Electronic Supplementary Information

Short Peptide Based Hydrogels: Incorporation of Graphene into the Hydrogel

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**Synthetic Procedure of Peptides:**

**Synthesis of Peptide 1:**

(i) **Boc-Tyr-OH**: A solution of L-Tyr (3.621 g, 20 mmol) in a mixture of dioxane (40 mL), water (20 mL) and 1M NaOH (20 mL) was stirred and cooled in an ice water bath. Di-tert-butyl pyrocarbonate (4.8 g, 22 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was concentrated in vacuum to about 20–25
mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 20 mL), and
acidified with a dilute solution of KHSO₄ to pH 2-3 (congo red). The aqueous phase was
extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate
extract were pooled, washed with water, dried over anhydrous Na₂SO₄ and evaporated in
vacuum. The pure material was obtained as a waxy solid.
Yield: 5.204 g (18.5 mmol, 92.5%).

(ii) Boc-Tyr-Asp-(OMe)₂: 4.782 g (17 mmol) of Boc-Tyr-OH was dissolved in 20 mL of
dry DMF in an ice-water bath. H-Asp-(OMe)₂ was isolated from 5.76 g (34 mmol) of the
corresponding methyl ester hydrochloride by neutralization; subsequent extraction with
ethyl acetate and ethyl acetate extract was concentrated to 15 mL. It was then added to
the reaction mixture, followed immediately by 3.5 g (17 mmol) of dicyclohexyl
carbodiimide (DCC) and 2.30 g (17 mmol) of HOBt. The reaction mixture was allowed
to come to room temperature and stirred for 2 days. The residue was taken up in ethyl
acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was
washed with 1 M HCl (3 × 30 mL), brine (2 × 30 mL), 1M sodium carbonate (3 × 30 mL)
and brine (2 × 30 mL) respectively. This washed organic solution was dried over
anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained.
Yield: 6.069 g (14.30 mmol, 84.12%).

¹H NMR (300 MHz, CDCl₃, 25º C, TMS): δ 7.17 (d, 3J(H, H) = 7.83 Hz, 1H; NH), δ
6.94–6.91 (d, 2H; aromatic H), ), δ 6.69–6.66 (d, 2H; aromatic H), δ 5.24 (d, 3J(H, H) =
7.68 Hz, 1H; NH), δ 4.74 (br, 1H; αCH), δ 4.28 (br, 1H; αCH), δ 3.63 (s, 3H; OCH₃), δ
3.58 (s, 3H; OCH₃), δ 2.92 – 2.73 (m, 4H; βCH₂), δ 1.33 (s, 9H; Boc–CH₃); HRMS: m/z
425.07 [M+H]⁺, 447.04 [M+Na]⁺; ¹³C NMR (75 MHz, CDCl₃, 25º C): δ 171.83 (1C of
COOMe), δ 171.21 (1C of COOMe), δ 170.69 (C of CONH), δ 155.62 (C of CONH), δ 155.45 (1C, aromatic C of Tyr), δ 130.22 (1C, aromatic C of Tyr), δ 127.03 (2C, aromatic C of Tyr), δ 115.55 (2C, aromatic C of Tyr), δ 80.26 (1C, tertiary C of Boc), δ 77.58-76.74 (C of CDCl₃), δ 52.72 (1C, α C), δ 51.99 (1C, α C), δ 48.95 (1C, C of OCH₃), 48.62 (1C, C of OCH₃), δ 37.26 (1C, C of β CH₂), δ 35.85 (1C, C of β CH₂), δ 28.31 (3C, primary C of Boc).

(iii) Boc-Tyr-Asp-(OH)₂: To 5.093 g (12 mmol) of Boc-Tyr-Asp-(OMe)₂ were added 40 mL MeOH and 30 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2 × 50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2 × 50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 4.205 g (10.608 mmol, 88.40 %).

