Supporting information

Self-recovering dual cross-linked hydrogels based on bioorthogonal click chemistry and ionic interactions

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Fig. S1 Oscillatory strain sweep measurements of different dual cross-linked hydrogel compositions (normalization to a strain of 0.1%).

Fig. S2 Storage moduli (G’ value) of CC (100c), PC (100p) and DC (xyp/yya) hydrogels after two times of mechanical rupture. (n = 3; * p<0.033, ** p<0.002, ***p<0.001, one-way Anova)
**Fig. S3** Swelling ratios of pure chemical, physical and DC hydrogels at 1 h, 3 h, 7 h and 24 h. (n = 3; * p<0.033, ** p<0.002, one-way Anova)

**Fig. S4** Dry mass of PC and DC hydrogels at 1 h and 24 h.

**Fig.S5** Cryo-SEM images of star-PEG-DBCO/star-PEG-N₃ (20 mg/mL, left) and star-PEG-AA/Ca²⁺ (30 mg/mL, right) cross-linked hydrogel systems. The scale bars represent 10 μm.
Fig. S6 Mesh size distribution of hydrogels.
**Fig. S7** Cryo-SEM images of the 100% physically cross-linked hydrogels at different polymer concentration. The scale bars represent 10 μm.

**Fig. S8** Cryo-SEM images of the 100% physically cross-linked hydrogel systems at different Ca\(^{2+}\) concentration (1 eq polymer combined with 10 eq, 15 eq, 20 eq, 30 eq or 40 eq Ca\(^{2+}\)). The scale bars represent 10 μm.
Fig. S9 Confocal microscopy images of cell morphology after 5-day culture inside different hydrogel systems.

Fig. S10 MALDI-TOF spectra of star-PEG-alendronic acid.
Fig. S11 $^{31}$P NMR spectra of star-PEG-alendronic acid.

Figure S12. MALDI-TOF spectra of star-PEG-DBCO.

Fig. S13 $^1$H NMR spectra of star-PEG-DBCO.
Fig. S14 Mass spectrometry spectra of azido-RGDS.
Fig. S15 MALDI-TOF spectra of (A) star-PEG-N₃, (B) star-PEG-RGDS-N₃ and (C) star-PEG-CF-N₃.
**Fig. S16** $^1$H NMR spectra of (A) star-PEG-N$_3$, (B) star-PEG-RGDS-N$_3$ and (C) star-PEG-CF-N$_3$. 