Supporting Information

Filled and peptide-modified single-walled carbon nanotubes: synthesis, characterization, and in vitro test for cancer cell targeting

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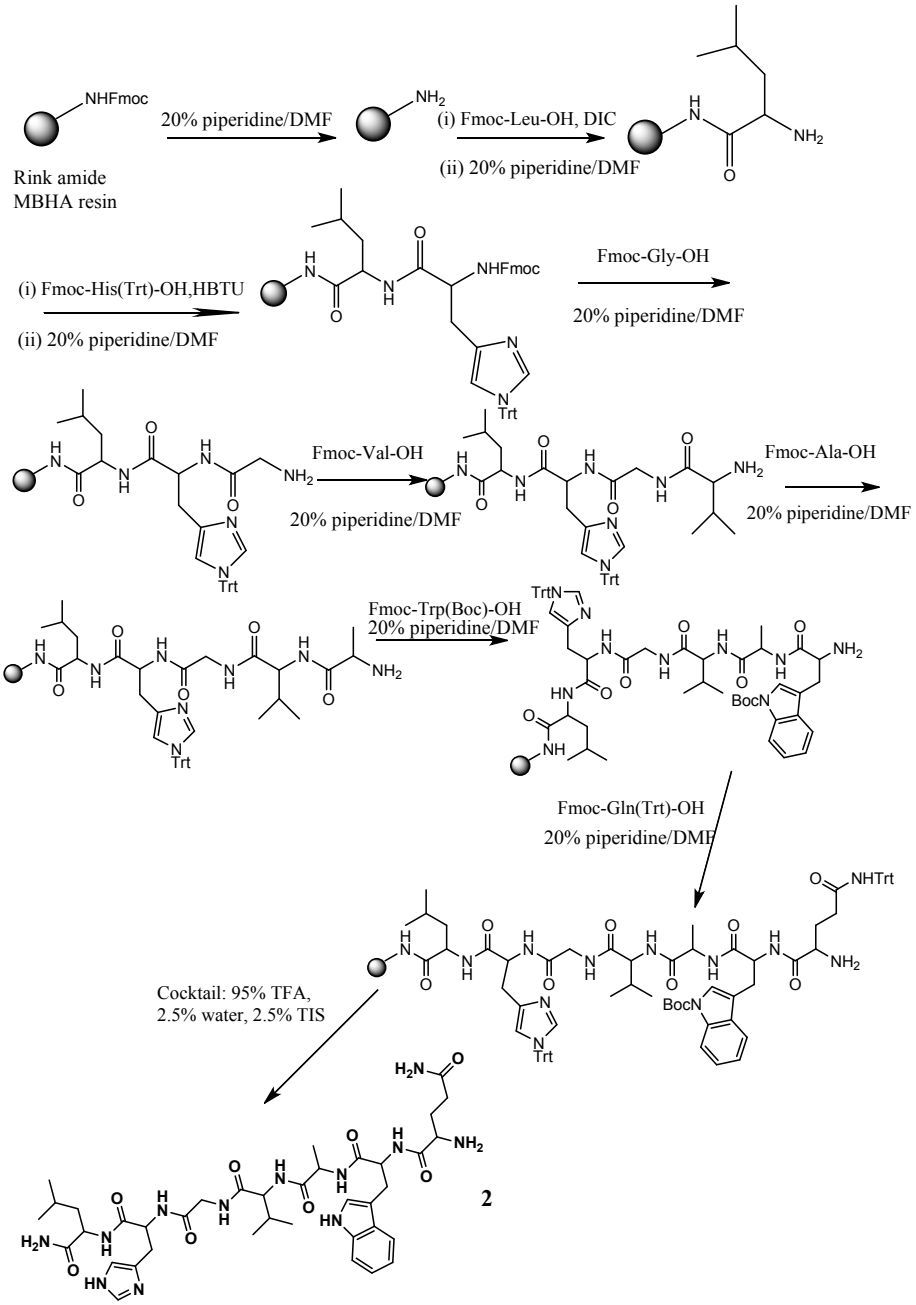
1. Steaming purification of SWNTs

This method was based on literature method by Malcolm L H Green.[1, 2] 250 mg arc-discharge made SWNTs (CarboLex) was kept in a glove box fed with argon gas for two days to remove oxygen absorbed on surface of carbon nanotubes.

