Supporting Information for:

Macroporous Uniform Azide- and Alkyne-functional Polymer Microspheres with Tuneable Surface Area: Synthesis, In-depth Characterization and *Click*-Modification

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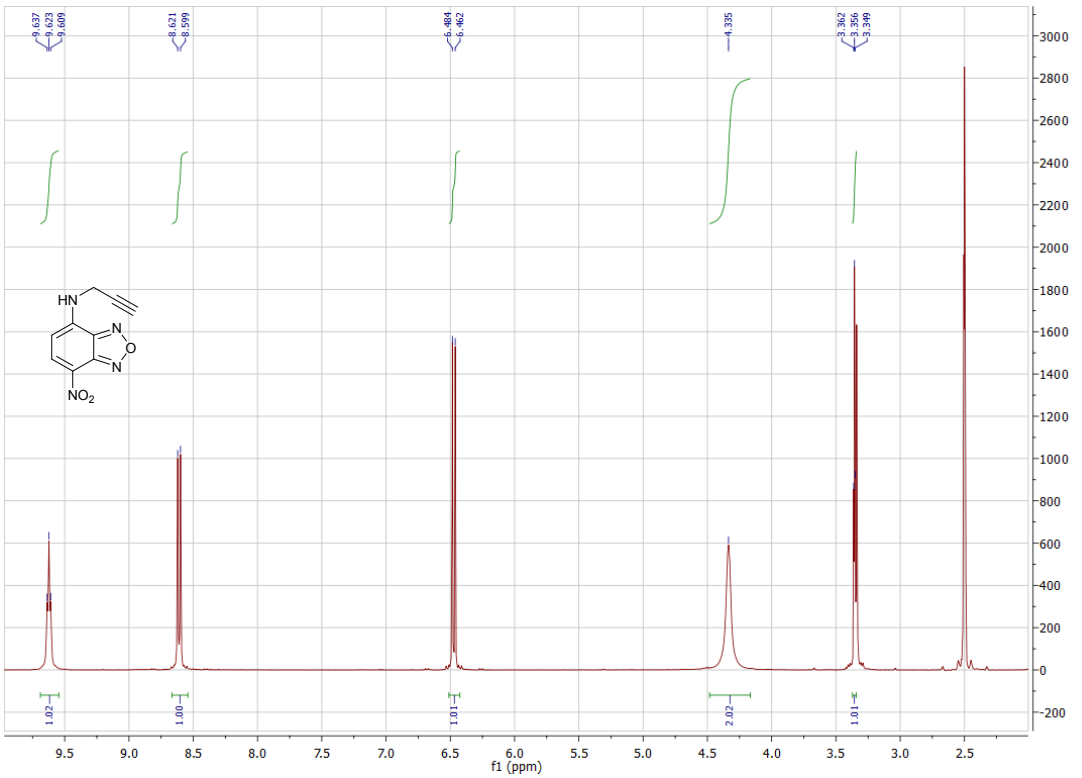

Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of NBD alkyne reagent (**6**)

