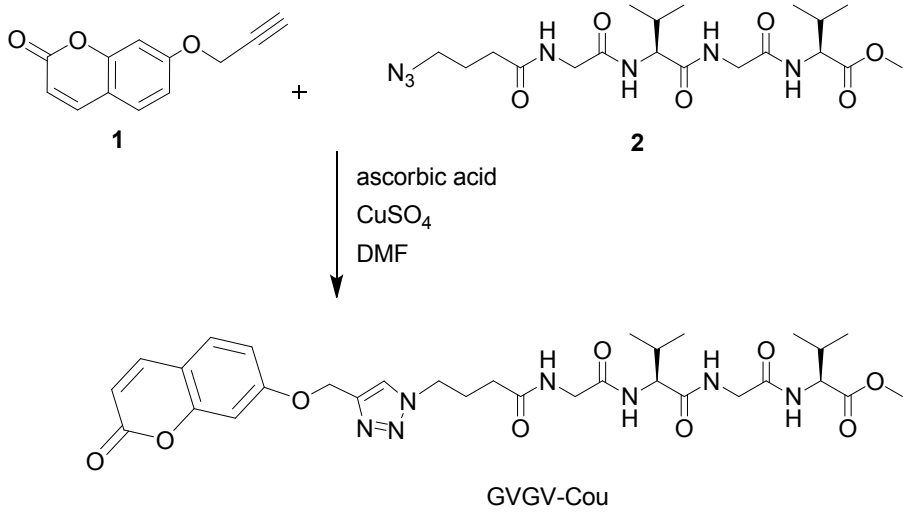
Supporting Information

Tetrapeptide-coumarin conjugate 3D networks based on hydrogen-bonded charge transfer complex: gel formation and dye release

Zongxia Guo, Ruiying Gong, Yi Jiang and Xiaobo Wan

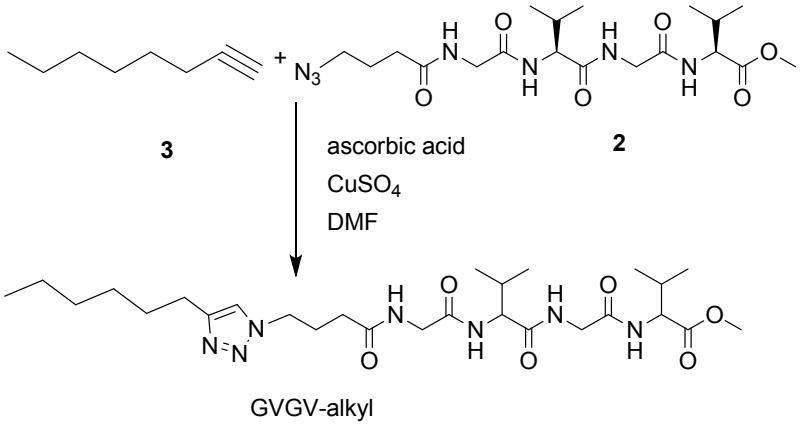
The Synthesis of Gly-(L-Val)-Gly-(L-Val)-Coumarin conjugate



Scheme S1 The Synthesis of Gly-(L-Val)-Gly-(L-Val)-Coumarin conjugate.

The mixture of compound **1**[1] (200 mg, 1 mmol) and **2**[2] (455 mg, 1 mmol) in 5ml DMF was stirred in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ (25 mg) and ascorbic acid (70mg) at room temperature overnight. Et_2O (30 ml) was added to the mixture, and the precipitate was filtered and washed with Et_2O to afford **GVGV-Cou** 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



Scheme S2 The Synthesis of Gly-(L-Val)-Gly-(L-Val)-alkyl conjugate.

The mixture of compound **3** (11 mg, 0.1 mmol) and **2** (45.5 mg, 0.1 mmol) in 5ml DMF was stirred in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ (1.7 mg) and ascorbic acid (2.5 mg) at room temperature overnight. Et_2O (30 ml) was added to the mixture, and the precipitate was filtered and washed with Et_2O to afford **GVGV-alkyl** as a pale solid in 99% yield. ^{1}H 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.