¹H NMR (300 MHz, [D₆]DMSO, 25º C): δ 9.15 (br, 1H; Tyr−OH), δ 8.13 (d, ³J(H, H) = 7.8 Hz, 1H; NH), δ 7.10−6.95 (m, aromatic H, 2H; NH), δ 6.75 (d, ³J(H, H) = 7.9 Hz, 1H; NH), δ 6.69−6.62 (m, aromatic H, 2H; NH), δ 4.53−4.51 (m, 1H; α CH), δ 4.06−3.99 (m, 1H; α CH), δ 3.45−3.43 (m, 2H; β CH), δ 2.85−2.61 (m, 2H; β CH), δ 1.31 (s, 9H; Boc−CH₃); HRMS: m/z 419.15 [M+Na]+, 433.16 [M+K]+; ¹³C NMR (75 MHz, [D₆]DMSO, 25º C): δ 172.81 (C of COOH), δ 172.19 (C of COOH), δ 172.11 (C of CONH), δ 156.16 (C of CONH), δ 155.60 (1C, aromatic C of Tyr), δ 130.54 (1C, aromatic C of Tyr), δ 128.59 (2C, aromatic C of Tyr), δ 115.25 (2C, aromatic C of Tyr), δ 78.48 (1C, tertiary C of Boc), δ 60.20 (1C, α C), δ 56.34 (1C, α C), δ 40.75−39.08 (C of...
[D₆]DMSO), δ 37.05 (1C, C of β CH₂), δ 36.70 (1C, C of β CH₂), δ 28.31 (3C, primary C of Boc).

(iv) H-Tyr-Asp-(OH)₂: To 3.5676 g (9 mmol) of Boc-Tyr-Asp-(OH)₂ was added 4 mL of 98% formic acid, and the removal of the Boc group was monitored by TLC. After 8 h, formic acid was removed under a vacuum. The residue was taken in water (20 mL) and washed with diethyl ether (2×30 mL). The pH of the aqueous solution was then adjusted to 7 with 30% aqueous NH₃. The aqueous solution was lyophilized to yield white solid product. Yield: 2.374 g (8.01 mmol, 89%).

¹H NMR (300 MHz, [D₆]DMSO, 25ºC): δ 8.36 (1H, NH), δ 8.13 (1H; NH), δ 7.01–6.61 (m, 5H; aromatic H), δ 4.06–3.98 (m, 1H; α CH), δ 3.66–3.52 (m, 1H; α CH), δ 2.95–2.88 (m, H; β CH₂), δ 2.74–2.62 (m, 1H; β CH), δ 2.27–2.15 (m, H; β CH₂), δ 1.96 (m, 1H; β CH); HRMS: m/z 297.05 [M+H]⁺.

(v) Fmoc-Tyr-Asp-(OH)₂: 1.777 g of (6 mmol) of H-Tyr-Asp-(OH)₂ was dissolved in a basic sodium carbonate solution (15 mL). It was cooled in an ice-water bath. Cooled solution of Fmoc-Cl (2.31 g) in dioxane (15 mL) was added to it. The reaction mixture was allowed to come to room temperature and it was stirred for 24 hrs. Then the solution was concentrated in vacuum to about 15 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 30 mL), and acidified with a dilute HCl to neutral pH. The aqueous phase was extracted with ethyl acetate and this operation was done twice. The ethyl acetate extract were pooled, dried over anhydrous Na₂SO₄ and evaporated in vacuum. A white material was obtained. Yield: 2.83 g (5.45 mmol, 91%); m.p. 135ºC.
\( ^1H \) NMR (300 MHz, [D\(_6\)]DMSO, 25º C): \( \delta \) 12.59 (br, 2H; COOH), \( \delta \) 9.13 (s, 1H; aromatic OH), \( \delta \) 8.33 (d, \(^3J(H, H) = 7.8\) Hz, 1H; NH), \( \delta \) 7.87–7.85 (m, 2H; aromatic CH), \( \delta \) 7.65–7.60 (m, 2H; aromatic CH), \( \delta \) 7.53 (d, \(^3J(H, H) = 9\) Hz, 1H; NH), \( \delta \) 7.41–7.37 (m, 2H; aromatic CH), \( \delta \) 7.33–7.27 (m, 2H; aromatic CH), \( \delta \) 7.10–7.08 (m, 2H; aromatic CH of Tyr), \( \delta \) 6.64–6.61 (m, 2H; aromatic CH of Tyr), \( \delta \) 4.57–4.54 (m, 1H; \( \alpha \) CH), \( \delta \) 4.18–4.09 (m, 4H; CH, CH\(_2\) and \( \alpha \) CH), \( \delta \) 3.58–3.55 (m, 2H; \( \beta \) CH\(_2\)), \( \delta \) 2.92–2.87 (m, 1H; \( \beta \) CH\(_2\)), \( \delta \) 2.69–2.56 (m, 1H; \( \beta \) CH\(_2\)); HRMS: m/z 541.32 [M+Na]\(^+\), 557.26 [M+K]\(^+\); \( ^{13}C \) NMR (75 MHz, [D\(_6\)]DMSO, 25ºC): \( \delta \) 172.87 (2C, C of COOH), \( \delta \) 172.21 (C, C of CONH), \( \delta \) 156.29 (C of CONH), \( \delta \), \( \delta \) 144.37 (C, aromatic C), \( \delta \) 141.19 (2C, aromatic C), \( \delta \) 130.72 (2C, aromatic C), \( \delta \) 128.73 (C, aromatic C), \( \delta \) 128.17 (2C, aromatic C), \( \delta \) 127.62 (2C, aromatic C), \( \delta \) 125.91 (2C, aromatic C), \( \delta \) 120.61 (2C, aromatic C), \( \delta \) 120.41 (2C, aromatic C), \( \delta \) 115.37 (2C, aromatic C), \( \delta \) 66.20 (C of CH\(_2\)), \( \delta \) 56.87 (C, \( \alpha \) C), \( \delta \) 49.13 (C, \( \alpha \) C), \( \delta \) 47.11 (C of CH), \( \delta \) 40.88–39.49 (C of [D\(_6\)]DMSO), \( \delta \) 37.29 (C, \( \beta \) C), \( \delta \) 36.57 (C, \( \beta \) C).

