Secondary structures of PEG-functionalized random copolymers derived from (*R*)- and (*S*)- families of alkyne polycarbodiimides

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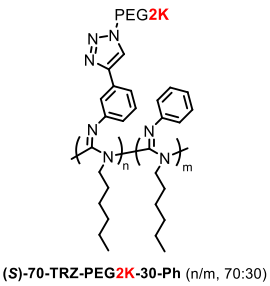
General Methods: tapping mode atomic force microscopy (TMAFM) investigation of thin film morphology was carried out using a Nanoscope IV-Multimode Veeco, equipped with an E-type vertical engage scanner. Thin film was prepared by spin-coating techniques from $CHCl_3$ stock solutions in the range of final concentrations varying from 0.156 mg/mL to 10 mg/mL on Si-wafer (orientation 100) substrate. Solutions of PEG-polymers were used for spin-coating immediately. The AFM images were acquired at room temperature by using silicon cantilevers with nominal spring constant of 42 N x m^{-1} and nominal resonance frequency of 320 kHz (standard silicon OTESPa tips obtainable from Bruker). Amplitude set point values varied from 425 to 273 mV and scan rates of 0.99 and 1.99 Hz were used. Scanning electron microscopy (SEM) images were collected on the Zeiss Supra 40 SEM at UTD Nano Characterization Facility. The samples were mounted on silicon wafers and coated with conductive Pd/Au film. The potential applied to the inspection sample was 10 kV. Transmission electron micrographs were acquired on both Tecnai Spirit electron microscope under 200 kV at UT Southwestern Medical School and High Resolution Transmission Electron Microscope – JEOL 2100 TEM operating at a voltage of 200 kV (University of Pennsylvania, Singh Center for Nanotechnology, Philadelphia, PA, USA). The samples were mounted on the carbon coated copper grid and negative staining with 2% aqueous uranyl acetate was applied to the specimens. Synthesis of compound (*S*)-PPMC-*b*-TRZ-PEG20K-TRZ-*b*-(*S*)-PPMS was described elsewhere.[S1] Single crystal X-ray diffraction data was collected on a crystal of 1-(hex-5-ynyl)-3-(3-(2-(triisopropylsilyl)ethynyl)phenyl)thiourea (TIPS-thiourea)[9d] at room temperature using a Bruker Kappa Apex-II DUO diffractometer (microfocus Cu Kα radiation source, CCD detector). Afterwards, the data was integrated, scaled, and evaluated for space group selection using Bruker SAINT, SADABS (multi-scan absorption correction), and XPREP. A preliminary model was generated using SIR97 (direct methods).[S2] Refinement of this model was carried out with SHELXL2014/7.[S3] $C_{24}H_{36}N_2SSi$, M_r = 412.70 g mol^{-1}, monoclinic, a = 24.712 (7) Å, b = 8.4842 (15) Å, c = 24.907 (6) Å, β = 101.616 (10)°, V = 5115 (2) $Å^3$, T = 299 K, space group $I2/a$, Z = 8, μ(Cu$K\alpha$) = 1.64 mm^{-1}, 16729 measured reflections, 4474 independent reflections (R_{int} = 0.032). The final R_1 values were 0.047 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.133 ($I > 2\sigma(I)$). The final R_1 values were 0.061 (all data). The final $wR(F^2)$ values were 0.147 (all data). The goodness of fit on F^2 was 1.05, CCDC 1566196 (see Figure 2S31).

Polymer encapsulated SWCNTs` aqueous suspension: PEG-polymer (5 mg) and HiPco raw single-walled carbon nanotubes (alternatively, 5 mg of NanoIntegris SWCNTs, 9.4 wt%, batch # HR26-075) were mixed with water (1 mL) in a microcentrifuge tube (1.5 mL). The mixture was sonicated at low temperature using 1/8" tapered microtip (Sonics Vibracell, Sonics and Materials) for 20 minutes at 40% amplitude. The resulting dark black suspension was centrifuged at 30,000 rcf (Eppendorf Centrifuge 5430R) for 30 minutes at 20 °C and the pellet was discarded to remove unsuspended material. The supernatant was collected and the centrifugation was repeated. To remove excess of polymer, the supernatant was filtered using a centrifugal filter membrane (100 kD MWCO, Millipore) twice. The black residue was collected and suspended in water (1mL) to obtain polymer encapsulated carbon nanotube suspension.

The SWCNTs suspensions were characterized using visible-near infrared absorbance and near infrared fluorescence measurements using a previously reported method. (1) Briefly, a dilute aqueous suspension of nanotube (100 µL) was taken in disposable cuvette (UVette 200 Eppendorf) for absorbance measurements using a JASCO V-670 spectrophotometer (Jasco, