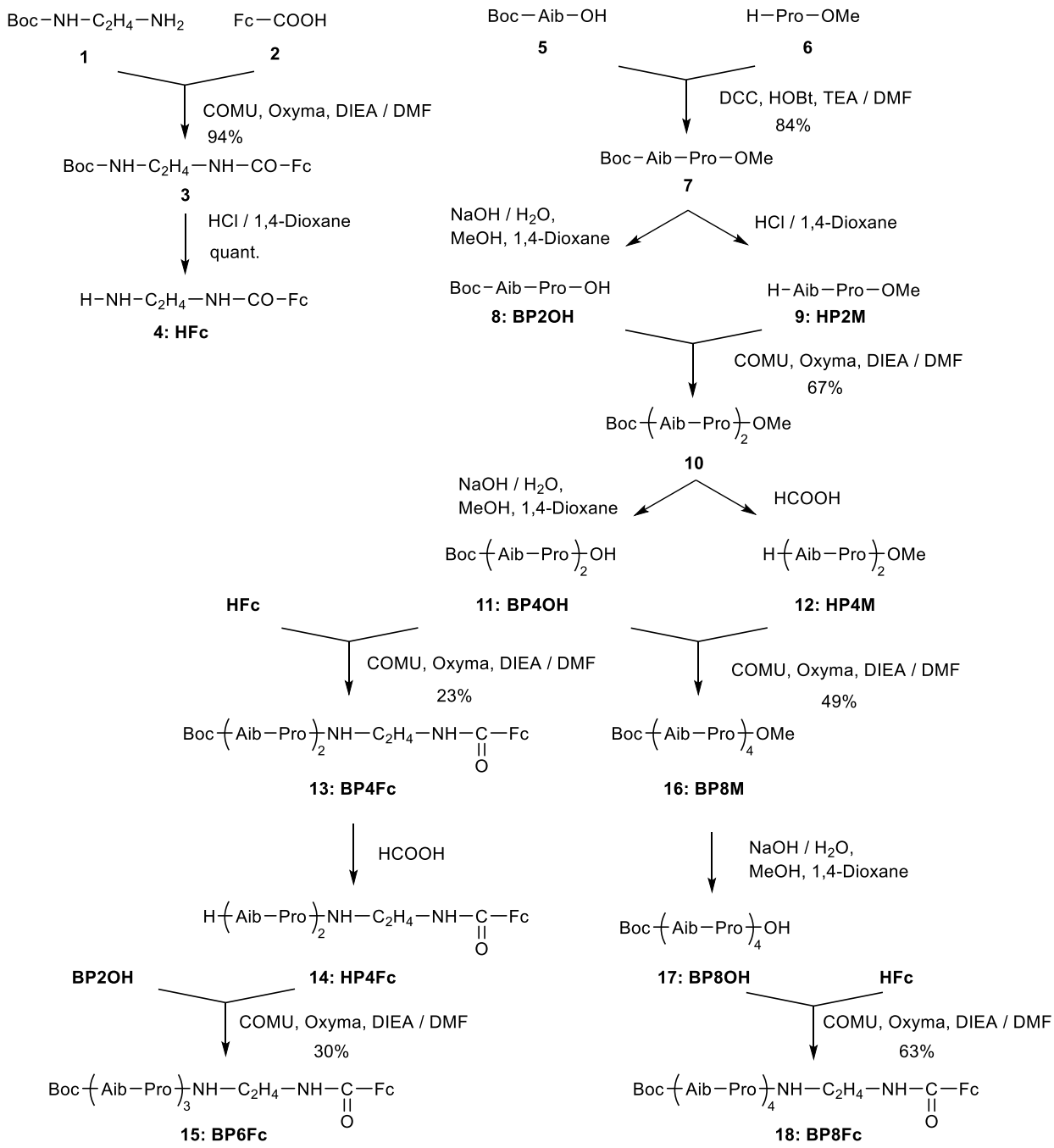
DIEA: *N*,*N*-diisopropylethylamine

DMF: *N*,*N*-dimethylformamide

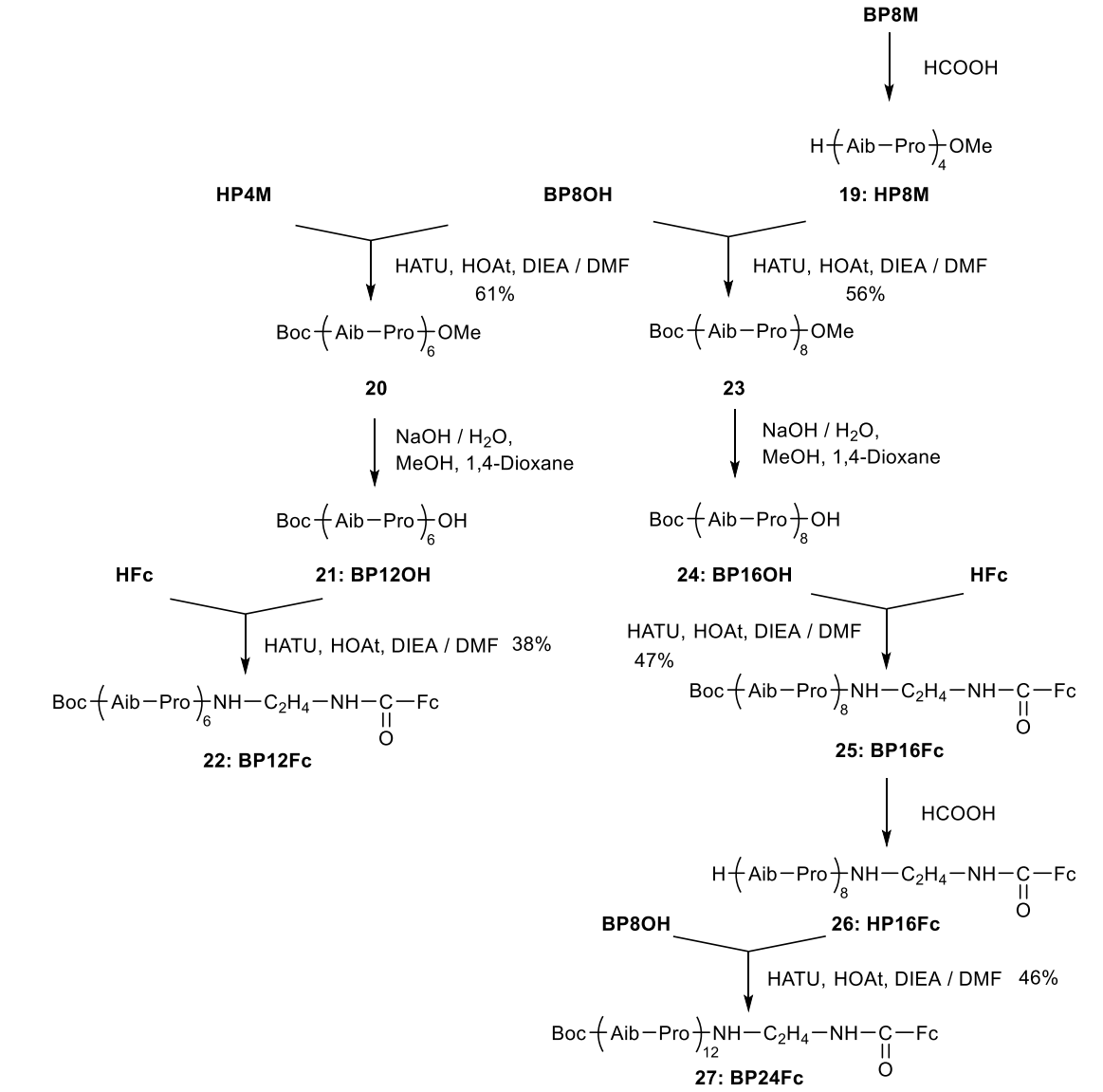
COMU: (1-cyano-2-ethoxy-2-oxoethylidenaminooxy)dimethylaminomorpholinocarbenium hexafluorophosphate

Oxyma: ethyl (hydroxyimino)cyanoacetate

TEA: triethylamine



Scheme S1. Synthetic schemes of Aib-Pro peptides.



Scheme S2. Synthetic schemes of Aib-Pro peptides.

Boc-NH-$(CH_2)_2$-NH-CO-Fc (3)

Compound **1** (4.00 g, 17.3 mmol) and Compound **2** (3.33 g, 20.8 mmol) were dissolved in minimum amount of DMF. The mixed solution of COMU (11.1 g, 26.0 mmol) and Oxyma (3.69 g, 26 .0 mmol) in minimum amount of DMF, and DIEA (12.1 ml, 69.3 mmol) were added in this order at 0 °C under Ar atmosphere. The reaction mixture was stirred at r.t. for 24 h, and the solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with 4 wt% $KHSO_4$ aq. and sat. $NaHCO_3$ aq. for three times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 40/1 v/v). Yield: 6.10 g, 16.3 mmol (94%).

Boc-Aib-Pro-OMe (7)

Compound **5** (20.0 g, 98.4 mmol) and compound **6** (19.6 g, 118 mmol) were dissolved in minimum amount of DMF. The mixed solution of DCC (30.5 g, 148 mmol) and HOBt (19.9 g, 148 mmol) in minimum amount of DMF, and TEA (30.2 mL, 217 mmol) were added in this order at 0 °C. After stirring at r. t. for 15 h, the solvent was removed under reduced pressure and the residue was filtered with ethyl acetate. The filtrate was washed with 4 wt% $KHSO_4$ aq. and with sat. $NaHCO_3$ aq. for four times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: chloroform/ethyl acetate = 10/1 v/v). Yield: 26.0 g, 82.7 mmol (84%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.42 (s, 9H, BocCH_3), 1.56 (d, 6H, AibC$^{\beta}H_3$), 1.92 (m, 2H, ProC$^{\gamma}H_2$), 2.07 (m, 2H, ProC$^{\beta}H_2$), 3.71 (s, 3H, OMe), 3.66, 3.76 (m, 2H, Pro C$^{\delta}H_2$), 4.37 (t, 1H, ProC$^{\alpha}H$), 5.10 (s, 1H, urethane).

Boc-(Aib-Pro)$_2$-OMe (10)

The OMe group of compound **7** (10.0 g, 31.8 mmol) was deprotected by treating with 1 N NaOH aq. (165 mL) in the mixed solution of methanol (330 mL) and 1,4-dioxane (330 mL). The reaction mixture was stirred for 6 h. After the pH of the reaction mixture was adjusted to 7 by adding 1 N HCl aq., the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with 4 wt% $KHSO_4$ aq. once and with brine. The organic phase was dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure to obtain the deprotected product **BP2OH**. Compound **7** (11.6 g, 36.9 mmol) was dissolved in chloroform (10.0 mL) and the Boc group of compound **7** was deprotected by treating with 4 N HCl/1,4-dioxane (100 mL). The reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure, the crude product was washed with diisopropyl ether and concentrated under reduced pressure to obtain the deprotected product **HP2M**. **BP2OH** and **HP2M** were dissolved in minimum amount of DMF. The mixed solution of COMU (20.3 g, 47.4 mmol) and Oxyma (6.74 g, 47.4 mmol) in minimum amount of DMF, and DIEA (22.0 mL, 127 mmol) were added in this order at 0 °C under Ar atmosphere. The reaction mixture was stirred at r. t. for 24 h, and the solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with 4 wt% $KHSO_4$ aq. and sat. $NaHCO_3$ aq. for four times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 40/1 v/v). Yield: 10.5 g, 21.2 mmol (67%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 21H, BocCH_3, AibC$^{\beta}H_3$), 1.82-2.20 (m, 8H, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.72 (s, 3H, OMe), 3.46-3.80 (m, 4H, Pro C$^{\delta}H_2$), 4.49, 4.58 (m, 2H, ProC$^{\alpha}H$), 4.82 (s, 1H, urethane), 7.64 (s, 1H,

AibN*H*).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{26}N_2O_5$, 497.30; found, 497.30.

