The Synthesis of Gly-(L-Val)-Gly-(L-Val)-Coumarin conjugate

The mixture of compound 1 (200 mg, 1 mmol) and 2 (455 mg, 1 mmol) in 5 ml DMF was stirred in the presence of a catalytic amount of CuSO$_4$·5H$_2$O (25 mg) and ascorbic acid (70 mg) at room temperature overnight. Et$_2$O (30 ml) was added to the mixture, and the precipitate was filtered and washed with Et$_2$O to afford GVGVCou as a pale solid in 97% yield. $^1$H NMR (600 MHz, DMSO-d$_6$): 8.31 (s, 1H), 8.27 (t, $J$ = 5.8, 1H), 8.12 (t, $J$ = 5.8, 1H), 8.04-8.00 (m, 2H), 7.86 (d, $J$ = 8.6, 1H), 7.65 (d, $J$ = 8.6, 1H), 7.17 (d, $J$ = 2.1, 1H), 7.04-7.02 (m, 1H), 5.26 (s, 2H), 4.40 (t, $J$ = 6.8, 2H), 4.19-4.15 (m, 2H), 3.83-3.73 (m, 4H), 3.63 (s, 3H), 2.16 (t, $J$ = 7.2, 2H), 2.07-2.01 (m, 4H), 0.87-0.84 (m, 12H). HR-MS(ESI) Calcd: 678.2858 for [M+Na$^+$]; Found: 678.2858 for [M+Na$^+$].
The Synthesis of Gly-(L-Val)-Gly-(L-Val)-alkyl conjugate

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\begin{align*}
\text{Scheme S2} & \quad \text{The Synthesis of Gly-(L-Val)-Gly-(L-Val)-alkyl conjugate.} \\
\text{3} & \quad \text{ascorbic acid} \\
\text{CuSO}_4 & \quad \text{DMF} \\
\text{GVGV-alkyl} & \\
\end{align*}
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The mixture of compound 3 (11 mg, 0.1 mmol) and 2 (45.5 mg, 0.1 mmol) in 5 ml DMF was stirred in the presence of a catalytic amount of CuSO\(_4\)-5H\(_2\)O (1.7 mg) and ascorbic acid (2.5 mg) at room temperature overnight. Et\(_2\)O (30 ml) was added to the mixture, and the precipitate was filtered and washed with Et\(_2\)O to afford GVGV-alkyl as a pale solid in 99% yield. \(\text{\textsuperscript{1}H} \text{ NMR (600 MHz, DMSO-d}_6\): 7.65 (d,} J = 3.9, 1H), 7.48 (m, 2H), 7.37 (s, 1H), 7.07 (m, 1H), 4.53 (m, 1H), 4.48 (m, 1H), 4.43 (m, 2H), 4.04-4.22 (m, 4H), 3.70 (s, 3H), 2.73-2.71 (t,} J = 7.5, J = 3.9, 2H), 2.24 (m, 6H), 1.38 (m, 2H), 1.35 (m, 6H), 0.89-0.98 (m, 15H).

Gel formation test in Ethanol of GVGV-alkyl

To check if the triazole affects the gel formation of GVGV-Cou in ethanol, the GVGV-alkyl has been synthesized (Scheme S2). It was found that GVGV-alkyl could not form a gel under the same condition where GVGV-Cou CT gel is formed. Then it can be suggested that triazole serves only as a linker during the formation of GVGV-Cou CT gel.
The $^1$H NMR spectrum of GVGV-Cou (600 MHz, DMSO-d$_6$).
Fig. S2 The $^1$H NMR spectrum of GVGV-alkyl (600MHz, CDCl$_3$-d$_6$).
Fig. S3 SEM images of co-xerogels.
Fig. S4 XRD spectra of GVGV-Cou xerogel and co-xerogels.

References