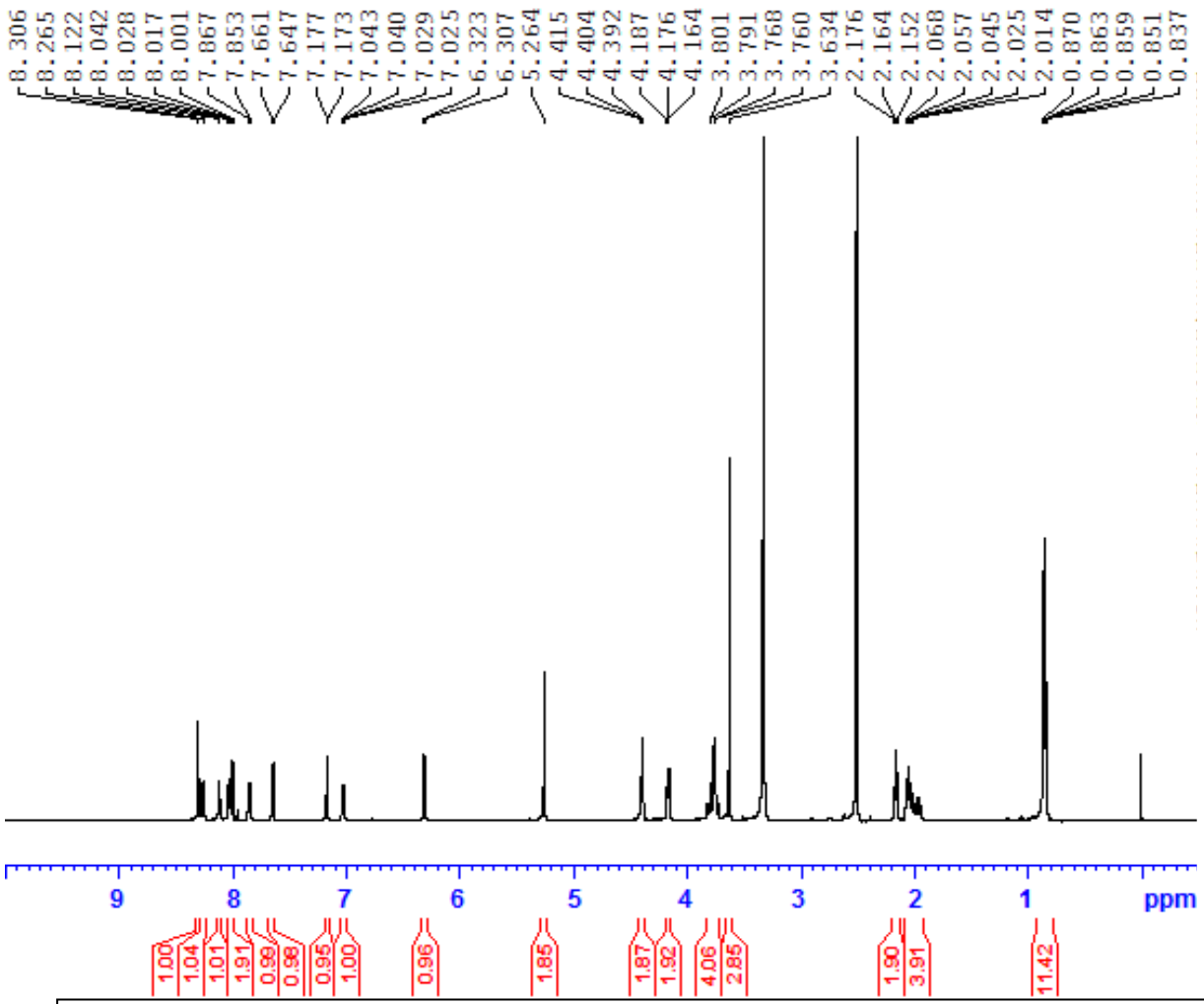


Fig. S1 The ^{1}H NMR spectrum of **GVGV-Cou** (600MHz, DMSO-d*6*).