Boc-(Aib-Pro)$_2$-NH-(CH)$_2$-NH-Fc (13)

The OMe group of compound **10** (500 mg, 1.01 mmol) was deprotected by treating with 1 N NaOH aq. (5.00 mL) in the mixed solution of methanol (10.0 mL) and 1,4-dioxane (10.0 mL). The reaction mixture was stirred for 8 h. After the pH of the reaction mixture was adjusted to 7 by adding 1 N HCl aq., the solvent was removed under reduced pressure. The residue was dissolved in chloroform and washed with 4 wt% $KHSO_4$ aq. once and with brine. The organic phase was dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure to obtain the deprotected product **BP4OH**. The Boc group of compound **3** was deprotected by treating with HCOOH (10 mL). The reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure, the crude product was washed with diisopropyl ether and concentrated under reduced pressure to obtain the deprotected product **HFc**. **BP4OH** (130 mg, 269 μmol) and **HFc** (99.8 mg, 323 μmol) were dissolved in minimum amount of DMF. The mixed solution of COMU (173 mg, 404 μmol) and Oxyma (57.4 mg, 404 μmol) in minimum amount of DMF, and DIEA (197 μL, 1.13 mmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with 4 wt% $KHSO_4$ aq. and sat. $NaHCO_3$ aq. for four times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 45.6 mg, 61.5 μmol (23%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 21H, BocCH_3, AibC$^{\beta}H_3$), 1.82-2.20 (m, 8H, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.46-3.80 (m, 8H,CH_2CH_2, Pro C$^{\delta}H_2$), 4.58 (m, 2H, ProC$^{\alpha}H$), 4.21-4.95 (s, 9H, Fc), 5.51 (s, 1H, urethane), 7.22, 7.62 (t, 2H, N*H*EtN*H*), 7.83 (s, 1H, AibN*H*).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{52}FeN_6O_7$, 736.32; found, 736.32.

Boc-(Aib-Pro)$_3$-NH-(CH)$_2$-NH-Fc (15)

The Boc group of compound **13** was deprotected by treating with HCOOH (30.0 mL). The reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure, the crude product was washed with diisopropyl ether and concentrated under reduced pressure to obtain the deprotected product **HP4Fc**. **BP2OH** (396 mg, 1.32 mmol) and **HP4Fc** (300 mg, 440 μmol) were dissolved in minimum amount of DMF. The mixed solution of COMU (282 mg, 659 μmol) and Oxyma (93.7 mg, 659 μmol) in minimum amount of DMF, and DIEA (460 μL, 2.64 mmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Then, the residue was further purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 40/1 then 10/1 v/v). Yield: 121 mg, 131 μmol (30%).

ESI-MS *m/z*: $[M+H]^+$ calcd for $C_{45}H_{66}FeN_8O_9$, 918.43; found, 918.43.

Lipoic acid-(Aib-Pro)$_3$-NH-(CH)$_2$-NH-Fc (P6)

The Boc group of compound **15** (80 mg, 87.1 mmol) was deprotected by treating with HCOOH (10 mL). The reaction mixture was stirred for 5 h. Then HCl/ethyl acetate (500 μL) was added and stirred for 10 min. The solvent was removed under reduced pressure, and then residual HCOOH was treated by NH_3/methanol (10.0 mL). The

crude product was washed with diethyl ether and concentrated under reduced pressure to obtain the deprotected product **HP6Fc**. **HP6Fc** and lipoic acid (52.9 mg, 256 μmol) were dissolved in minimum amount of DMF. The mixed solution of COMU (165 mg, 385 μmol) and Oxyma (54.7 mg, 385 μmol) in minimum amount of DMF, and DIEA (134 μL, 769 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with 4 wt% $KHSO_4$ aq. and sat. $NaHCO_3$ aq. for three times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Then, the residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 30/1 then 10/1 v/v). Further, the residue was purified by column chromatography (Sephadex LH20, eluent: methanol), again. Yield: 41.4 mg, 41.1 μmol (48%).

^{1}H NMR (400 MHz, $CDCl_3$, δ) 1.36-1.61 (m, 18H, AibC$^{\beta}H_3$), 1.65-2.55 (m, 22H, CH_2CH_2CH_2, SSCH$_2$CH_2CH, CH_2CO, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.08-3.95(m, 13H, SSCH_2CH$_2$CH, SSCH$_2$CH$_2$CH, CH_2CH_2, ProC$^{\delta}H_2$), 4.58 (m, 3H, ProC$^{\alpha}H$), 4.22-4.95(s, 9H, Fc), 7.32, 7.62(t, 2H, NHEtNH), 6.88, 7.98 (s, 3H, AibNH).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{48}H_{70}FeN_8O_8S_2$, 1007.41; found, 1007.41.

Boc-(Aib-Pro)$_4$-OMe (14: BP8M)

Compound **10** (520 mg, 1.05 mmol) was dissolved in chloroform (1.00 mL) and the Boc group of compound **10** was deprotected by treating with HCOOH (15.0 mL). The reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure, the crude product was washed with diisopropyl ether and concentrated under

reduced pressure to obtain the deprotected product **HP4M**. **BP4OH** (484 mg, 1.12 mmol) and **HP4M** (450 mg, 932 μmol) were dissolved in minimum amount of DMF. The mixed solution of COMU (599 mg, 1.04 mmol) and Oxyma (199 mg, 1.40 mmol) in minimum amount of DMF, and DIEA (650 μL, 3.73 mmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with 4 wt% $KHSO_4$ aq. and sat. $NaHCO_3$ aq. for four times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol), and the solution was removed under reduced pressure. Yield: 390 mg, 45.3 μmol (49%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 33H, BocCH_3, AibC$^{\beta}H_3$), 1.82-2.20 (m, 16H, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.72 (s, 3H, OMe), 3.46-3.80 (m, 8H, ProC$^{\delta}H_2$), 4.49, 4.58 (m, 4H, ProC$^{\alpha}H$), 4.82 (s, 1H, urethane), 7.64, 7.83 (s, 3H, AibNH).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 23.87, 23.97, 24.67, 24.86, 25.10, 26.26, 26.55, 26.69 (Aib$C^{\beta}H_3$), 25.71, 25.92, 26.08 (Pro$C^{\gamma}H_2$), 28.12, 28.65, 28.99, 29.19 (Pro$C^{\beta}H_2$), 28.27 (BocC(CH_3)$_3$), 47.71, 48.02, 48.12, 48.55 (Pro$C^{\delta}H_2$), 51.87 (OCH_3), 56.47, 56.55, 56.70 (AibC^{α}(CH_3)$_2$), 60.56, 62.13, 62.23, 62.56 (ProC^{α}H), 80.51 (Boc$C$(CH_3)$_3$), 155.16 (Boc$C$=O), 171.62, 172.07, 172.11, 172.40, 172.74, 172.77, 173.59 (Aib$C$=O, Pro$C$=O).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{42}H_{68}N_8O_{11}$, 860.50; found, 860.50.

