

Supplementary Information for:

Surface modification of polydopamine coated particles *via* glycopolymer brush synthesis for protein binding and FLIM testing

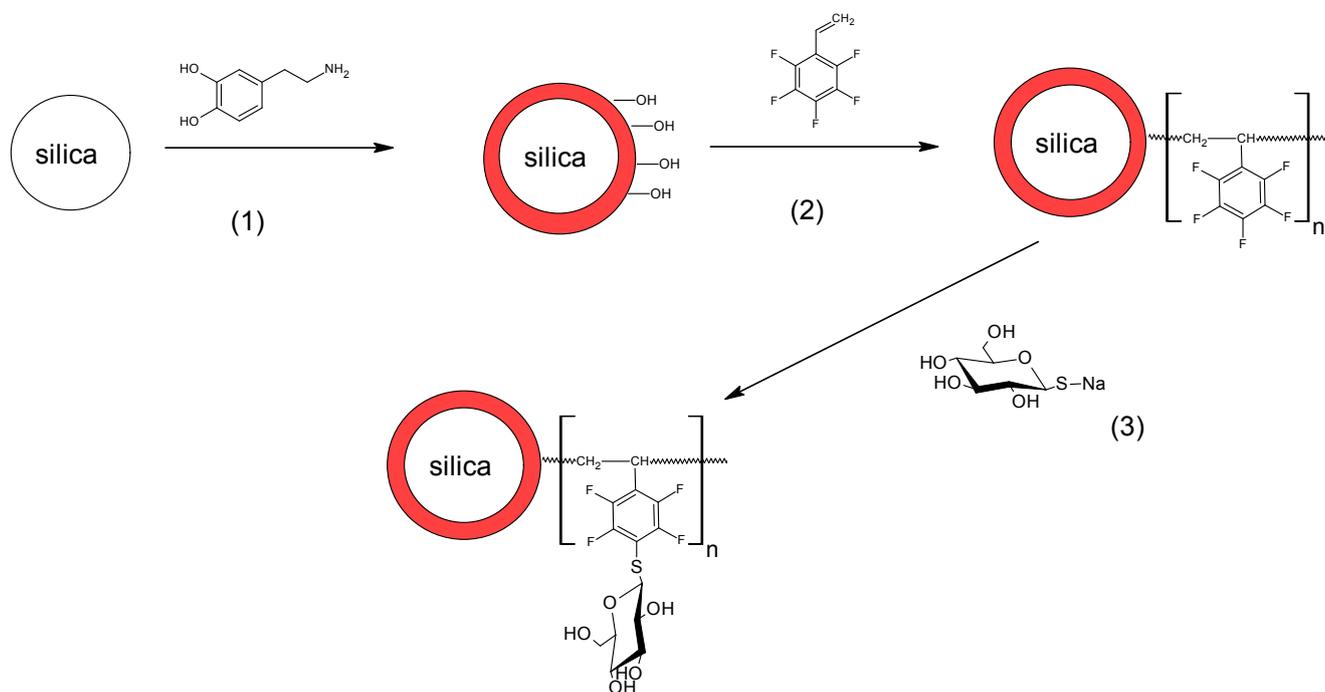
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Scheme S1 Detailed reaction procedures for the production of glycopolymer brushes on PDA@SiO₂ particles using a 'grafting from' approach.



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The scheme roughly depicts the (1) synthesis of polydopamine on silica templates using a TRIS buffered solution followed by the (2) 'grafting from' of PFS in fluorobenzene using a carbonyl azide RAFT agent and DBTDL to bind to catechol and amine moieties. The final step (3) involves the post-modification of PPFS chains with thioglucose sodium salt *via* thiol-*para*-fluorine 'click' chemistry in 20 DMF using triethylamine as a catalyst.

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Figure S1 NMR spectrum showing successful synthesis of BDMAATTC, solvent is CDCl₃.

