Supplementary Information

Modular co-assembly of peptides and polyoxometalates into underwater adhesives with photoluminescence and adjustable adhesion

Xinyan Wang, Yiwen Li, Junlian Nie, Guang Wen and Wen Li*

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University. Qianjin Avenue 2699, Changchun, 130012, China.
E-mail: wenli@jlu.edu.cn

1, Preparation of the single peptide/POM composite.

***Pep1/SiW$_9$V$_3$*:** Pep1 (112.64 mg) was dissolved in 0.35 ml of deionized water to form an aqueous solution (pH ~ 6.0). Then SiW_9V_3 solution (316 mg of SiW_9V_3 dissolved in 0.25 ml of deionized water), was mixed with the peptide solution at 25 °C. The charge ratio of SiW_9V_3 to Pep1 was 4:3, and the final pH value of the mixed solution was controlled at about 6.0. The resulting turbid solution with orange-red appearance was heated to 65 °C with ultrasonication, followed by cooling down to 25 °C for 5 min, giving rise to the formation of an orange-red stiff solid. Elemental analysis (EA) revealed that the lyophilized Pep1/SiW_9V_3 solid powder possessed 17.17% C, 5.24% N, and 3.02% H. Thermogravimetric analysis (TGA) showed a mass loss of 4.85% from 25 to 183.2℃ arising from crystal water. Combining EA and TGA, Pep1/SiW_9V_3 should correspond to a tentative formula: $[H_2(C_{19}H_{29}N_5O_3)]_{2.7\sim2.8}K_{0.6\sim1.4}[SiW_9V_3O_{40}]\cdot8\sim11(H_2O)$.

***Pep2/SiW$_9$V$_3$*:** Pep2 (102.11 mg) was dissolved in 0.35 ml of deionized water to form an aqueous solution (pH ~ 6.0). Then SiW_9V_3 solution (316 mg of SiW_9V_3 dissolved in 0.25 ml of deionized water), was mixed with the peptide solution at 25 °C. The charge ratio of SiW_9V_3 to Pep2 was 4:3, and the final pH value of the mixed solution was controlled at about 6.0. The resulting turbid solution with orange-red appearance was heated to 65 °C with ultrasonication, followed by cooling down to 25 °C for 5 min, giving rise to the formation of a fluid coacervate with orange-red appearance. Elemental analysis (EA) revealed that the lyophilized Pep2/SiW_9V_3 coacervate powder possessed 13.26% C, 6.58% N, and 2.82% H. Thermogravimetric analysis (TGA) showed a mass loss of 5.00% from 25 to 179.1℃ arising from crystal water. Combining EA and TGA, Pep2/SiW_9V_3 should correspond to a tentative formula: $[H_2(C_{14}H_{26}N_6O_4)]_{2.8}K_{0.4\sim1.4}[SiW_9V_3O_{40}]\cdot9\sim10(H_2O)$.

2, Characteristic.

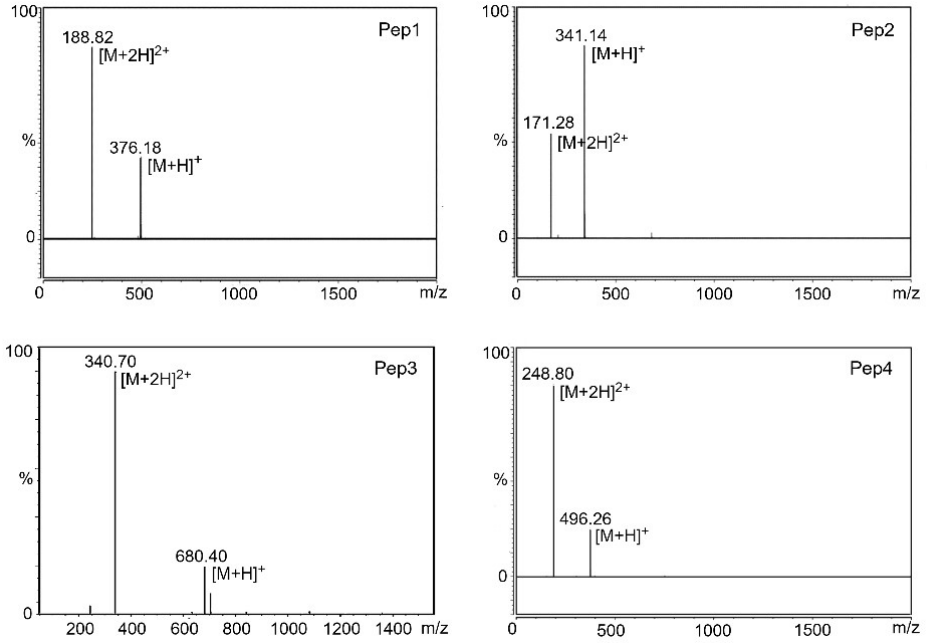

Fig. S1 ESI-MS spectra of the short peptides.

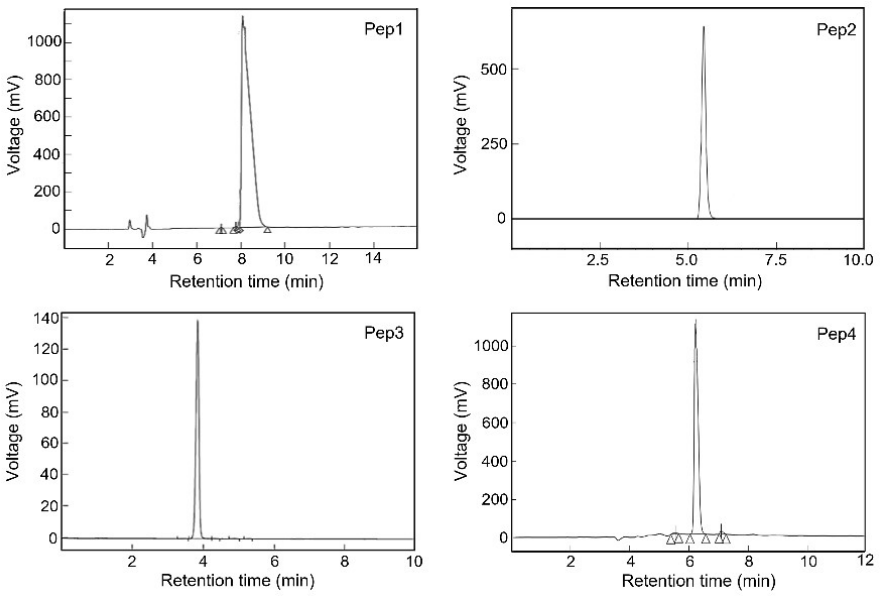

Fig. S2 HPLC curves of the short peptides.

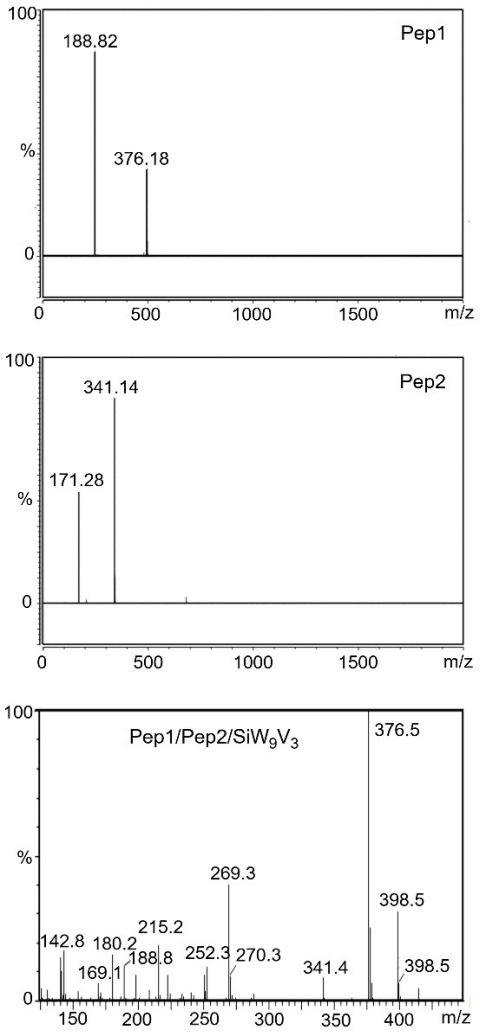

Fig. S3 ESI-MS spectra of Pep1, Pep2 and Pep1/Pep2/SiW_9V_3 adhesive.