Distilled water was first flushed with argon to remove dissolved oxygen. SWNTs were placed in a silica tube (9 mm diameter) and immobilised with silica wool at both sides. The sample was then put in the middle of quartz furnace tubes. The sample was kept under argon for 30 min. The steam was introduced by bubbling argon through boiling water (98 °C). After the whole system was purged by argon for 2 h, then the furnace was gradually then heated to 900 °C (15 °C/min). After 2 h steaming treatment, the steam was turned off, and the furnace was switched off, but argon flow was kept on until furnace decreased to room temperature to protect the sample from thermal oxidation. After steam treatment, sample was stirring in 16 % HCl overnight, and then the carbon nanotubes was filtered after the solution diluted with access distilled water, the solid was washed with access distilled water. Obtained carbon nanotubes solid was dried in oven at 60 °C overnight.

2. Synthesis of bombesin [7-13] peptide (2) (Scheme S1)

The bombesin (Gln-Trp-Ala-Val-Gly-His-Leu-NH_2) [7-13] peptide sequence was made by SPPS (Solid Phase Peptide Synthesis), involving the coupling of coupled fluorenylmethoxycarbonyl (Fmoc) amino acids onto Rink Amide Resin. Leucine, glycine, alanine and valine were used unprotected, Fmoc-Leu-OH, Fmoc-Gly-OH, Fmoc-Ala-OH and Fmoc-Val-OH. The side chain functional group of histidine and glutamine were protected by trityl and tert-butoxycarbonyl(Fmoc-His(Trt)-OH, Fmoc-Gln(Boc)-OH)and tryptophan protected by tert-Butyloxycarbonyl, Fmoc-Trp(Boc)-OH. The resulting product was then freeze-dried and stored in the fridge for further analysis. The white powder after freeze-drying was analyzed by mass spectroscopy: ESI/MS: *m/z* 809.44 $[M + H]^+$, 405.38 $[M +2H]^{2+}$.



Scheme S1: Procedure for the synthesis of bombesin[7-13]: Gln-Trp-Ala-Val-Gly-His-Leu-NH_2