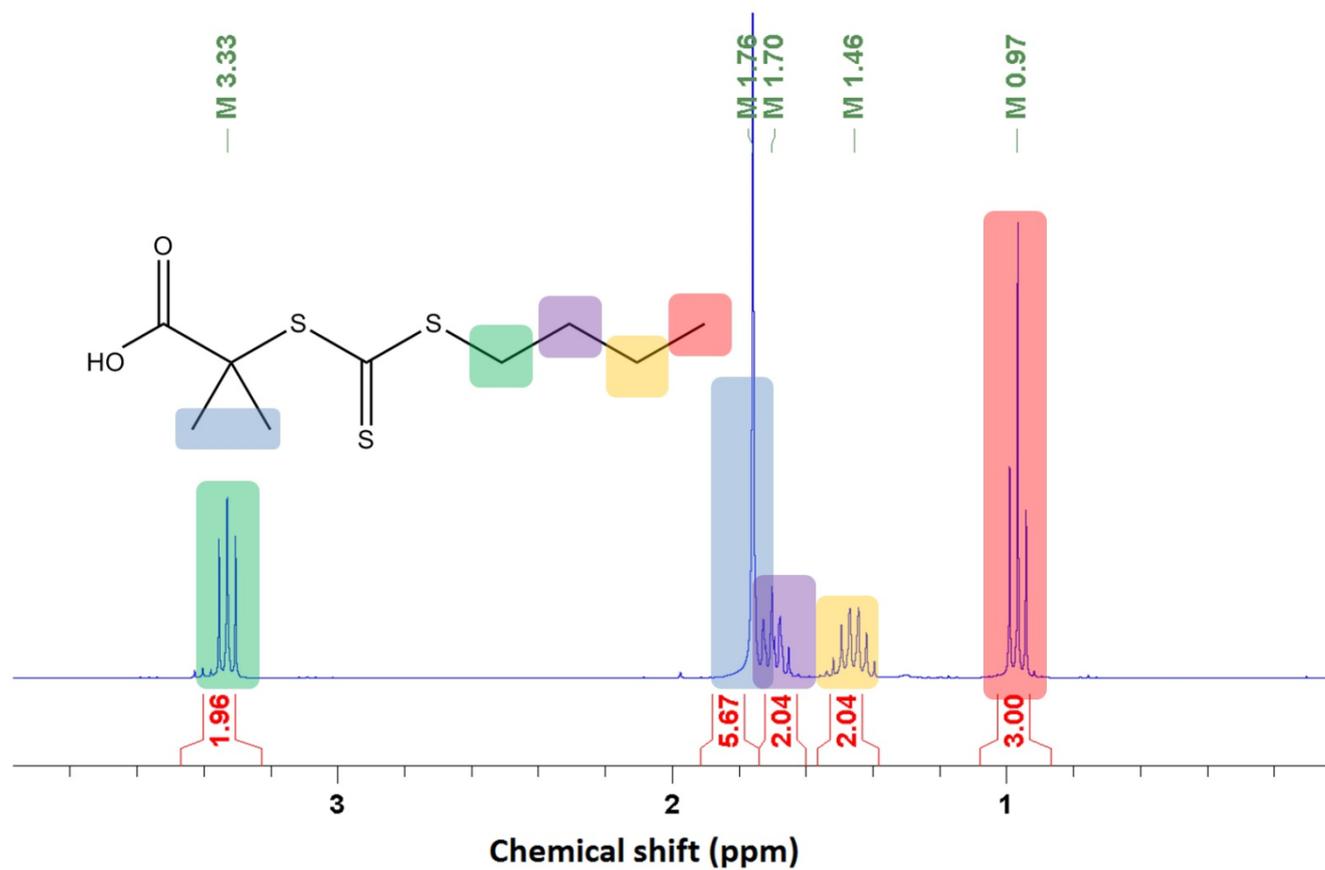
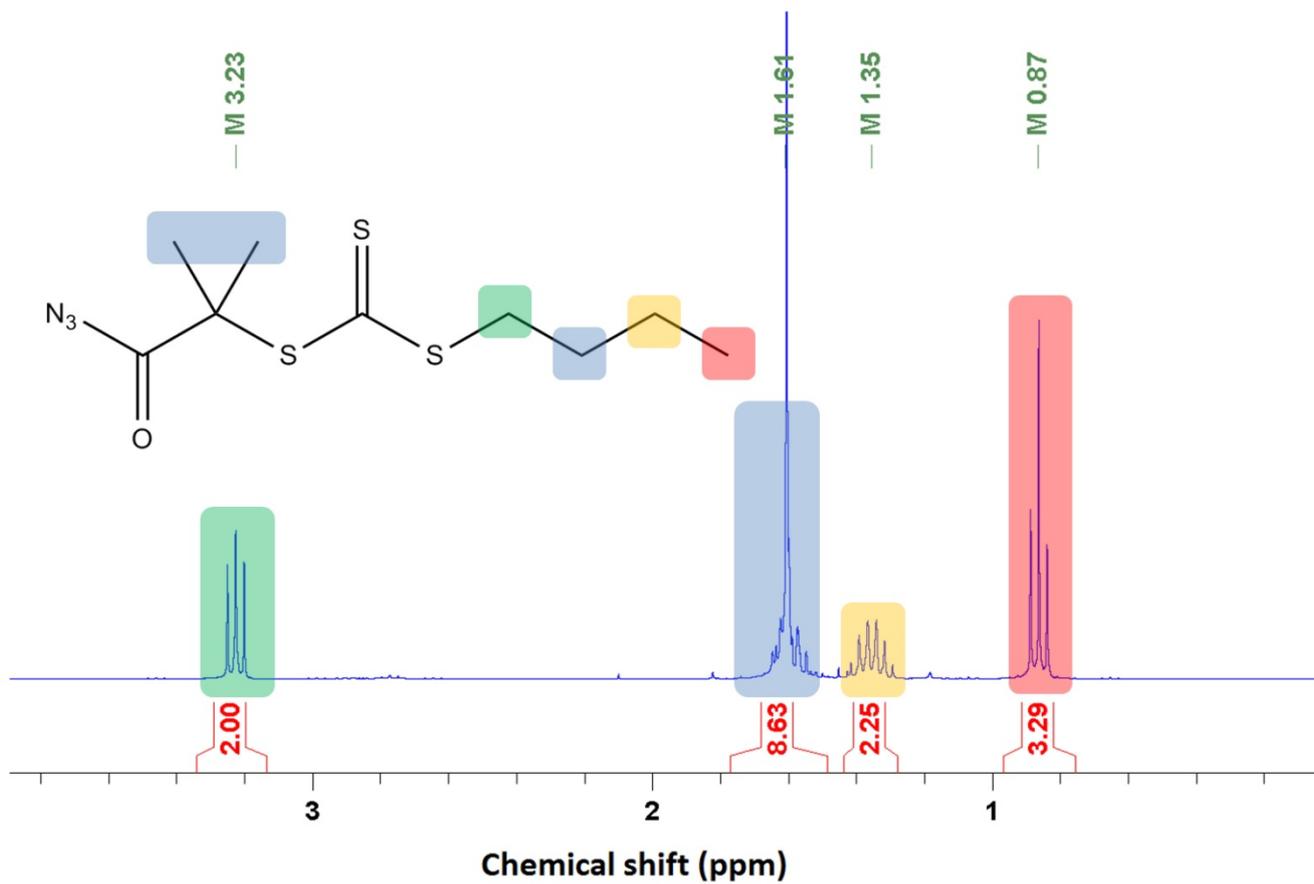


