

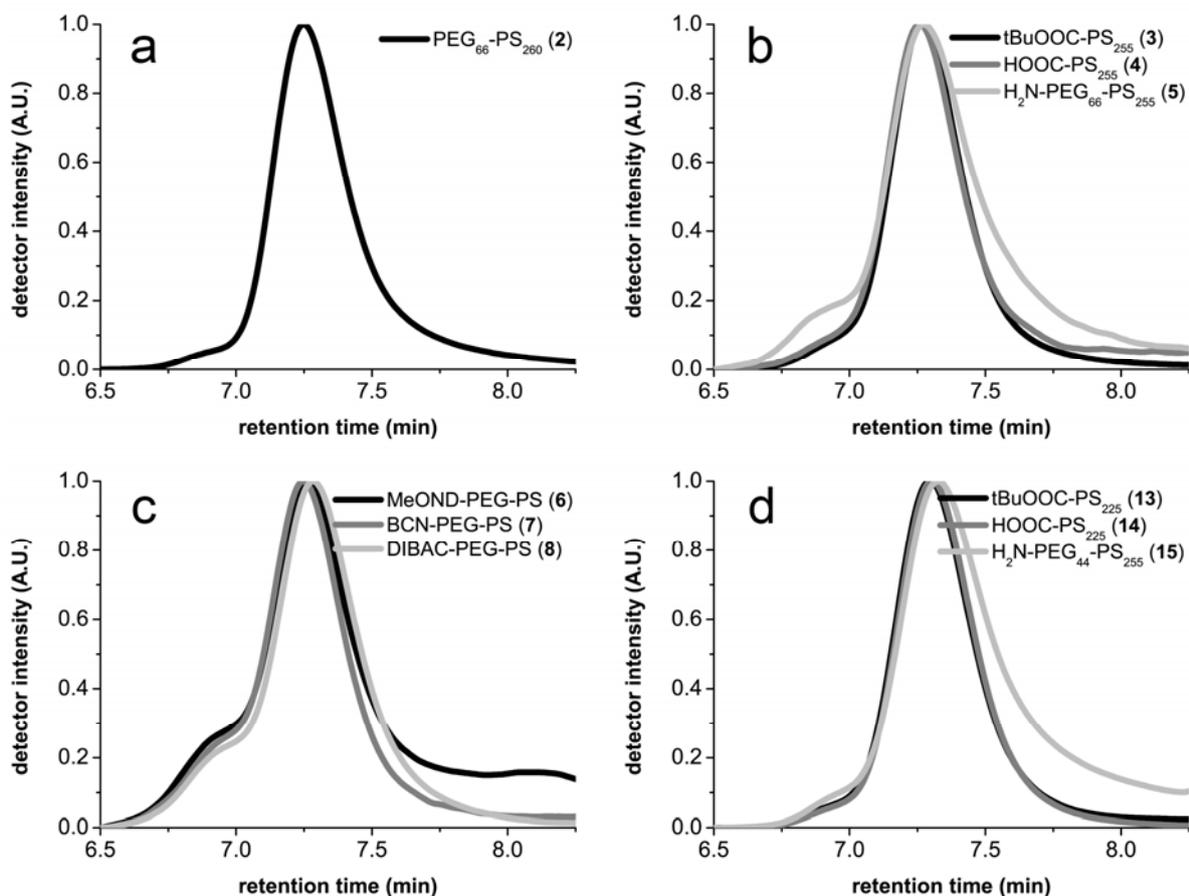
## Supporting Information

### Copper-free click chemistry on polymersomes: pre vs. post self-assembly functionalisation†

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#### I GPC chromatographs of polymers

The GPC chromatographs of the synthesised polymers are depicted in Figure S1.

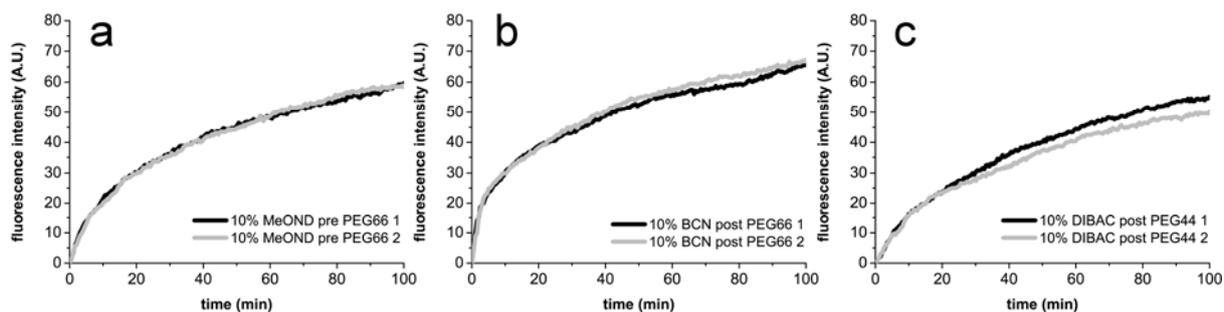


**Figure S1** GPC chromatographs of the polymers a) PEG<sub>44</sub>-*b*-PS<sub>260</sub> (2); b) tBuOOC-PS<sub>255</sub> (3), HOOC-PS<sub>255</sub> (4) and H<sub>2</sub>N-PEG<sub>66</sub>-*b*-PS<sub>255</sub> (5); c) MeOND-PEG<sub>66</sub>-*b*-PS<sub>255</sub> (6) and BCN-PEG<sub>66</sub>-*b*-PS<sub>255</sub> (7); d) tBuOOC-PS<sub>225</sub> (13), HOOC-PS<sub>225</sub> (14) and H<sub>2</sub>N-PEG<sub>44</sub>-*b*-PS<sub>225</sub>.

#### II Deviation in fluorogenic assays

All the SPAAC reactions between N<sub>3</sub>-coumarin-PEG<sub>44</sub> and the functional polymersomes were performed in *duplo* or *triplo*. The ultimate data were derived by taking the average of the individual

measurements. To demonstrate the reproducibility of these fluorogenic assays, three different *duplo* experiments are depicted in Figure S2; a maximum differentiation of 10 % was observed.



**Figure S2** Increase in fluorescence ( $\lambda = 418$  nm) during the SPAAC reaction between  $N_3$ -coumarin-PEG<sub>44</sub> and the polymersomes decorated with a) 10 wt% pre-functionalised MeOND-PEG<sub>66</sub>-PS, b) 10 wt% NH<sub>2</sub>-PEG<sub>66</sub>-PS post-functionalised with BCN-OSu or c) 10wt% NH<sub>2</sub>-PEG<sub>44</sub>-PS post-functionalised with DIBAC-OSu was measured in duplo.