## **Electronic Supplementary Information**

## Thermoresponsive hybrid double-crosslinked networks using magnetic iron oxide nanoparticles as crossing points

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## Synthesis of [*N*-methyl(dimethoxyphosphonyl)-(3-furanyl)]prop-2-yn-1-amine (2)

**2** was synthesised in 1 step as follow (Scheme S1-B). *N*-(3-furanylmethylene)prop-2-yn-1amine **1** (1.372 g; 10 mmoles; 1 eq) and dimethyl phosphite (1.11 g; 10 mmoles; 1 eq) were placed in a 25 mL round-bottom flask equipped with a magnetic stirrer and a condenser. The reaction mixture was heated for 8 h at 60 °C. The  $\alpha$ -aminophosphonate was purified by silica gel column chromatography eluted with acetonitrile (150 mL), then a gradient of ethyl acetate:acetonitrile, 80:20 (250 mL), and finally ethyl acetate (400 mL) to give the pure product as a yellow oil (55% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) (Fig. S2),  $\delta$  (ppm): 7.52 (m, 1H, O-C*H*=C); 7.43 (m, 1H, O-C*H*=CH); 6.54 (t, *J* = 3.42 Hz, 1H, O-CH=C*H*); 4.37 (d, *J* = 17.08 Hz, C*H*-P); 3.77 (m, 6H, C*H*<sub>3</sub>); 3.57-3.19 (m, 2H, C*H*<sub>2</sub>); 2.26 (t, *J* = 3.93 Hz, C=C*H*); 1.89 (s, N*H*). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 143.45; 141.85; 118.65; 110.25 (furan ring); 80.67 (*C*=CH); 72.50 (C=CH); 53.50 (CHP); 49.55 (d, *J* = 8.10 Hz, CH<sub>3</sub>); 35.70 (N-CH<sub>2</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>) (Fig. S3),  $\delta$  (ppm): 25.47.

## **Figures and Schemes**



Scheme S1. Synthesis of [*N*-methyl(dimethoxyphosphonyl)-(3-furanyl)]prop-2-yn-1-amine(2) in two steps.



Figure S1. <sup>1</sup>H NMR spectrum of *N*-(3-furanylmethylene)prop-2-yn-1-amine (1) in CDCl<sub>3</sub>.



**Figure S2.** <sup>1</sup>H NMR spectrum of [*N*-methyl(dimethoxyphosphonyl)-(3-furanyl)]prop-2-yn-1amine (**2**) in CDCl<sub>3</sub> (\*solvent residual peaks).



**Figure S3.** <sup>31</sup>P NMR spectrum of [*N*-methyl(dimethoxyphosphonyl)-(3-furanyl)]prop-2-yn-1-amine (**2**) in CDCl<sub>3</sub>.



**Figure S4** MALDI-TOF mass spectra of diazido-PEO (blue) and difuran-functionalized dimethylphosphonate PEO (red). The inset figure is an expanded region showing the constitutive unit of PEO; matrix: DCTB, NaTFA.



Scheme S2. Dealkylation of difuran-functionalized dimethylphosphonate-terminated PEO.



**Figure S5.** <sup>1</sup>H NMR (left) and <sup>31</sup>P NMR (right) spectra of difuran-functionalized dimethylphosphonate-terminated PEO (blue) and difuran-functionalized diphosphonic acid-terminated PEO (red).



Figure S6. TEM image of iron oxide nanoparticles.



**Figure S7.** DSC scanning of oxanorbornene-functionalized dimethylphosphonate-terminated PEO at 36 % w/w in DMSO.



**Figure S8.** Frequency dependence of the storage **G**' and loss **G**'' moduli of 3D doublecrosslinked network at 120 °C.