Figure S2 NMR spectrum showing successful synthesis of BIAzTC, solvent is CDCl₃.

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Figure S3 GPC traces of the kinetics samples for PPFS polymerized with BIAzTC.

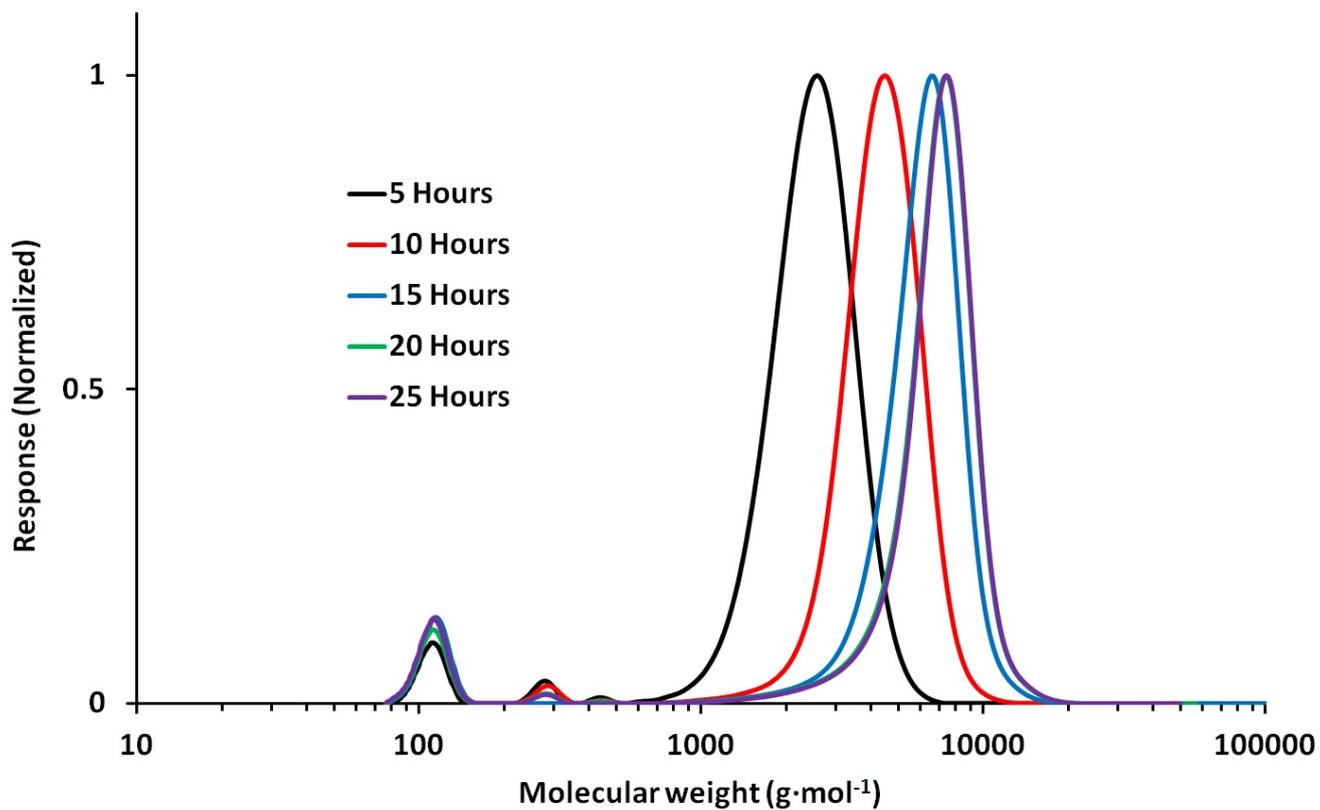


Figure S4 Dispersivity vs Time and Pseudo-first order kinetic plot of PPFS

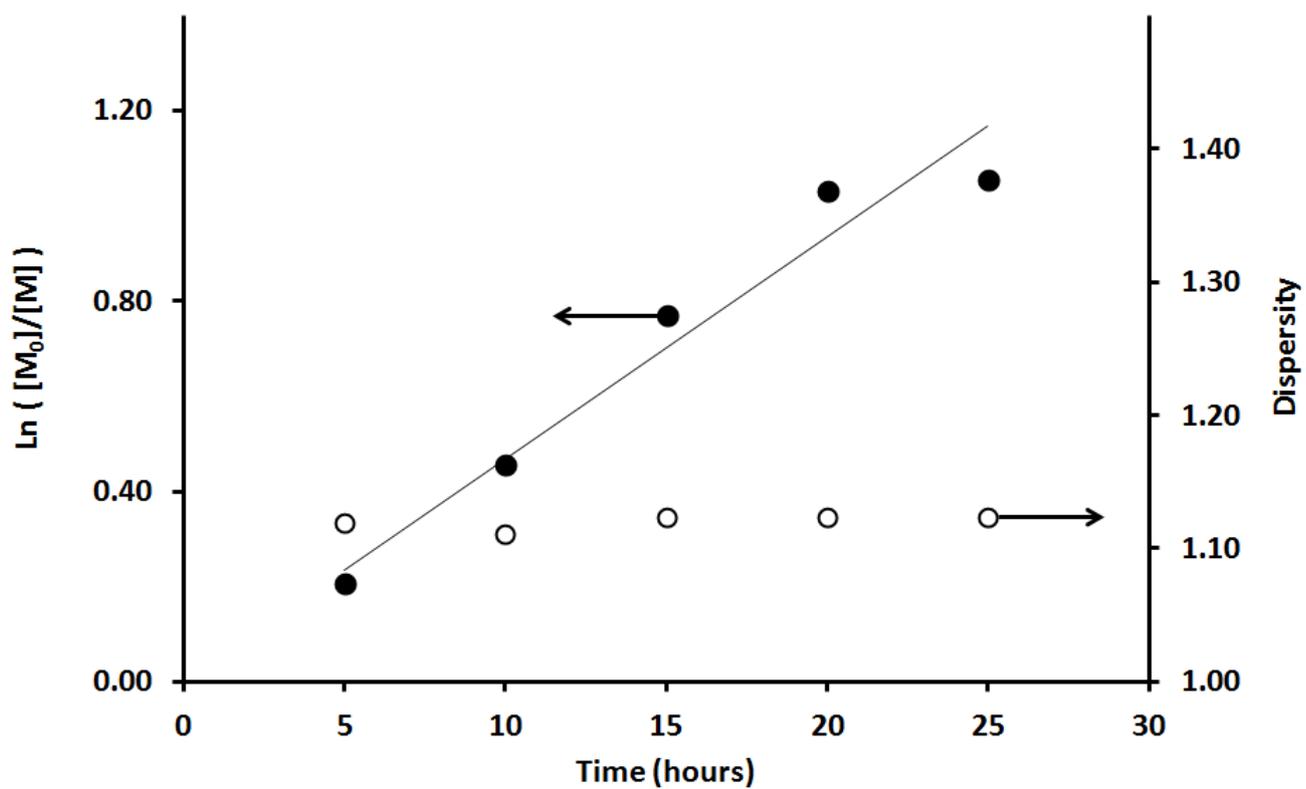


Figure S5 ATR-FTIR spectrum showing the stable isocyanate moiety on the PPFS polymer chains grown with BIAzTC.