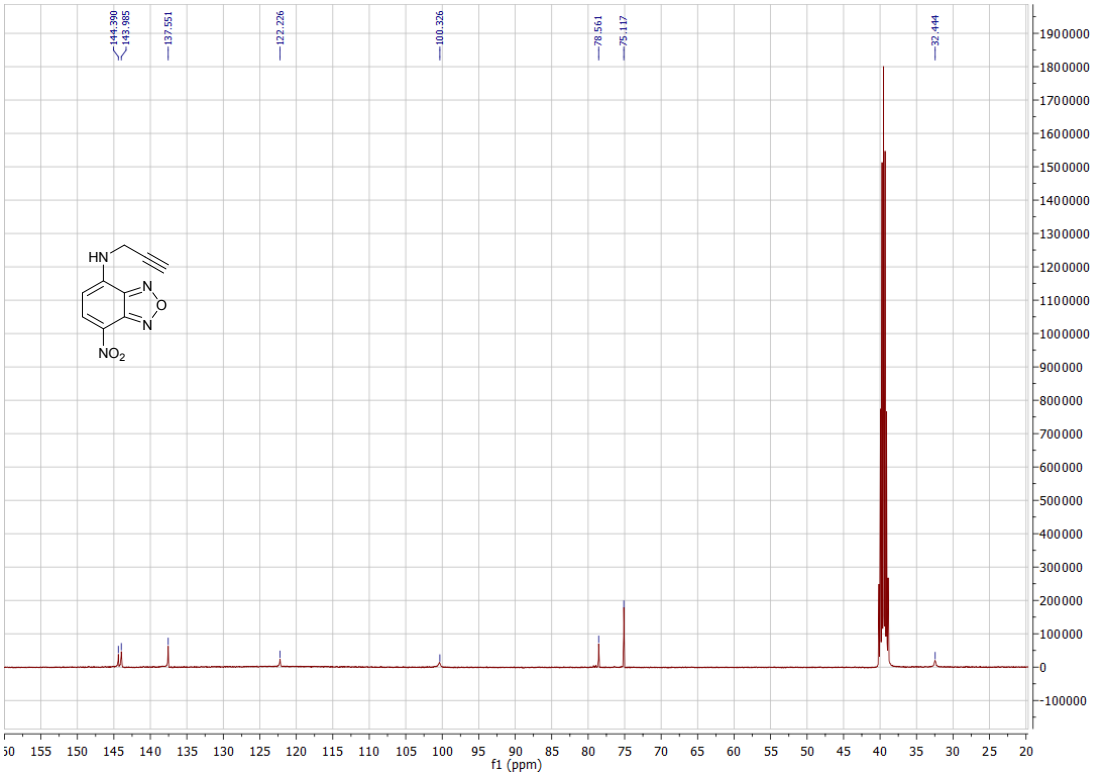

Figure S2. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of NBD alkyne reagent (**6**)

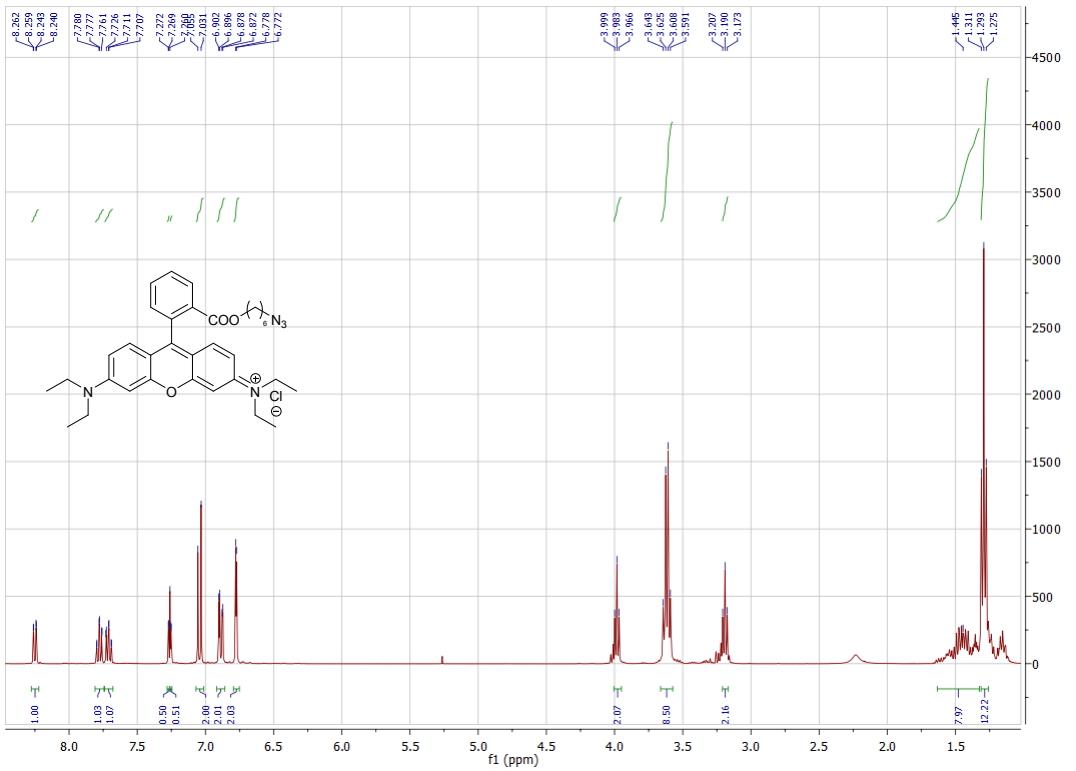

Figure S3. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of Rhodamine B azide reagent (**7**)