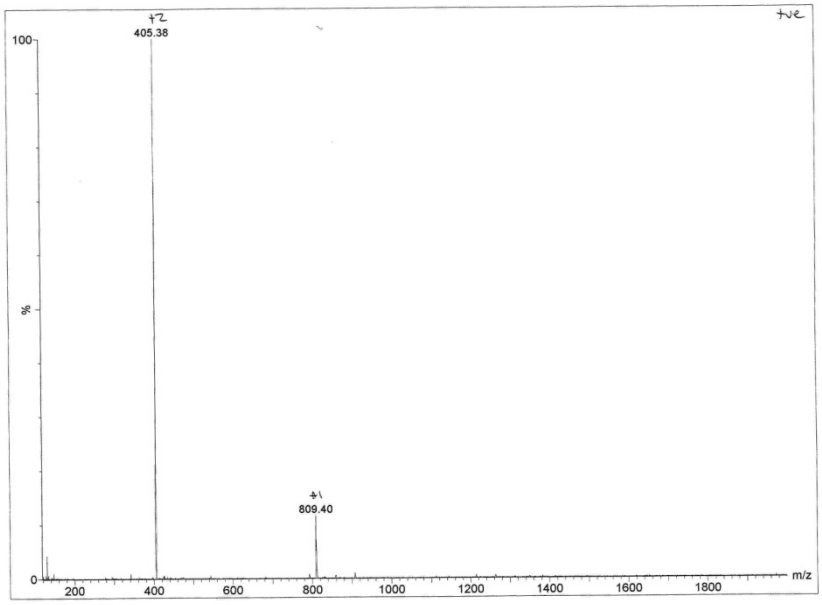
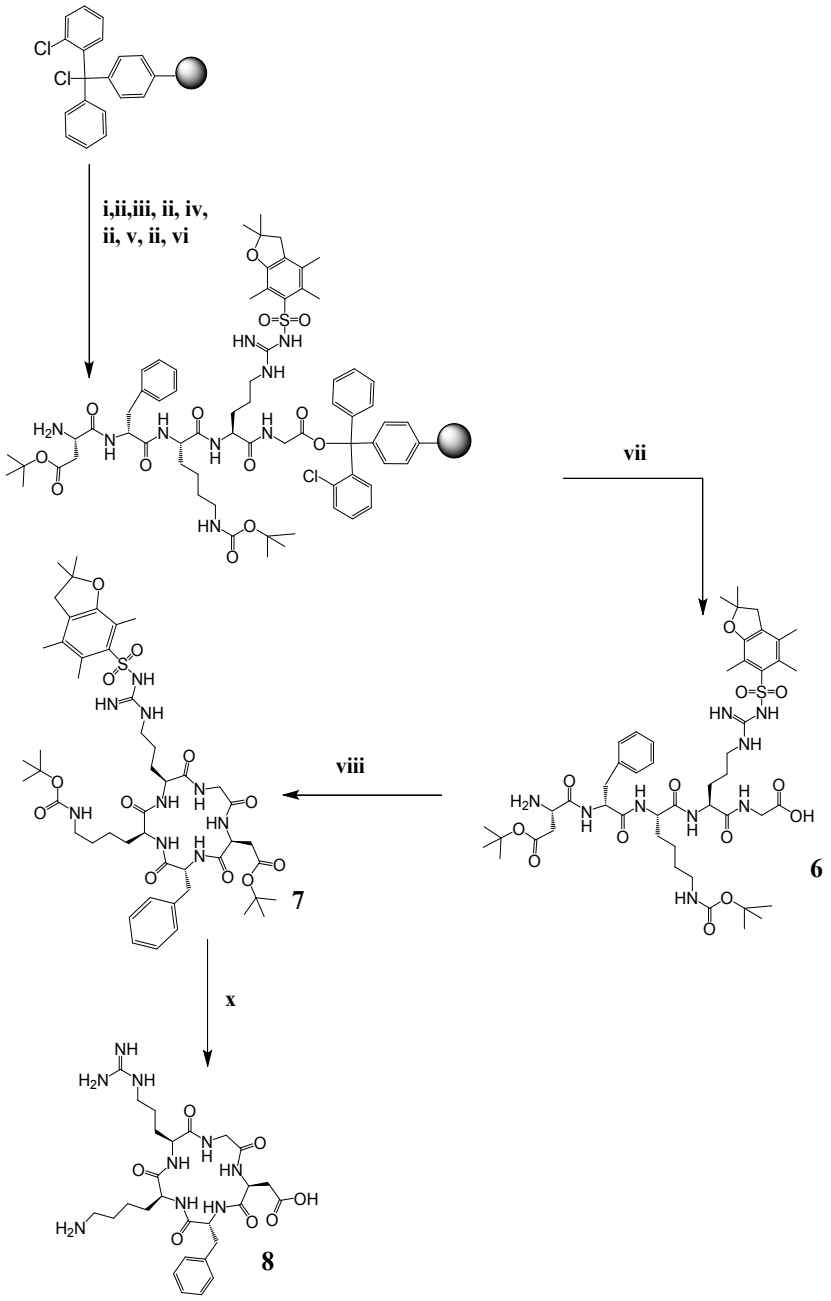


Figure S1. The ESI/MS spectrum of Bombesin[7-13] showing two peaks at *m/z* 809.44 and 405.38 corresponding to$[M]^{2+}$ and $[M]^{+}$.