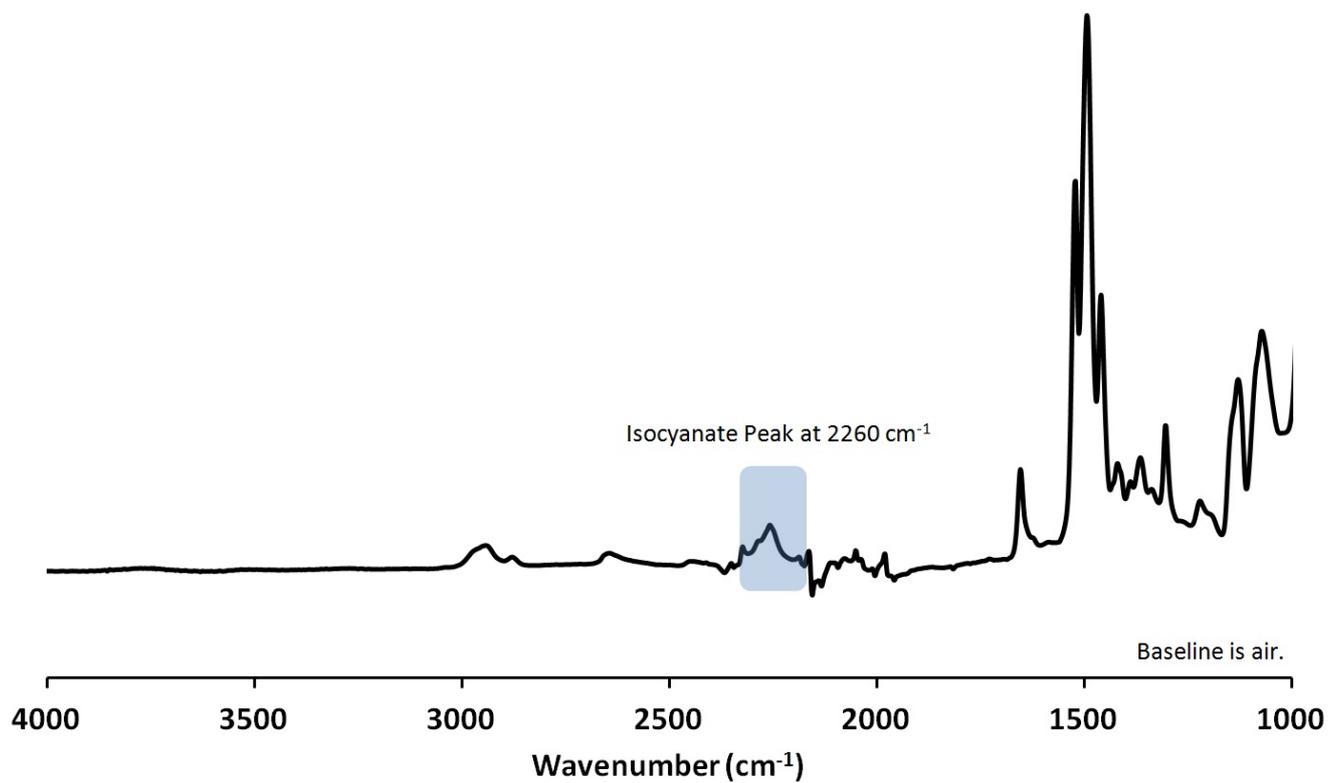
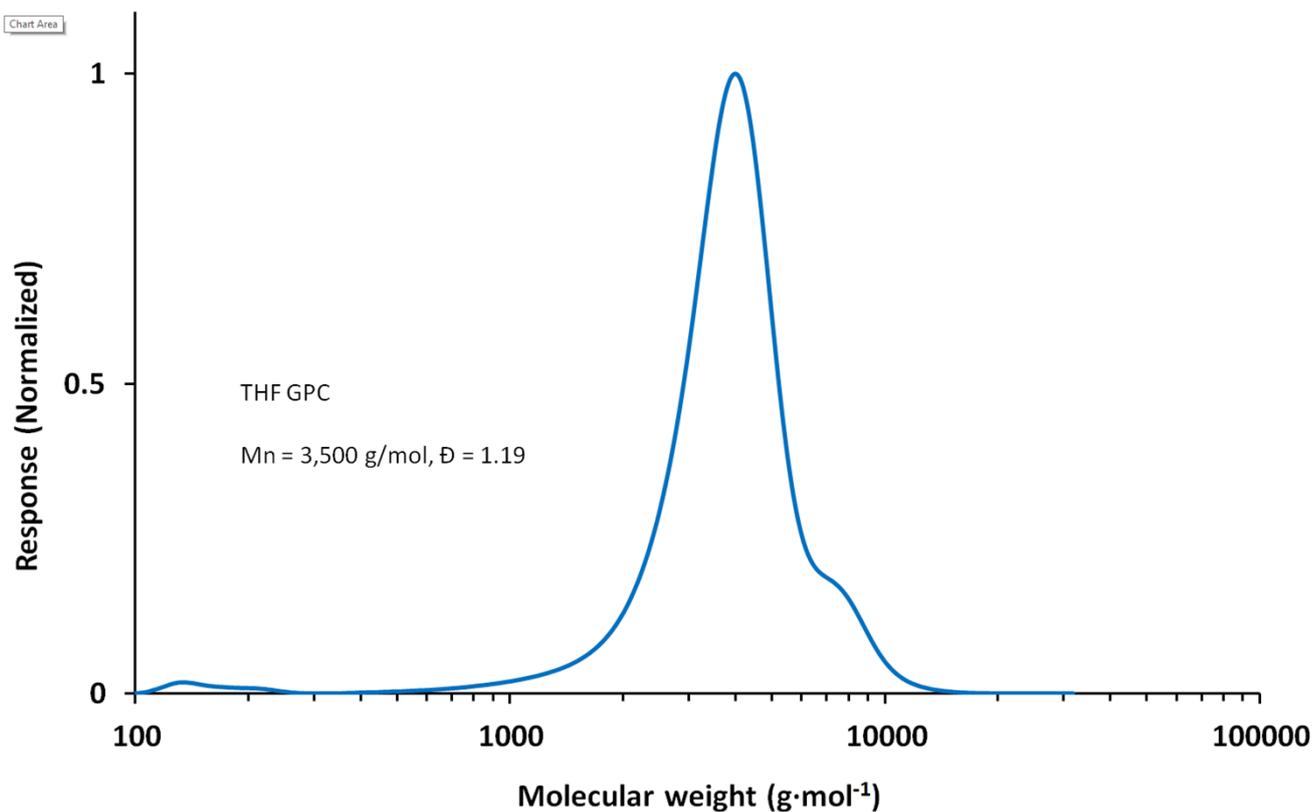