Boc-(Aib-Pro)$_4$-NH-(CH)$_2$-NH-Fc (18)

The OMe group of **BP8M** was deprotected by treating with 1 N NaOH aq. (695 μL) in the mixed solution of

methanol (1.40 mL) and 1,4-dioxane (1.40 mL). The reaction mixture was stirred for 8 h. After the pH of the reaction mixture was adjusted to 7 by adding 1 N HCl aq., the solvent was removed under reduced pressure. The residue was dissolved in chloroform and washed with 4 wt% $KHSO_4$ aq. once and with brine. The organic phase was dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure to obtain the deprotected product **BP8OH**. **BP8OH** (60.0 mg, 70.8 μmol) and **HFc** (65.6 mg, 213 μmol) were dissolved in minimum amount of DMF. The mixed solution of COMU (45.5 mg, 106 μmol) and Oxyma (15.1 mg, 106 μmol) in minimum amount of DMF, and DIEA (74.0 μL, 425 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol) twice. The residue was further purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 40/1 then 10/1 v/v). Yield: 49.0 mg, 44.5 μmol (63%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 33H, BocC*H*$_3$, AibC$^{\beta}$*H*$_3$), 1.82-2.20 (m, 16H, ProC$^{\gamma}$*H*$_2$, ProC$^{\beta}$*H*$_2$), 3.46-3.80 (m, 12H,C*H*$_2$C*H*$_2$, ProC$^{\delta}$*H*$_2$), 4.49, 4.58 (m, 4H, ProC$^{\alpha}$*H*), 4.12-4.79 (s, 9H, Fc), 4.82 (s, 1H, urethane), 7.32, 7.62 (t, 2H, N*H*EtN*H*), 7.64, 7.83 (s, 3H, AibN*H*).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{54}H_{80}FeN_{10}O_{11}$, 1101.54; found, 1101.53.

Lipoic acid-(Aib-Pro)$_4$-NH-(CH)$_2$-NH-Fc (P8)

The Boc group of compound **18** (60.0 mg, 54.4 μmol) was deprotected by treating with HCOOH (10.0 mL). The reaction mixture was stirred for 5 h. Then HCl/ethyl acetate (500 μL) was added and stirred for 10 min. The solvent was removed under reduced pressure, and then residual HCOOH was treated by NH_3/methanol (10.0 mL). The

crude product was washed with diethyl ether and concentrated under reduced pressure to obtain the deprotected product **HP8Fc**. **HP8Fc** (45.0 mg, 45.0 μmol) and lipoic acid (27.8 mg, 135 μmol) were dissolved in minimum amount of DMF. The mixed solution of HATU (74.1 mg, 202 μmol) and HOAt (27.5 mg, 202 μmol) in minimum amount of DMF, and DIEA (78.3 μL, 450 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred for at r. t. 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). The residue was dissolved in chloroform, and the solution was washed with 4 wt% $KHSO_4$ aq. and sat. $NaHCO_3$ aq. for four times each. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol/chloroform 1/1 v/v). Then, the residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 40/1 then 10/1 v/v), and further purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 35.3 mg, 29.7 μmol (66%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 24H, AibC$^{\beta}H_3$), 1.65-2.55 (m, 26H, CH_2CH_2CH_2, SSCH$_2$CH_2CH, CH_2CO, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.08-3.21 (m, 2H, SSCH_2CH$_2$CH), 3.25-3.40 (m, 1H, SSCH$_2$CH$_2$C*H*), 3.46-3.80 (m, 12H,CH_2CH_2, ProC$^{\delta}H_2$), 4.49, 4.58 (m, 4H, ProC$^{\alpha}H$), 4.12-4.79 (s, 9H, Fc), 7.32, 7.62 (t, 2H, N*H*EtN*H*), 6.88, 7.64, 7.83 (s, 4H, AibN*H*).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{57}H_{84}FeN_{10}O_{10}S_2$, 1189.52; found, 1189.53.

Boc-(Aib-Pro)$_6$-OMe (20)

BP8OH (200 mg, 263 μmol) and **HP4M** (152 mg, 315 μmol) were dissolved in minimum amount of DMF. The

mixed solution of HATU (144 mg, 394 μmol) and HOAt (53.7 mg, 394 μmol) in minimum amount of DMF, and DIEA (206 μL, 1.18 mmol) were added in this order at 0 °C under Ar atmosphere. The reaction mixture was stirred at r. t. for 24 h, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol/chloroform 1/1 v/v) twice. Yield: 58.9 mg, 27.6 μmol (61%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 45H, BocCH_3, AibC$^{\beta}H_3$), 1.82-2.20 (m, 24H, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.72 (s, 3H, OMe), 3.46-3.80 (m, 12H, ProC$^{\delta}H_2$), 4.49, 4.58 (m, 6H, ProC$^{\alpha}H$), 4.82 (s, 1H, urethane), 7.64 (s, 5H, AibNH).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{60}H_{96}N_{12}O_{15}$, 1225.72; found, 1225.73.

Boc-(Aib-Pro)$_6$-NH-(CH)$_2$-NH-Fc (22)

The OMe group of compound **20** (150 mg, 122 μmol) was deprotected by treating with 1 N NaOH aq. (245 μL) in the mixed solution of methanol (490 μL) and 1,4-dioxane (490 μL). The reaction mixture was stirred at 35 °C for 12 h. After the pH of the reaction mixture was adjusted to 7 by adding 1 N HCl aq., the solvent was removed under reduced pressure. The residue was dissolved in chloroform and washed with 4 wt% $KHSO_4$ aq. for three times and with brine. The organic phase was dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced pressure to obtain the deprotected product **BP12OH**. **BP12OH** (100 mg, 82.5 μmol) and **HFc** (76.4 mg, 248 μmol) were dissolved in minimum amount of DMF. The mixed solution of HATU (136 mg, 371 μmol) and HOAt (50.6 mg, 371 μmol) in minimum amount of DMF, and DIEA (144 μL, 825 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 46.0 mg,

31.4 μmol (38%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 45H, BocCH_3, AibC$^{\beta}H_3$), 1.82-2.20 (m, 24H, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.46-3.80 (m, 16H,CH_2CH_2, ProC$^{\delta}H_2$), 4.58 (m, 6H, ProC$^{\alpha}H$), 4.21-4.95 (s, 9H, Fc), 5.51 (s, 1H, urethane), 7.22-8.00 (t, 7H, N*H*EtN*H*, AibN*H*).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{72}H_{108}FeN_{14}O_{15}$, 1465.75; found, 1465.75.

