Supplemental Material: Annu. Rev. Mater. Res. 2015. 45:277–310 doi: 10.1146/annurev-matsci-070214-020815 Citrate-Based Biomaterials and Their Applications in Regenerative Engineering Tran, Yang, and Ameer

A)
$$HO \longrightarrow OH$$

$$120^{\circ}C \longrightarrow N_2$$

$$HO \longrightarrow OH$$

$$HO \longrightarrow OH$$

$$120^{\circ}C \longrightarrow N_2$$

$$HO \longrightarrow OH$$

Supplemental Figure 1. Citrate-based biomaterial combinational crosslinking mechanisms. A) Poly(octamethylene citrate) – Click (POC-Click) materials can be crosslinked using a thermal synchronous binary (TSB) crosslinking mechanism: thermal click reaction between azide and alkyne groups and esterification between –COOH and –OH groups. B) Citrate-based biomaterials synthesized with vinyl containing monomers offer a dual crosslinking mechanism (DCM): free radical polymerization between unsaturated functional groups and/or thermal esterification between –COOH and –OH groups.

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Supplemental Figure 2. Representative synthesis schematic of crosslinked urethane-doped polyesters (CUPE). A) First, citric acid is reacted with 1,8-octanediol to create a poly(octamethylene citrate) (POC) pre-polymer. B) Next, hexamethylene diisocyanate (HDI) is doped into the pre-polymer network and acts as a chain extender for pre-POC. The resulting material is a soft and elastic polyester network containing degradable ester bonds with urethane linkages. Adapted from Figure 1 of reference (29) with permission.

HOCCH₂CCH₂COOH
OH
HO
$$\downarrow$$
OH
 \downarrow

Supplemental Figure 3. Schematic of the synthesis of diazenium diolated CBBs for the prolonged release of nitric oxide (NO). NO release profile can be controlled with the choice of diol, with hydrophobic diols resulting in slower NO release.