Figure S6 GPC trace of PPFS polymer generated during 'grafting from' reactions in the presence of PDA@SiO₂ particles

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The GPC trace in Figure S6 shows a slight shoulder. This shoulder is not seen in any of the GPC traces of PPFS polymer chains analyzed in the same THF GPC instrument. The presence of the polydopamine surface, in the form of a particle or a flat surface could result in a small amount of polymer to coupling due to aminolysis of the RAFT chain ends. A small amount of residual monomer is seen for the trace.

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Figure S7 NMR spectrum of free PPFS synthesized during a 'grafting from' reaction, using BIAzTC on the surface of PDA@SiO₂, solvent is CDCl₃.

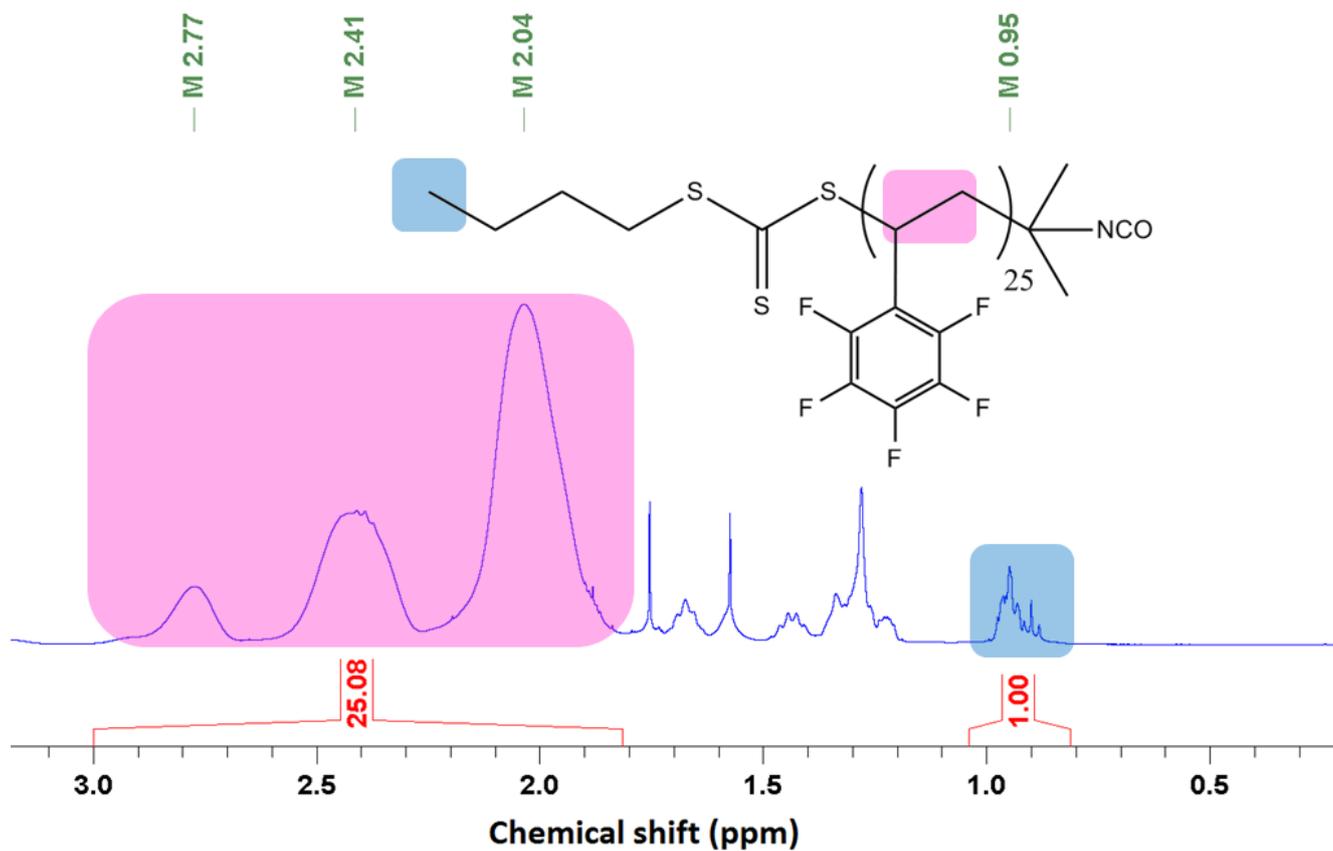
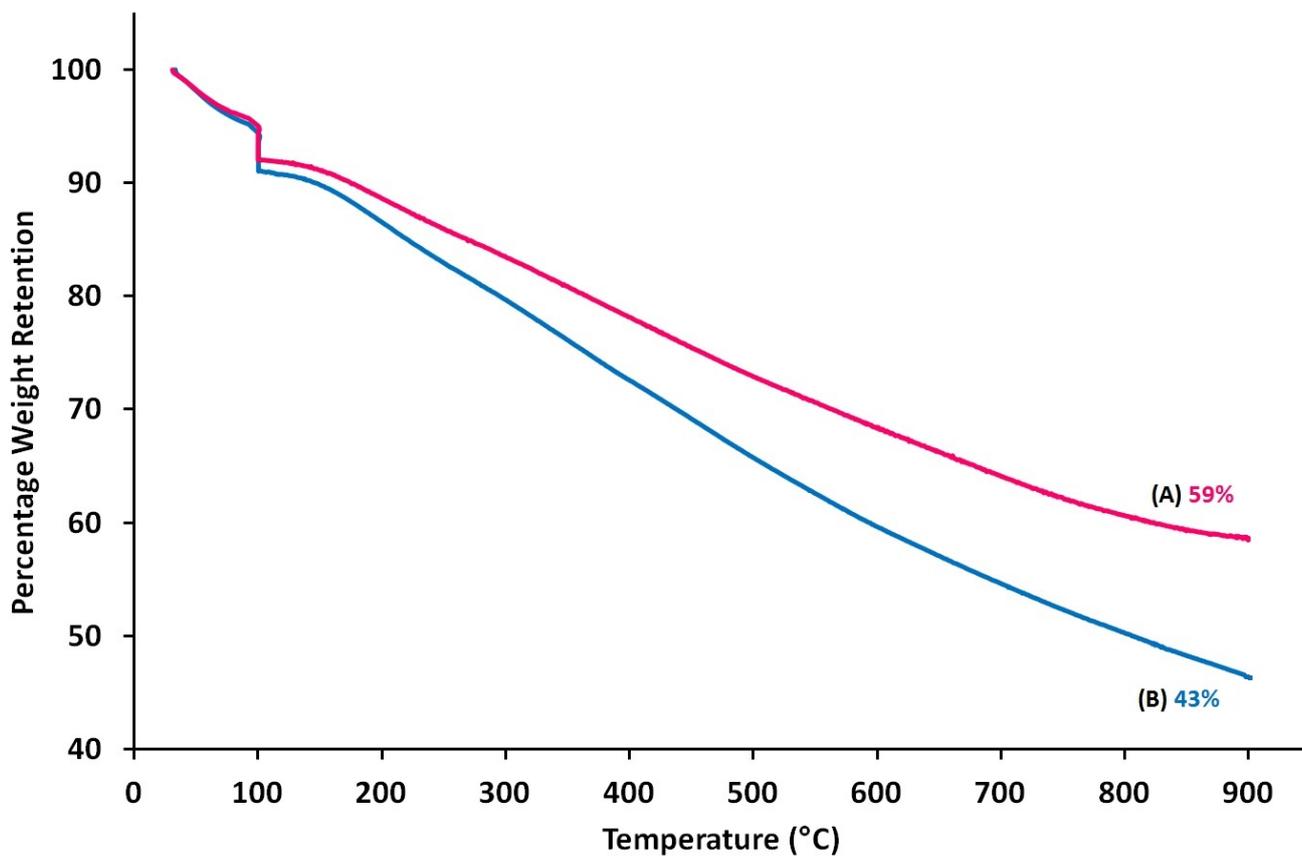
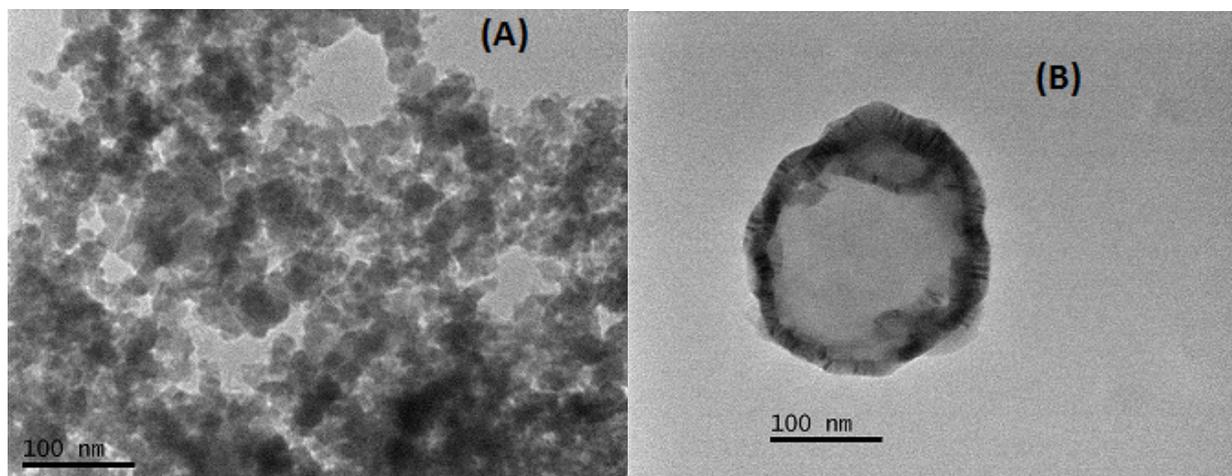