Lipoic acid-(Aib-Pro)$_6$-NH-(CH)$_2$-NH-Fc (P12)

The Boc group of compound **22** was deprotected by treating with HCOOH. The reaction mixture was stirred for 12 h. Then HCl/ethyl acetate (500 μL) was added and stirred for 10 min. The solvent was removed under reduced pressure, and then residual HCOOH was treated by NH_3/methanol (10.0 mL). The crude product was washed with diethyl ether and concentrated under reduced pressure to obtain the deprotected product **HP12Fc**. **HP12Fc** (120 mg, 81.9 μmol) and lipoic acid (50.7 mg, 246 μmol) were dissolved in minimum amount of DMF. The mixed solution of HATU (135 mg, 368 μmol) and HOAt (50.2 mg, 368 μmol) in minimum amount of DMF, and DIEA (143 μL, 819 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Then, the residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 50/1, 30/1 then 10/1 v/v) and further purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 73.8 mg, 47.5 μmol (58%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.43-1.68 (m, 36H, AibC$^{\beta}H_3$), 2.19-2.49 (m, 34H, CH_2CH_2CH_2, SSCH_2CH_2CH, CH_2CO, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.10-3.90 (m, 19H, SSCH_2CH$_2$CH, SSCH$_2$CH$_2$C*H*, CH_2CH_2, ProC$^{\delta}H_2$), 4.58 (m, 3H,

ProC$^{\alpha}$*H*), 4.22-4.95 (s, 9H, Fc), 7.42, 7.62 (t, 2H, N*H*EtN*H*), 6.91, 7.95-8.08 (s, 6H, AibN*H*).

MALDI-MS (*m/z*): $[M+H]^+$ calcd for $C_{75}H_{112}FeN_{14}O_{14}S_2$, 1553.73; found, 1553.71.

Boc-(Aib-Pro)$_8$-OMe (23)

BP8OH (200 mg, 236 μmol) and **HP8M** (216 mg, 283 μmol) were dissolved in minimum amount of DMF and chloroform. The mixed solution of HATU (129 mg, 354 μmol) and HOAt (48.2 mg, 354 μmol) in minimum amount of DMF, and DIEA (173 mL, 992 μmol) were added in this order at 0 °C under Ar atmosphere. The reaction mixture was stirred at r. t. for 24 h, and the solvent was removed under reduced pressure. The residue was purified by column chromatograpy (Sephadex LH20, eluent: methanol/chloroform 1/1 v/v) Then, the residue was purified by column chromatography (Sephadex LH20, eluent: methanol) twice. Yield: 210 mg, 132 μmol (56%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.42-1.59 (m, 57H, BocC*H*$_3$, AibC$^{\beta}$*H*$_3$), 1.80-2.20 (m, 32H, ProC$^{\gamma}$*H*$_2$, ProC$^{\beta}$*H*$_2$), 3.72 (s, 3H, OMe), 3.63-3.86 (m, 16H, ProC$^{\delta}$*H*$_2$), 4.51- 4.59 (m, 8H, ProC$^{\alpha}$*H*), 4.97 (s, 1H, urethane), 7.63-8.02 (s, 7H, AibN*H*).

ESI-MS (*m/z*): $[M+H]^+$ calcd for $C_{78}H_{124}N_{16}O_{19}$, 1589.93; found, 1589.94.

Boc-(Aib-Pro)$_8$-NH-(CH)$_2$-NH-Fc (25)

The OMe group of compound **23** (72.0 mg, 45.3 μmol) was deprotected by treating with 1 N NaOH aq. (190 μL) in the mixed solution of methanol (380 μL) and 1,4-dioxane (380 μL). The reaction mixture was stirred at 35 °C for 12 h. After the pH of the reaction mixture was adjusted to 7 by adding 1 N HCl aq., the solvent was removed under reduced pressure. The residue was dissolved in chloroform and washed with 4 wt% $KHSO_4$ aq. for three times and with brine. The organic phase was dried over anhydrous $MgSO_4$, then filtered and concentrated under reduced

pressure to obtain the deprotected product **BP16OH**. **BP16OH** (60.0 mg, 38.1 μmol) and **HFc** (31.0 mg, 114 μmol) were dissolved in minimum amount of DMF. The mixed solution of HATU (41.7 mg, 114 μmol) and HOAt (15.6 mg, 114 μmol) in minimum amount of DMF, and DIEA (59.7 μL, 343 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 32.7 mg, 17.9 μmol (47%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.36-1.61 (m, 57H, BocCH_3, AibC$^{\beta}H_3$), 1.82-2.20 (m, 32H, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.46-3.80 (m, 20H, CH_2CH_2, ProC$^{\delta}H_2$), 4.58 (m, 8H, ProC$^{\alpha}H$), 4.21-4.92 (s, 9H, Fc), 5.50 (s, 1H, urethane), 7.22-8.03 (t, 9H, N*H*EtN*H*, AibN*H*).

MALDI-MS (*m/z*): $[M+H]^+$ calcd for $C_{90}H_{136}FeN_{18}O_{19}$, 1829.96; found, 1829.98.