**Synthesis of Peptide 2:**

(i) Boc-Phe-OH: A solution of L-Phe (3.303 g, 20 mmol) in a mixture of dioxane (40 mL), water (20 mL) and 1M NaOH (20 mL) was stirred and cooled in an ice water bath. Di-tert-butyl pyrocarbonate (4.8 g, 22 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was concentrated in vacuum to about 20-25 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 20 mL), and acidified with a dilute solution of KHSO\(_4\) to pH 2-3 (cono red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate
extract were pooled, washed with water, dried over anhydrous Na₂SO₄ and evaporated in vacuum. The pure material was obtained as a waxy solid.
Yield: 4.931 g (18.59 mmol, 93%).

(ii) Boc-Phe-Asp-(OMe)₂: 4.507 g (17 mmol) of Boc-Phe-OH was dissolved in 20 mL of dry DMF in an ice-water bath. H-Asp-(OMe)₂ was isolated from 5.76 g (34 mmol) of the corresponding methyl ester hydrochloride by neutralization; subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 15 mL. It was then added to the reaction mixture, followed immediately by 3.5 g (17 mmol) of dicyclohexyl carbodiimide (DCC) and 2.30 g (17 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 2 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1 M HCl (3 × 30 mL), brine (2 × 30 mL), 1M sodium carbonate (3 × 30 mL) and brine (2 × 30 mL) respectively. This washed organic solution was dried over anhydrous sodium sulfate and evaporated in vacuum. A white material was obtained.
Yield: 6.939 g (14.501 mmol, 85.3%).

¹H NMR (300 MHz, CDCl₃, 25° C, TMS): δ 7.16–7.00 (m, 5H; aromatic H and 1H; NH), δ 6.84 (d, ³J(H, H) = 9.6 Hz, 1H; NH), δ 4.73–4.69 (m, 1H; α CH), δ 4.31 (br, 1H; α CH), δ 3.64 (s, 3H; OCH₃), δ 3.55 (s, 3H; OCH₃), δ 3.04 – 2.88 (m, 2H; β CH₂), δ 2.77 – 2.73 (m, 2H; β CH₂), δ 1.37 (s, 9H; Boc–CH₃); HRMS: m/z 430.96 [M+Na]⁺, 431.97 [M+Na+H]⁺, 446.93 [M+K]⁺; ¹³C NMR (75 MHz, CDCl₃, 25° C): δ 171.27 (1C of COOMe), δ 171.14 (1C of COOMe), δ 170.30 (1C of CONH), δ 155.32 (C of CONH), δ 136.46 (1C, aromatic C of Phe), δ 129.61 (1C, aromatic C of Phe), δ 129.42 (1C,
aromatic C of Phe), δ 128.71 (1C, aromatic C of Phe), δ 128.40 (1C, aromatic C of Phe), δ 127.11 (1C, aromatic C of Phe), δ 80.26 (1C, tertiary C of Boc), δ 77.41–76.90 (C of CDCl₃), δ 55.61 (1C, α C), δ 48.83 (1C, α C), δ 38.31 (1C, β C), δ 36.01 (1C, C of β C), δ 28.02 (3C, primary C of Boc).