3. Cyclic deprotected RGDfK peptide

The protected linear peptide RGDfK(Arg(Pbf)-Gly-Asp(OtBu)-D-Phe-Lys(Boc)) was obtained by using solid phase peptide synthesis by Fmoc strategy on the highly acid-labile chlorotrityl polystyrene resin. 84 % resin loading was obtained by treating the resin with a solution of Fmoc-Gly-OH and DIPEA. Each amino acid was coupled with PyBOP and DIPEA in DMF to obtain the linear protected peptide after removing it from the solid support in 85% overall yield and high purity. Cleavage from the resin was achieved by treatment with TFA / DCM (7 mL; 1 : 99 v/v) for 10 × 2 min. Cyclisation of the protected linear peptide was achieved by using PyBOP and DIPEA in DCM, and gave the cyclic protected RGDfK as a white solid in 94% yield. The protected groups of Cyclo(-RGDfK) were removed by dissolving product in a TFA deprotection cocktail (TFA/CH_2Cl_2, 1: 1, 5 mL), and the solution was stirred for 2 h. It gave a resulting product of deprotected Cyclo(-RGDfK). ESI-MS: *m/z* calcd for $C_{27}H_{42}N_9O_7$: 604.31 $[M+H]^+$; found 604.3910.



Scheme S2. Synthesis of deprotected cyclic RGDfK peptide **8**, (i):Fmoc-Gly-OH, DIPEA,CH_2Cl_2 (ii):20%(v/v) piperidine in DMF; (iii):Fmoc-Arg(Pbf)-OH, PyBop, DIPEA,CH_2Cl_2; (iv): Fmoc-Lys(Boc)-OH, PyBop, DIPEA, CH_2Cl_2; (v): Fmoc-D-Phe-OH PyBop, DIPEA,CH_2Cl_2; (vi):Fmoc-Asp(OtBu)-OH, PyBop, DIPEA,CH_2Cl_2; (vii):TFA/ DCM (10 mL; 1 : 99 v/v) for 10×2 min, pyridine/MeOH (10 mL ; 1 : 9 v/v); (viii): PyBOP, DIPEA, 72 h rt; (x):TFA/CH_2Cl_2 (1:1), rt, 2 h.