Lipoic acid-(Aib-Pro)$_8$-NH-(CH)$_2$-NH-Fc (P16)

The Boc group of compound **25** was deprotected by treating with HCOOH. The reaction mixture was stirred for 12 h. Then HCl/Ethyl acetate (500 μL) was added and stirred for 10 min. The solvent was removed under reduced pressure, and then residual HCOOH was treated by NH_3/methanol (10.0 mL). The crude product was washed with diethyl ether and concentrated under reduced pressure to obtain the deprotected product **HP16Fc**. **HP16Fc** (77.0 mg, 44.5 μmol) and lipoic acid (27.6 mg, 134 μmol) were dissolved in minimum amount of DMF. The mixed solution of HATU (73.4 mg, 200 μmol) and HOAt (27.3 mg, 200 μmol) in minimum amount of DMF, and DIEA (77.5 μL, 445 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography

(Sephadex LH20, eluent: methanol). Then, the residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 40/1 then 10/1 v/v) and further purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 38.4 mg, 21.4 μmol (48%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.44-1.68 (m, 48H, AibC$^{\beta}$*H*$_3$), 1.65-2.55 (m, 31H, C*H*$_2$C*H*$_2$C*H*$_2$, SSCH$_2$C*H*$_2$CH, C*H*$_2$CO, ProC$^{\gamma}$*H*$_2$, ProC$^{\beta}$*H*$_2$), 3.08-3.95 (m, 23H, SSC*H*$_2$CH$_2$CH, SSCH$_2$CH$_2$C*H*, C*H*$_2$C*H*$_2$, ProC$^{\delta}$*H*$_2$), 4.58 (m, 8H, ProC$^{\alpha}$*H*), 4.22-4.95 (s, 9H, Fc), 7.32, 7.62 (t, 2H, N*H*EtN*H*), 6.88, 7.98-8.08 (s, 8H, AibN*H*).

MALDI-MS (*m/z*): $[M+H]^+$ calcd for $C_{93}H_{140}FeN_{18}O_{18}S_2$, 1917.94; found, 1917.89.

Boc-(Aib-Pro)$_{12}$-NH-(CH)$_2$-NH-Fc (26)

BP8OH (162 mg, 191 μmol) and **HP16Fc** (110 mg, 63.6 μmol) were dissolved in minimum amount of DMF and chloroform. HATU (105 mg, 286 μmol), HOAt (39.0 mg, 286 μmol) and DIEA (111 μL, 636 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol) twice. Yield: 61.0mg, 23.8 μmol (46%).

MALDI-TOF (*m/z*): $[M+H]^+$ calcd for $C_{126}H_{192}FeN_{26}O_{27}$, 2558.92; found, 2558.85.

Lipoic acid-(Aib-Pro)$_{12}$-NH-(CH)$_2$-NH-Fc (P24)

The Boc group of compound **27** (140 mg, 54.8 μmol) was deprotected by treating with HCOOH. The reaction mixture was stirred for 12 h. Then HCl/ethyl acetate (500 μL) was added and stirred for 10 min. The solvent was removed under reduced pressure, and then residual HCOOH was treated by NH_3/methanol (10.0 mL). The crude product was washed with diethyl ether and concentrated under reduced pressure to obtain the deprotected product

HP24Fc. **HP24Fc** (120 mg, 48.8 μmol) and lipoic acid (30.2 mg, 146 μmol) were dissolved in minimum amount of DMF. HATU (80.4 mg, 220 μmol), HOAt (30.0 mg, 220 μmol) and DIEA (85.0 μL, 488 μmol) were added in this order at 0 °C under Ar atmosphere, and the reaction mixture was stirred at r. t. for 24 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Sephadex LH20, eluent: methanol). Then, the residue was purified by column chromatography (silica gel, eluent: chloroform/methanol = 100/0, 30/1, 20/1 then 10/1 v/v) and further purified by column chromatography (Sephadex LH20, eluent: methanol). Yield: 30.2 mg, 11.4 μmol (23%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.45-1.65 (m, 72H, AibC$^{\beta}H_3$), 1.82-2.49 (m, 68H, CH_2CH_2CH_2, SSCH$_2$CH_2CH, CH_2CO, ProC$^{\gamma}H_2$, ProC$^{\beta}H_2$), 3.10-3.87 (m, 31H, SSCH_2CH$_2$CH, SSCH$_2$CH$_2$C*H*, CH_2CH_2, ProC$^{\delta}H_2$), 4.58 (m, 12H, ProC$^{\alpha}$*H*), 4.22-4.95 (s, 9H, Fc), 7.42, 7.62 (t, 2H, N*H*EtN*H*), 6.91, 7.95-8.08 (s, 12H, AibN*H*).

MALDI-MS (*m/z*): $[M+H]^+$ calcd for $C_{129}H_{196}FeN_{26}O_{26}S_2$, 2646.36; found, 2646.25.

High performance liquid chromatography (HPLC).

The purities of Aib-Pro peptides were confirmed by HPLC analysis. The measurements were carried out under following conditions (column: TOSOH TSKgel ODS-12OT, eluent: methanol/water 7/3 to 10/0 v/v gradient in ten min, column temperature: 40 °C, flow rate: 0.1 mL/min). The HPLC chromatogram are shown in Figure S1. Their purities were evaluated based on the peak areas and confirmed to be >95%.

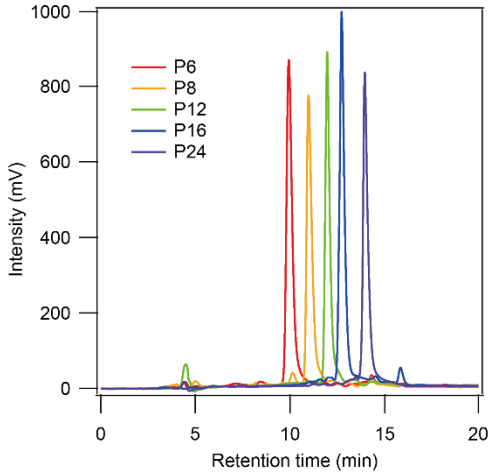


Figure S1. HPLC chromatogram of synthesized Aib-Pro peptides.

Theoretical calculation.