(iii) Boc-Phe-Asp-(OH)$_2$: To 4.9014 g (12 mmol) of Boc-Phe-Asp-(OMe)$_2$ were added 40 mL MeOH and 30 mL of 1(M) NaOH and the progress of saponification was monitored by thin-layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 50 mL of water and washed with diethyl ether (2×50 mL). The pH of the aqueous layer was then adjusted to 2-3 using 1(N) HCl, the aqueous layer was extracted with ethyl acetate (2×50 mL). The extract were pooled, dried over anhydrous sodium sulfate and evaporated in vacuum. Yield: 3.9425 g (10.364 mmol, 86.37%).

$^1$H NMR (300 MHz, [D$_6$]DMSO, 25ºC): δ 8.87 (d, 1H; NH), δ 7.30–7.15 (m, aromatic H, 5H), δ 7.01 (d, 1H; NH), δ 4.21–4.19 (m, 1H; α CH), δ 4.01 (m, 1H; α CH), δ 3.11–3.06 (m, 2H; β CH), δ 2.98–2.88 (m, 2H; β CH), δ 1.30 (s, 9H; Boc–CH$_3$); HRMS: m/z 403.14 [M+Na]$^+$.  

(iv) H-Phe-Asp-(OH)$_2$: To 3.4225 g (9 mmol) of Boc-Phe-Asp-(OH)$_2$ was added 4 mL of 98% formic acid, and the removal of the Boc group was monitored by TLC. After 8 h, formic acid was removed under a vacuum. The residue was taken in water (20 mL) and washed with diethyl ether (2×30 mL). The pH of the aqueous solution was then adjusted to 7 with 30% aqueous NH$_3$. The aqueous solution was lyophilized to yield white solid product. Yield: 2.205 g (7.867 mmol, 87.40%).
$^1$H NMR (300 MHz, [D$_6$]DMSO, 25ºC): $\delta$ 8.25 (d, 1H, $^3$J(H, H) = 6.3 Hz, NH), $\delta$ 8.13 (d, 
$^3$J(H, H) = 6.3 Hz, 1H; NH), $\delta$ 7.22–6.93 (m, 5H; aromatic H), $\delta$ 4.10–4.07 (m, 1H; $\alpha$ CH), 
$\delta$ 3.62–3.58 (m, 1H; $\alpha$ CH), $\delta$ 3.05–2.92 (m, H; $\beta$ CH$_2$), $\delta$ 2.85–2.80 (m, 1H; $\beta$ CH), 
$\delta$ 2.70–2.63 (m, H; $\beta$ CH$_2$), $\delta$ 2.41–2.30 (m, 1H; $\beta$ CH); HRMS: m/z 281.26 [M+H]$^+$, 
303.25 [M+Na]$^+$; $^{13}$C NMR (75 MHz, [D$_6$]DMSO, 25ºC): $\delta$ 173.89 (C of COOH), $\delta$
173.33 (C of COOH), $\delta$ 171.47 (C of CONH), $\delta$ 137.69 (1C, aromatic C of Phe), $\delta$ 130.73 
(1C, aromatic C of Phe), $\delta$ 130.00 (1C, aromatic C of Phe), $\delta$ 128.83(1C, aromatic C of 
Phe), $\delta$ 128.63 (1C, aromatic C of Phe), $\delta$ 127.24 (1C, aromatic C of Phe), $\delta$ 55.38 (C, $\alpha$
C), $\delta$ 49.37 (C, $\alpha$ C), $\delta$ 40.79–38.77 (C of [D$_6$]DMSO and 2 $\beta$ C).

(v) Fmoc-Phe-Asp-(OH)$_2$: 1.682 g of (6 mmol) of H-Phe-Asp-(OH)$_2$ was dissolved in a 
basic sodium carbonate solution (15 mL). It was cooled in an ice-water bath. Then cooled 
solution of Fmoc-Cl (2.31 g) in dioxane (15 mL) was added to it. The reaction mixture 
was allowed to come to room temperature and stirred for 24 hrs. Then the solution was 
concentrated in vacuum to about 15 mL, cooled in an ice water bath, covered with a layer 
of ethyl acetate (about 30 mL), and acidified with a dilute HCl to neutral pH. The 
aqueous phase was extracted with ethyl acetate and this operation was done twice. The 
ethyl acetate extract were pooled, dried over anhydrous Na$_2$SO$_4$ and evaporated in 
vacuum. A white material was obtained. Yield: 2.755 g (5.487 mmol, 91.45 %); m.p.
149ºC.

