## **Supplementary Information**

## Dual-cross-linked dynamic hydrogels with cucurbit[8]uril and imine linkages

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Fig. S1 <sup>1</sup>H NMR spectrum of Phe-EPL in  $D_2O$ . The substitution degree of Phe-EPL is 21.5% based on the integration corresponding peaks.



Fig. S2 FT-IR spectra of EPL, Phe and Phe-EPL.



Fig. S3 <sup>1</sup>H NMR spectrum of DF-PEG in CDCl<sub>3</sub>.



Fig. S4 FT-IR spectra of DF-PEG and PEG. Compare with the spectrum of PEG, DF-PEG has a characteristic peak at 1715 cm<sup>-1</sup>, which can be attributed to the stretching vibtation of C=O bond in the aldehyde and carbonyl groups.



Fig. S5 ITC titration plot of CB[8] titrated with Phe-EPL. Phe-EPL was used with the concentration of Phe of 2 mM, and the concentration of CB[8] is 0.1 mM. The experiment was performed at 25 °C in 10 mM PBS (pH = 7.0). The titration plot was

fitted with the sequential binding sites model.



Fig. S6 a) Oscillatory amplitude sweeps at 1 Hz and (b) frequency sweeps with strain of 0.02 of the DF-PEG cross-linked Phe-EPL hydrogel with varied Phe-EPL concentration. The solid marks represent storage modulus (G') and the hollow marks represent loss modulus (G'').



Fig. S7 Oscillatory amplitude sweeps of the single/dual-cross-linked hydrogels at 1 Hz.



Fig. S8 a) Oscillatory amplitude sweeps at 1 Hz and (b) frequency sweeps with strain of 0.02 of the dual-cross-linked Phe-EPL hydrogel with varied Phe-EPL concentration. The solid marks represent storage modulus (G') and the hollow marks represent loss modulus (G'').



Fig. S9 a) Oscillatory amplitude sweeps at 1 Hz and (b) frequency sweeps with strain of 0.02 of the dual-cross-linked Phe-EPL hydrogel with fixed CB[8] to phenylalanine molar ratio (0.5) and varied aldehyde to amine molar ratio of DF-PEG. The concentration of Phe-EPL is fixed at 5 wt%. The solid marks represent storage modulus (G') and the hollow marks represent loss modulus (G'').



Dual-cross-linked hydrogels



DF-PEG cross-linked hydrogel



CB[8] cross-linked network

Fig. S10 SEM images of a) the dual-cross-linked hydrogel with aldehyde to amine molar ratio 0.10, b) the dual-cross-linked hydrogel with aldehyde to amine molar ratio 0.13, c) the dual-cross-linked hydrogel with aldehyde to amine molar ratio 0.20, d) DF-PEG cross-linked Phe-EPL hydrogel and e) CB[8] cross-linked Phe-EPL network.