Figure S8 TGA traces for glycopolymers (30 hours of glucosylation) from 'grafting to' and one-pot 'grafting from' of PPFS on PDA@SiO₂ particles.



Glycopolymer from 'grafting to' sample showed 59% residual weight and (B) glycopolymer from one-pot 'grafting from' sample showed 43% residual weight.

Figure S9 TEM images of (A) PDA@SiO₂ and (B) glycopolymer graphed PDA@SiO₂ particles.



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The dense brush layer, visible as a darker band around the particle exterior, is visible in image B. The thickness of this band is roughly 20nm for the glycopolymer brush, which is slightly thicker than the 13nm thickness for a fully extended PPFS brush. The difference could easily be attributable to the increased steric hinderance of the glycopolymer brush compared to the PPFS brush.

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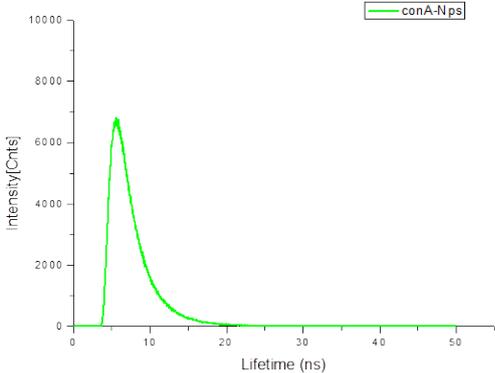
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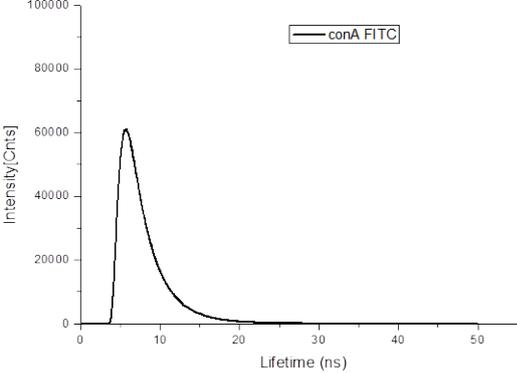
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Figure S10 Decay profile figures for the FLIM analysis performed on (A) ConA bound to nanoparticles and (B) FITC-ConA alone



(A)



(B)