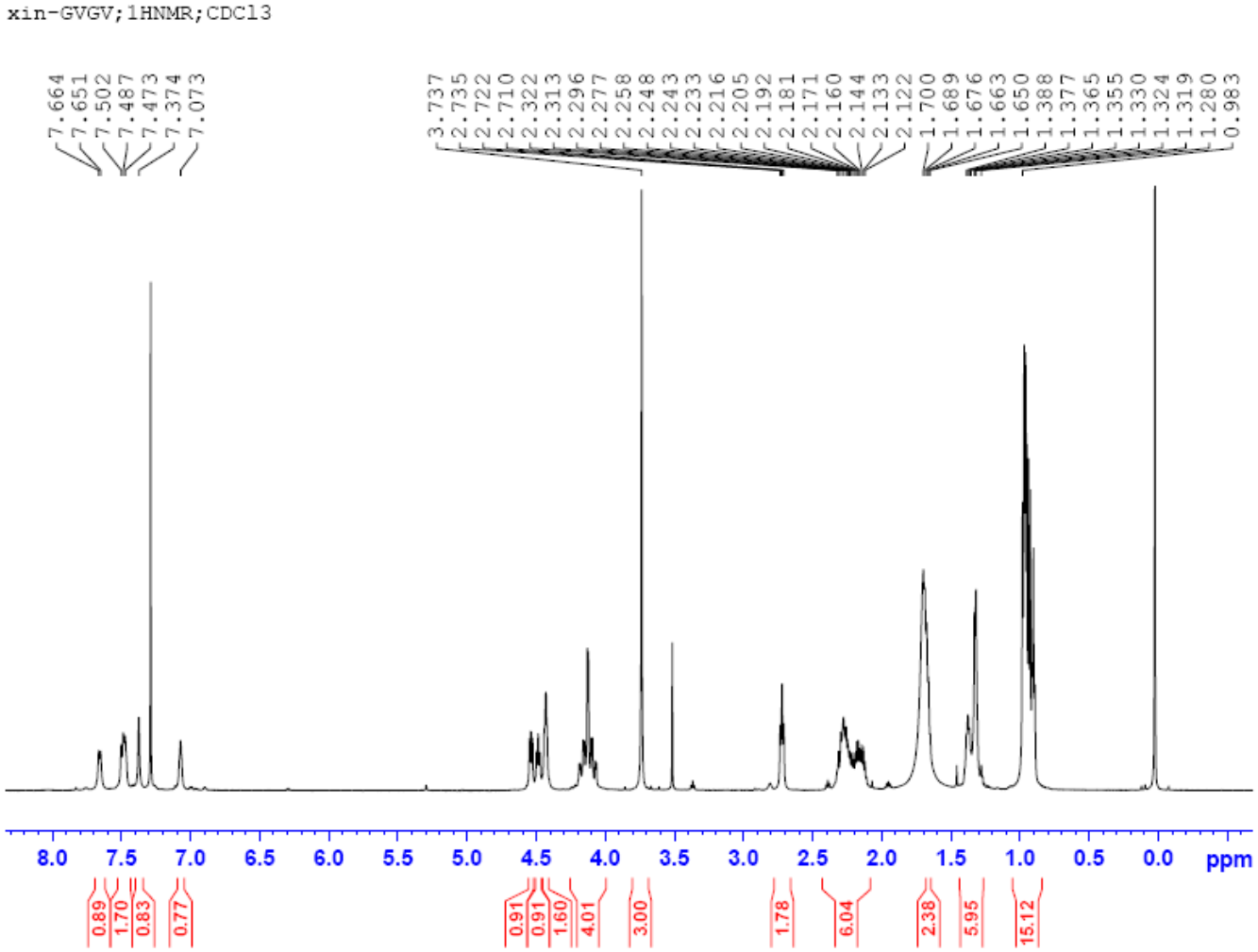


Fig. S2 The ^{1}H NMR spectrum of **GVGV-alkyl** (600MHz, $CHCl_3$-d*6*).