The initial geometry of **BP8M** was generated, in which the dihedral angles of the peptide backbone were set to be ω = 180°, ϕ = -80°, and ψ = -6°, respectively, to produce a 3_{10} helical structure. The first principle calculations of geometric optimization were carried out using the Gaussian 09 package[1] within the DFT framework under the ωB98XD/6-31G+ (d, p) level. The dihedral angles of the optimized peptide backbone were determined to be (ϕ, ψ) = (-50.4, -38.3), (-84.3, -1.9), (-49.9, -41.4), (-86.9, -5.0), (-52.7, -38.4), (-94.9, -0.1), (-60.1, -42.1) from the N terminal residue, to be confirmed as a β-bend ribbons spiral.[2] The molecular lengths of the peptides were calculated by the helix length and the length of the rest parts. The helix lengths were estimated with 2.0 Å per residue obtained by the optimized **BP8M** structure. Since the conformation of the parts other than the helix is unknown, the half of the length of the longest extended conformation was used as approximation. Then the length of lipoic acid moiety was determined to be 8 Å, and that of Fc moiety was to be 6 Å. The molecular length was determined to be 26 Å, 30 Å, 38 Å, 46 Å, 62 Å for **P6**, **P8**, **P12**, **P16**, **P24**, respectively. The thicknesses of the monolayers were estimated by (molecular length) × cosγ, where γ is the tilt angle of helical axis from the surface normal obtained by IRRAS, to be 14 Å, 17 Å, 26 Å, 31 Å, 46 Å for **P6**, **P8**, **P12**, **P16**, **P24**, respectively.

The cross-sectional area of the helical peptide was estimated to be 0.54 nm^2 (8.3 Å diameter). The limiting surface density of helical peptide is estimated as 30.8×10^{-11} mol cm^{-2}, assuming hexagonal packing with a tilt angle of 0°. The theoretical surface densities were estimated by (limiting surface density) × cosγ to be 16.7, 17.1, 21.0, 21.1, 22.6×10^{-11} mol cm^{-2} for **P6**, **P8**, **P12**, **P16**, **P24**, respectively.

The coordinates of the optimized geometries

Table S1. The coordinates of the optimized geometry of **BP8M**

Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	8.345	0.978	-0.586
2	C	7.314	0.147	-0.785
3	O	6.174	0.479	-1.088
4	C	8.146	2.429	-0.504
5	N	7.686	-1.135	-0.556
6	C	6.811	-2.279	-0.8
7	C	5.415	-2.109	-0.151
8	O	4.438	-2.563	-0.739
9	H	8.654	-1.299	-0.327
10	C	6.635	-2.488	-2.309
11	C	7.469	-3.516	-0.171
12	H	6.012	-3.361	-2.51
13	H	7.62	-2.632	-2.762
14	H	6.157	-1.617	-2.762
15	H	6.83	-4.387	-0.325
16	H	7.635	-3.391	0.903
17	H	8.433	-3.713	-0.652
18	N	5.266	-1.527	1.074
19	C	3.925	-1.511	1.66
20	C	3.042	-0.35	1.194
21	O	1.886	-0.283	1.622
22	H	3.39	-2.423	1.389
23	C	4.194	-1.412	3.166
24	C	5.455	-0.55	3.222
25	C	6.279	-1.026	2.02
26	H	4.391	-2.412	3.565
27	H	3.343	-0.989	3.7
28	H	6.005	-0.647	4.16
29	H	5.192	0.506	3.092
30	H	6.97	-1.828	2.303
31	H	6.864	-0.211	1.597
32	N	3.564	0.55	0.345
33	C	2.831	1.75	-0.069
34	C	1.395	1.44	-0.558
35	O	0.493	2.221	-0.269
36	H	4.489	0.393	-0.047
37	C	2.75	2.714	1.122
38	C	3.588	2.425	-1.222
39	H	2.245	3.637	0.836
40	H	3.767	2.944	1.455

41	H	2.193	2.262	1.945
42	H	3.006	3.277	-1.58
43	H	3.774	1.744	-2.054
44	H	4.555	2.792	-0.868
45	N	1.149	0.359	-1.35
46	C	-0.208	0.186	-1.867
47	C	-1.146	-0.575	-0.926
48	O	-2.33	-0.705	-1.248
49	H	-0.672	1.161	-2.034
50	C	0.005	-0.601	-3.166
51	C	1.2	-1.491	-2.823
52	C	2.097	-0.588	-1.971
53	H	0.261	0.098	-3.969
54	H	-0.892	-1.149	-3.458
55	H	1.725	-1.871	-3.701
56	H	0.872	-2.352	-2.231
57	H	2.816	-0.048	-2.597
58	H	2.658	-1.162	-1.237
59	N	-0.631	-1.09	0.202
60	C	-1.421	-1.928	1.105
61	C	-2.758	-1.267	1.527
62	O	-3.744	-1.982	1.685
63	H	0.305	-0.817	0.491
64	C	-1.724	-3.261	0.408
65	C	-0.605	-2.195	2.378
66	H	-2.304	-3.91	1.065
67	H	-0.776	-3.747	0.157
68	H	-2.3	-3.096	-0.504
69	H	-1.193	-2.827	3.047
70	H	-0.332	-1.277	2.9
71	H	0.322	-2.719	2.122
72	N	-2.811	0.071	1.777
73	C	-4.06	0.642	2.278
74	C	-4.973	1.226	1.188
75	O	-6.032	1.749	1.519
76	H	-4.64	-0.131	2.783
77	C	-3.575	1.745	3.223
78	C	-2.346	2.29	2.492
79	C	-1.715	1.059	1.823
80	H	-3.293	1.295	4.181
81	H	-4.35	2.492	3.402
82	H	-1.64	2.798	3.153
83	H	-2.656	3.007	1.726
84	H	-0.87	0.672	2.399
85	H	-1.344	1.31	0.83
86	N	-4.525	1.148	-0.086
87	C	-5.269	1.654	-1.241

88	C	-6.647	0.967	-1.403
89	O	-7.621	1.622	-1.764
90	H	-3.699	0.589	-0.269
91	C	-5.473	3.168	-1.109
92	C	-4.447	1.369	-2.508
93	H	-5.977	3.558	-1.994
94	H	-4.491	3.643	-1.01
95	H	-6.08	3.403	-0.235
96	H	-4.986	1.758	-3.376
97	H	-4.256	0.305	-2.656
98	H	-3.479	1.877	-2.44
99	N	-6.758	-0.375	-1.22
100	C	-8.088	-0.966	-1.348
101	C	-9.11	-0.35	-0.403
102	O	-10.297	-0.298	-0.635
103	H	-8.477	-0.812	-2.359
104	C	-7.87	-2.462	-1.032
105	C	-6.375	-2.674	-1.287
106	C	-5.762	-1.365	-0.799
107	H	-8.518	-3.097	-1.639
108	H	-8.093	-2.656	0.022
109	H	-6.183	-2.804	-2.358
110	H	-5.969	-3.537	-0.755
111	H	-4.783	-1.178	-1.238
112	H	-5.647	-1.374	0.29
113	O	-8.54	0.046	0.733
114	C	-9.363	0.75	1.659
115	H	-8.679	1.116	2.423
116	H	-10.116	0.083	2.086
117	H	-9.857	1.585	1.158
118	C	7.619	2.975	-1.83
119	C	7.226	2.744	0.674
120	C	9.556	2.946	-0.237
121	H	8.272	2.665	-2.65
122	H	6.607	2.626	-2.035
123	H	7.616	4.068	-1.79
124	H	9.959	2.514	0.684
125	H	10.224	2.689	-1.064
126	H	9.537	4.034	-0.131
127	H	6.23	2.32	0.529
128	H	7.649	2.347	1.603
129	H	7.125	3.828	0.782