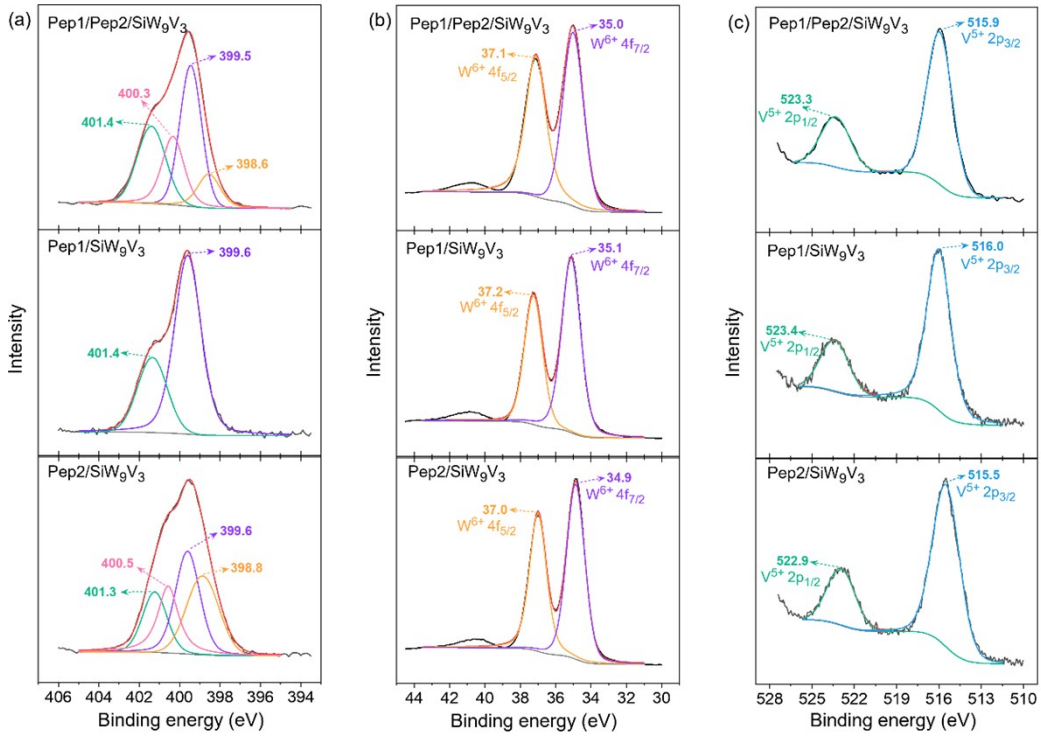

Fig. S4 XPS spectra of Pep1/Pep2/SiW_9V_3, Pep1/SiW_9V_3 and Pep2/SiW_9V_3: (a) N 1s level, (b) W 4f level, and (c) V 2p level.

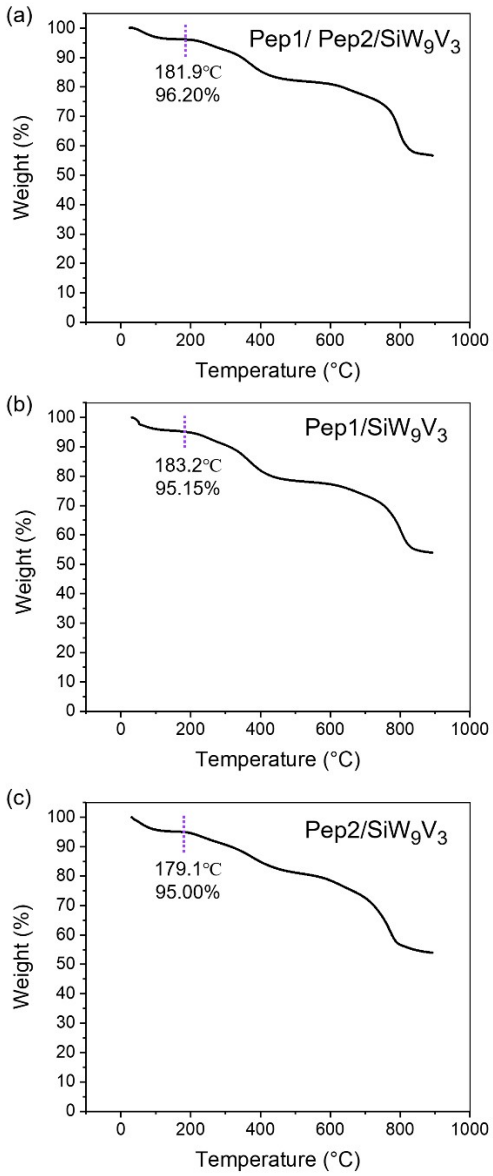

Fig. S5 TGA curves of the lyophilized Pep1/Pep2/SiW_9V_3 adhesive (a), Pep1/SiW_9V_3 solid (b) and Pep2/SiW_9V_3 coacervate (c).