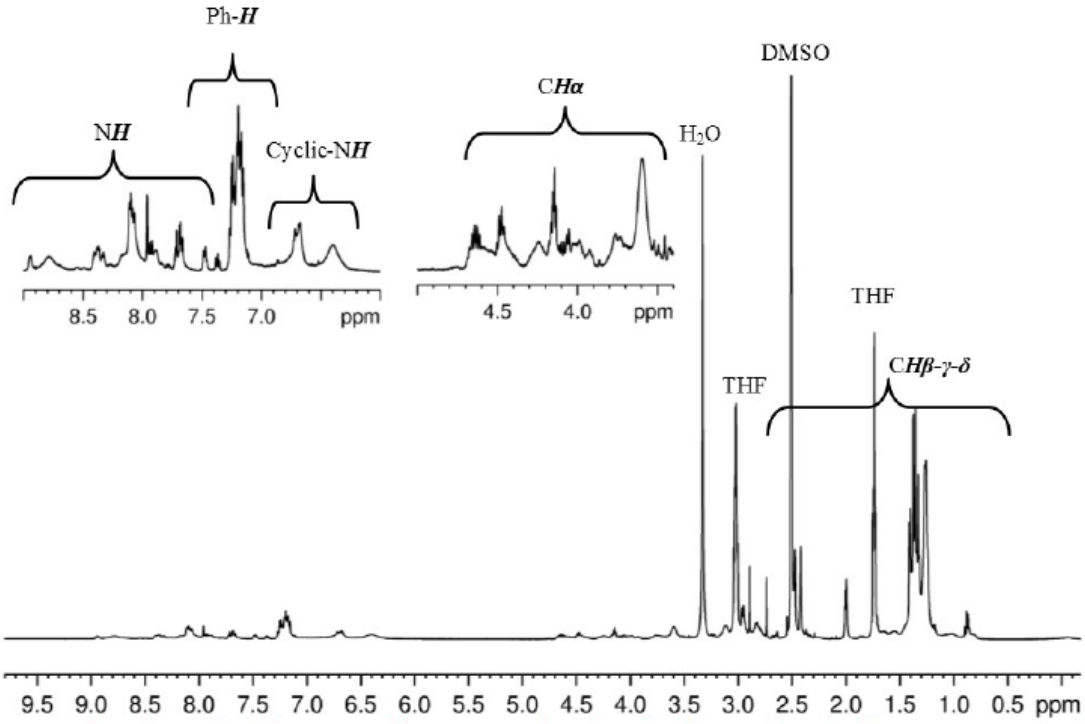


Figure S1 ^{1}H NMR of Cyclo-(RGDfK) (**8**). Inset shows expanded region of relevant proton nuclei in the high and low field of the spectrum.

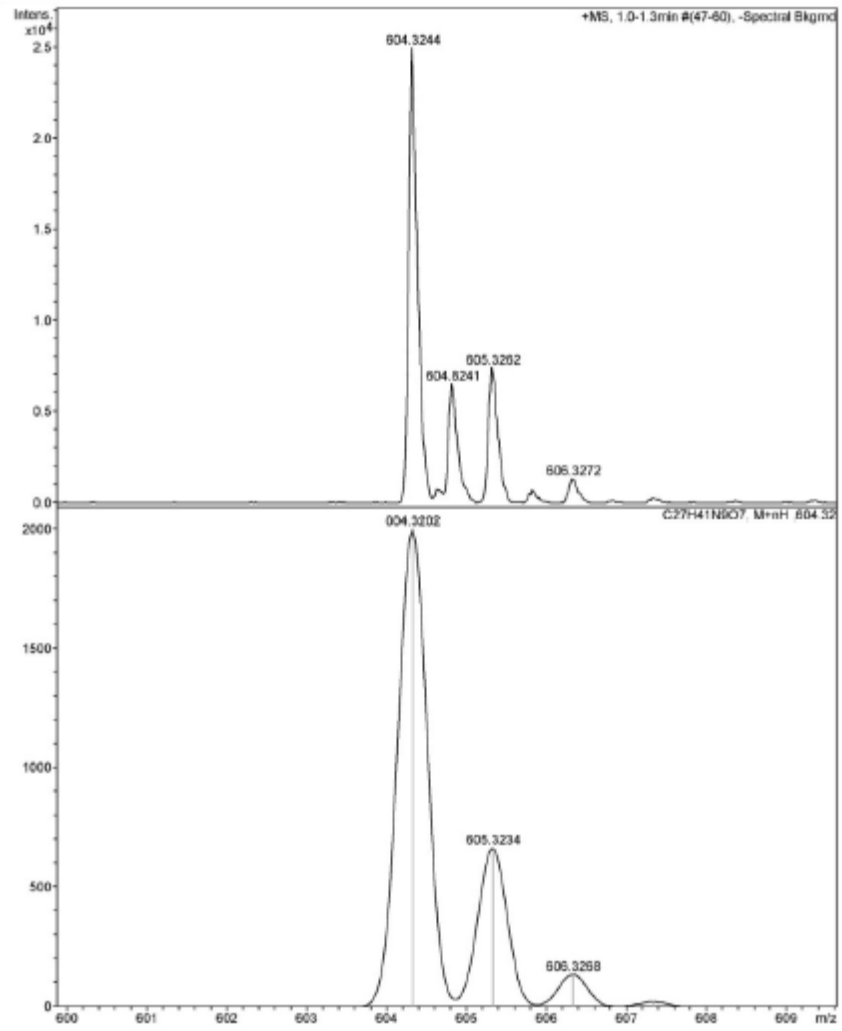


Figure S2 Mass spectrum of Cyclo-(RGDfK), (**8**) Observed (above) and calculated (below) isotopic pattern of (**8**) showing peak at *m/z* 604.32 corresponding to $[M+H]^+$.

1. B. Ballesteros, G. Tobias, L. Shao, et al., *Small*, 2008, **4**, 1501.
2. G. Tobias, L. Shao, C. G. Salzmann, et al., *J Phys Chem B*, 2006, **110**, 22318.