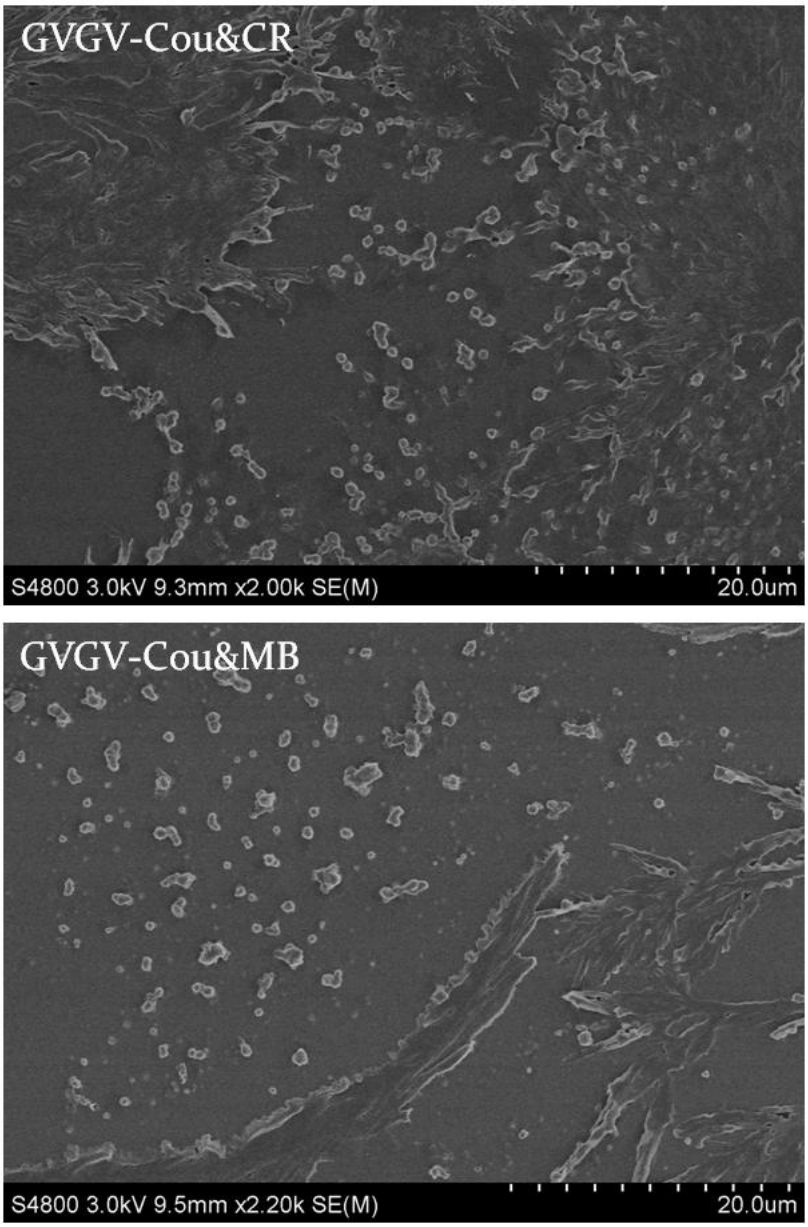


Fig. S3 SEM images of co-xerogels.

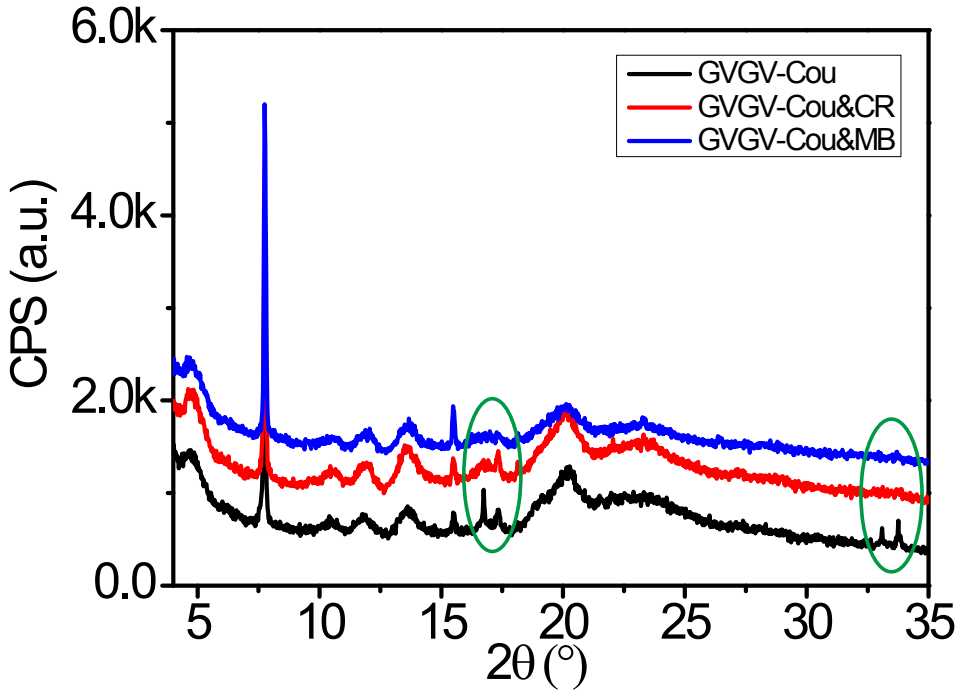


Fig. S4 XRD spectra of GVGV-Cou xerogel and co-xerogels.

References

(1) Y.Lin, J.Yuan, M.Hu, J.Cheng, J.Yin, S.Jin, S. H. Liu,*Organometallics*2009, **28**, 6402-6409.

(2) R. Gong, Y. Song, Z. Guo, M. Li, Y. Jiang and X. Wan, *Supramol. Chem.*, 2013, **25**, 269-275.