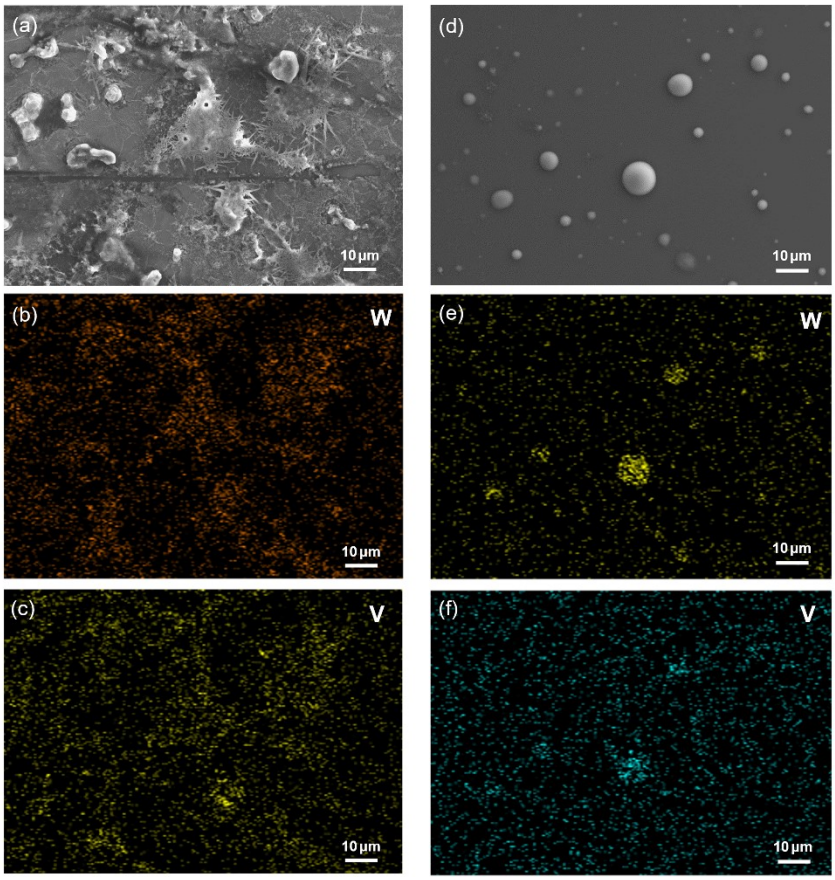

Fig. S6 FE-SEM (a, d) and EDS (b, e for tungsten element, and c, f for vanadium element) images of the lyophilized Pep1/SiW_9V_3 solid sample (a-c) and the lyophilized Pep2/SiW_9V_3 coacervate sample (d-f).

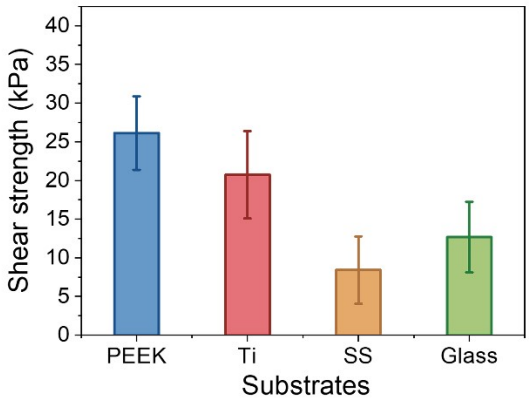

Fig. S7 The average shear adhesion strengths of Pep1/Pep2/SiW_9V_3 adhesive on various substrates at 37 °C.

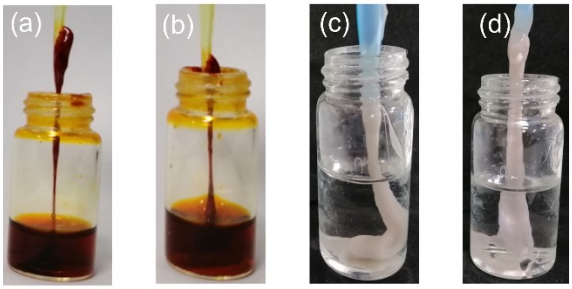

Fig. S8 Photographs of adhesives formed by different dual peptides and POMs: (a) Pep1/Pep3/SiW_9V_3; (b) Pep1/Pep4/SiW_9V_3; (c) Pep1/Pep2/PW_9 and (d) Pep1/Pep2/$EuPW_{11}$.

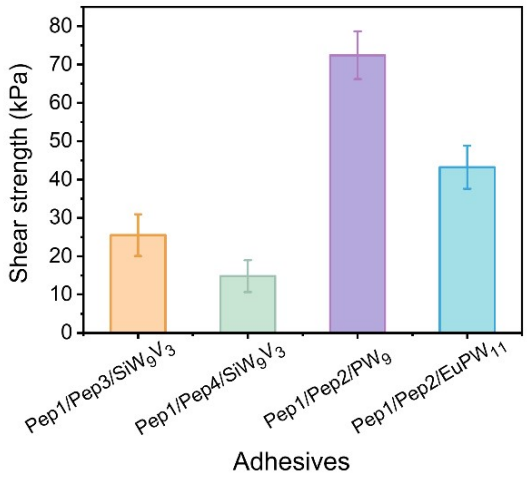

Fig. S9 Average shear adhesion strengths of the different dual peptides/POM adhesive against Ti substrates.