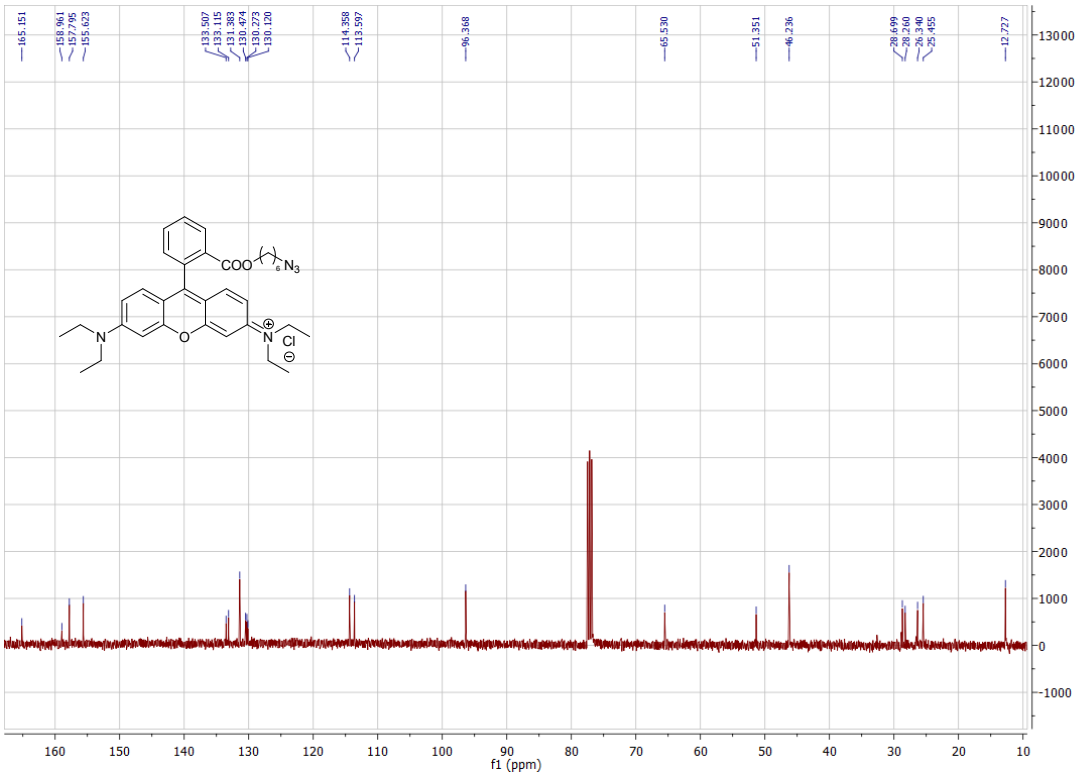

Figure S4. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of Rhodamine B azide reagent (**7**)

Swelling Step— optimal microscopy control

Completeness of the single swelling steps with dibutylphthalate (DBP) and monomer mixture with different amounts of styrene / divinylbenzene / toluene was observed by optical microscope. DBP was quickly and completely absorbed by the PS seed particles. The size of the microspheres significantly increased from 2.8 to 4.2 μm within ~ 90 min (Figure S5).

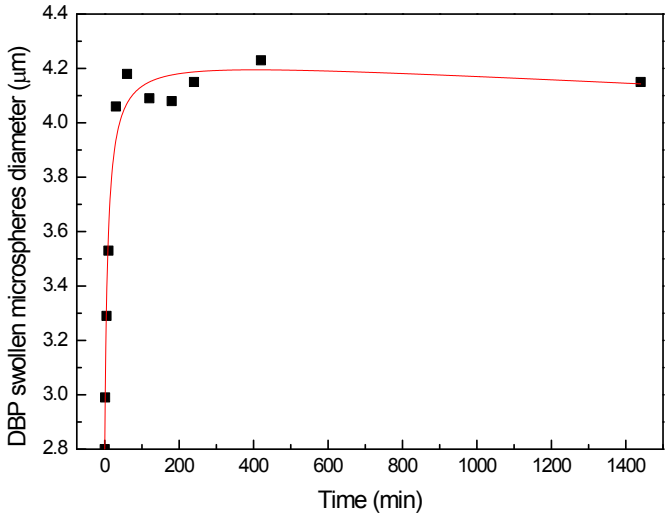

Figure S5. Plot of seed particle diameter during the swelling procedure with dibutylphthalate (DBP)