Table S2. The coordinates of the optimized geometry of **BA8M**

Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	8.266	0.345	-0.569
2	C	7.05	-0.148	-0.792
3	O	6.007	0.489	-0.844
4	C	8.467	1.77	-0.254
5	N	7.086	-1.508	-0.925
6	C	5.919	-2.216	-1.432
7	C	4.722	-2.125	-0.479
8	O	3.581	-2.219	-0.923
9	H	7.996	-1.936	-1.017
10	H	5.567	-1.748	-2.357
11	C	6.267	-3.679	-1.698
12	H	5.381	-4.205	-2.058
13	H	6.618	-4.173	-0.786
14	H	7.045	-3.755	-2.463
15	N	5.007	-1.942	0.828
16	C	4.007	-1.778	1.884
17	C	3.046	-0.612	1.562
18	O	1.925	-0.582	2.068
19	H	5.983	-1.846	1.072
20	C	3.206	-3.068	2.082
21	C	4.756	-1.403	3.17
22	H	2.464	-2.928	2.869
23	H	3.888	-3.874	2.366
24	H	2.688	-3.346	1.162
25	H	4.039	-1.247	3.978
26	H	5.334	-0.482	3.038
27	H	5.433	-2.213	3.462
28	N	3.503	0.375	0.764
29	C	2.658	1.504	0.421
30	C	1.387	1.105	-0.34
31	O	0.426	1.875	-0.327
32	H	4.405	0.298	0.303
33	H	2.283	1.958	1.343
34	C	3.45	2.535	-0.379
35	H	2.799	3.374	-0.631
36	H	3.843	2.098	-1.302
37	H	4.293	2.907	0.21
38	N	1.383	-0.082	-0.977
39	C	0.202	-0.623	-1.654
40	C	-1.007	-0.669	-0.695
41	O	-2.154	-0.643	-1.139
42	H	2.201	-0.681	-0.916
43	C	-0.153	0.207	-2.891

44	C	0.516	-2.072	-2.051
45	H	-1.031	-0.216	-3.382
46	H	0.692	0.193	-3.586
47	H	-0.373	1.24	-2.615
48	H	-0.364	-2.516	-2.522
49	H	0.793	-2.671	-1.179
50	H	1.347	-2.095	-2.761
51	N	-0.753	-0.796	0.625
52	C	-1.839	-0.867	1.584
53	C	-2.728	0.384	1.606
54	O	-3.876	0.279	2.04
55	H	0.199	-0.758	0.978
56	H	-2.521	-1.67	1.288
57	C	-1.285	-1.144	2.98
58	H	-2.108	-1.188	3.696
59	H	-0.587	-0.36	3.286
60	H	-0.753	-2.099	2.993
61	N	-2.206	1.536	1.144
62	C	-2.976	2.778	1.021
63	C	-4.215	2.591	0.109
64	O	-5.158	3.369	0.184
65	H	-1.272	1.527	0.742
66	C	-3.414	3.292	2.395
67	C	-2.074	3.811	0.33
68	H	-3.979	4.218	2.274
69	H	-2.525	3.484	3.004
70	H	-4.046	2.56	2.899
71	H	-2.628	4.744	0.205
72	H	-1.744	3.457	-0.651
73	H	-1.185	4.003	0.938
74	N	-4.138	1.592	-0.803
75	C	-5.185	1.312	-1.763
76	C	-6.023	0.075	-1.401
77	O	-6.787	-0.417	-2.229
78	H	-3.334	0.973	-0.816
79	H	-5.878	2.159	-1.732
80	C	-4.596	1.163	-3.165
81	H	-5.383	0.906	-3.875
82	H	-3.842	0.369	-3.175
83	H	-4.122	2.101	-3.466
84	N	-5.9	-0.404	-0.146
85	C	-6.626	-1.584	0.301
86	C	-8.118	-1.474	-0.05
87	O	-8.812	-2.414	-0.364
88	H	-5.26	0.033	0.508
89	C	-6.042	-2.85	-0.335
90	C	-6.526	-1.652	1.833

91	H	-6.577	-3.736	0.013
92	H	-4.987	-2.928	-0.059
93	H	-6.126	-2.798	-1.422
94	H	-7.07	-2.526	2.201
95	H	-6.94	-0.75	2.291
96	H	-5.476	-1.731	2.131
97	O	-8.589	-0.237	0.145
98	C	-9.958	-0.038	-0.195
99	H	-10.158	1.014	0.005
100	H	-10.605	-0.676	0.413
101	H	-10.117	-0.263	-1.252
102	C	8.027	2.633	-1.433
103	C	7.726	2.118	1.036
104	C	9.976	1.854	-0.052
105	H	8.533	2.313	-2.348
106	H	6.948	2.582	-1.585
107	H	8.304	3.673	-1.237
108	H	6.644	2.064	0.903
109	H	8.025	1.441	1.842
110	H	7.986	3.137	1.334
111	H	10.295	1.202	0.766
112	H	10.503	1.558	-0.962
113	H	10.256	2.882	0.192

Reference.

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, (2009) Gaussian, Inc., Wallingford, CT, USA.
2. B. Diblasio, V. Pavone, M. Saviano, A. Lombardi, F. Nastri, C. Pedone, E. Benedetti, M. Crisma, M. Anzolin and C. Toniolo, *J Am Chem Soc*, 1992, **114**, 6273-6278.