$^1$H NMR (300 MHz, [D$_6$]DMSO, 25ºC): $\delta$ 12.62 (br, 2H; COOH), $\delta$ 8.39 (d, $^3$J(H, H) = 
7.5 Hz, 1H; NH), $\delta$ $\delta$ 7.87–7.85 (m, 2H; aromatic CH), $\delta$ 7.69–7.61 (m, 3H; aromatic 
CH), $\delta$ 7.42–7.16 (m, 9H; aromatic CH and NH), $\delta$ 4.58–4.56 (m, 1H; $\alpha$ CH), $\delta$
4.29–4.24 (m, 1H, $\alpha$ CH), $\delta$ 4.18–4.08 (m, 3H; CH, CH$_2$), $\delta$ 3.05–3.01 (m, 2H; $\beta$ CH$_2$), $\delta$
2.79–2.63 (m, 2H; β CH₂); HRMS: m/z 525.45[M+Na]⁺, 541.44 [M+K]⁺; ¹³C NMR (75 MHz, [D₆]DMSO, 25°C): δ 172.94 (C, C of COOH), δ 172.29 (C, C of COOH), δ 172.03 (C, C of CONH), δ 156.32 (C of CONH), δ 144.32 (C, aromatic C), δ 141.20 (2C, aromatic C), δ 138.73 (2C, aromatic C), δ 129.82 (C, aromatic C), δ 128.57 (C, aromatic C), δ 128.18 (C, aromatic C), δ 127.62 (C, aromatic C), δ 127.34 (C, aromatic C), δ 126.78 (C, aromatic C), δ 125.85 (C, aromatic C), δ 120.62 (2C, aromatic C), δ 66.24 (C of CH₂), δ 56.55 (C, α C), δ 49.24 (C, α C), δ 47.11 (C of CH), δ 40.89–39.22 (C of [D₆]DMSO), δ 38.05 (C, β C), δ 36.86 (C, β C).

**Fig. S8** ¹H NMR Spectrum of the Peptide Boc-YD-(OMe)₂.
**Fig.S9** HRMS Spectrum of the Peptide Boc-YD-(OMe)$_2$.

**Fig.S10** $^{13}$C NMR Spectrum of the Peptide Boc-YD-(OMe)$_2$. 
Fig. S11 $^1$H NMR Spectrum of the Peptide Boc-YD-(OH)$_2$.

Fig. S12 HRMS Spectrum of the Peptide Boc-YD-(OH)$_2$. 
Fig. S13 $^{13}$C NMR Spectrum of the Peptide Boc-YD-(OH)$_2$.

Fig. S14 $^1$H NMR Spectrum of the Peptide H-YD-(OH)$_2$. 
**Fig. S15** HRMS Spectrum of the Peptide H-YD-(OH)$_2$.

**Fig. S16** $^1$H NMR Spectrum of the Peptide Fmoc-YD-(OH)$_2$. 
**Fig. S17** HRMS Spectrum of the Peptide Fmoc-YD-(OH)$_2$.

**Fig. S18** $^{13}$C NMR Spectrum of the Peptide Fmoc-YD-(OH)$_2$. 
**Fig. S19** $^1$H NMR Spectrum of the Peptide Boc-FD-(OMe)$_2$.

**Fig. S20** HRMS Spectrum of the Peptide Boc-FD-(OMe)$_2$. 
Fig. S21 $^{13}$C NMR Spectrum of the Peptide Boc-FD-(OMe)$_2$.

Fig. S22 $^1$H NMR Spectrum of the Peptide Boc-FD-(OH)$_2$. 
Fig. S23 HRMS Spectrum of the Peptide Boc-FD-(OH)₂.

Fig. S24 ¹H NMR Spectrum of the Peptide H-FD-(OH)₂.
Fig. S25 HRMS Spectrum of the Peptide H-FD-(OH)$_2$.

Fig. S26 $^{13}$C NMR Spectrum of the Peptide H-FD-(OH)$_2$. 
Fig. S27 $^1$H NMR Spectrum of the Peptide Fmoc-FD-(OH)$_2$.

Fig. S28 HRMS Spectrum of the Peptide Fmoc-FD-(OH)$_2$. 
Fig. S29 $^{13}$C NMR Spectrum of the Peptide Fmoc-FD-(OH)$_2$. 