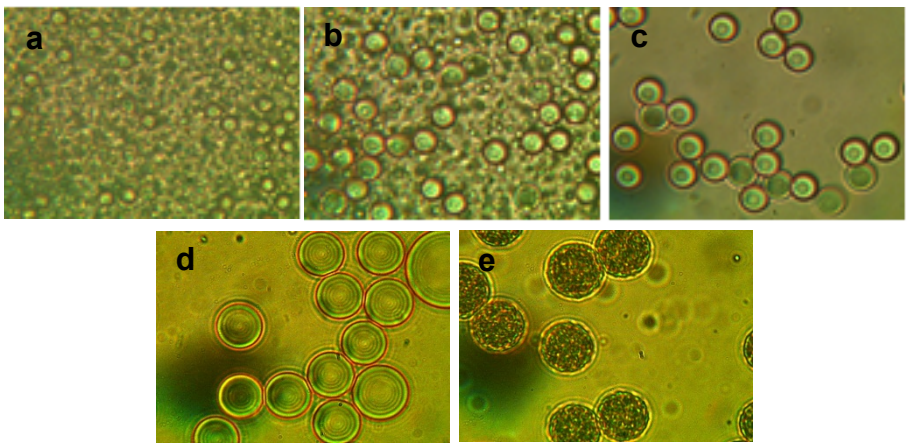

Figure S6. Optical microscope images of (a) seed particles with DBP droplets after 1 min., (b) after 10 minutes, (c) swollen PS seed after 240 min. showing size increase of seed particles, (d) after completed swelling with monomer mixture, (e) after polymerization showing porous morphology.

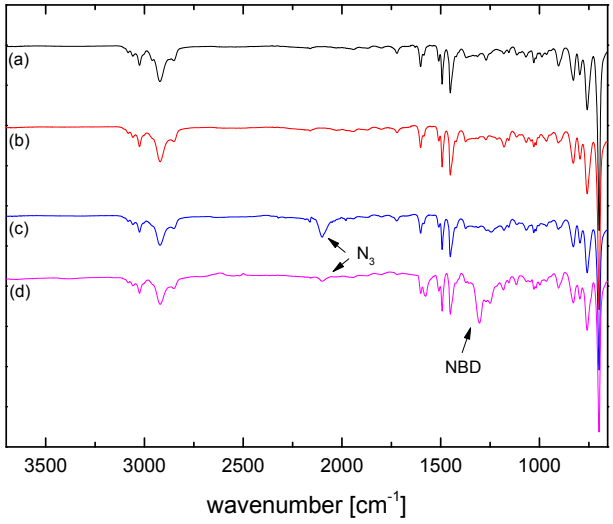

Figure S7. FT-IR spectra of porous particles MS3 (a), after hydrobromination (b), after bromide substitution with azide (c), and after clicking with NBD-alkyne (**6**) (d), with characteristic bands assigned.

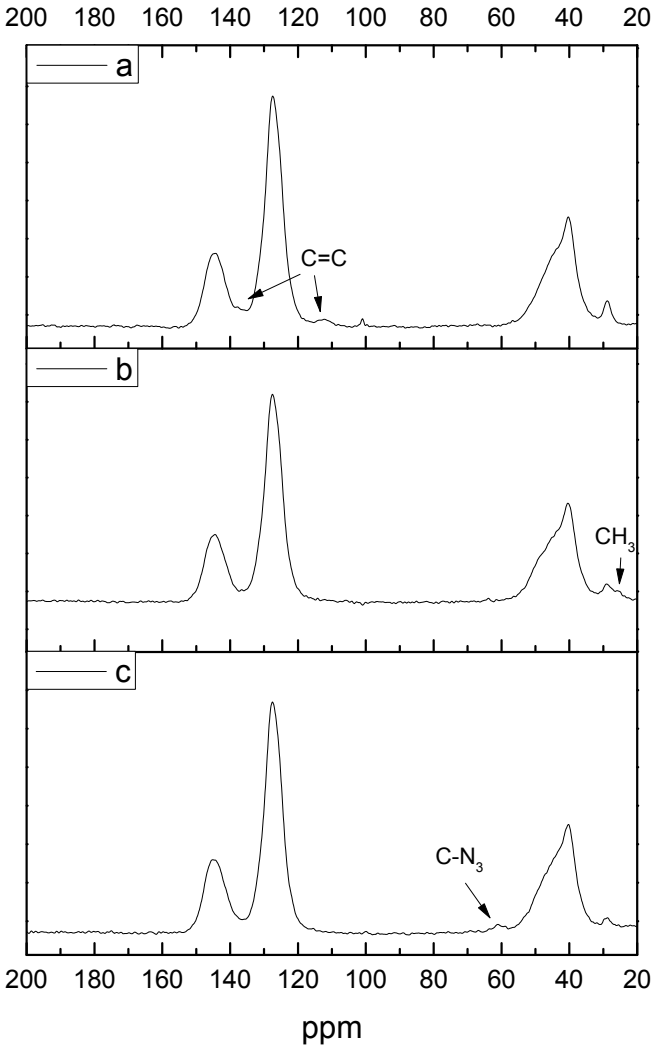

Figure S8. Solid state NMR spectra of porous particles MS3 exhibiting residual vinyl groups (a), after hydrobromination showing disappearance of vinyl groups and a shoulder at 26 ppm (–CHBr–CH_3) (b), and after bromide substitution by azide displaying a characteristic signal at 61 ppm (–CHN_3–CH_3).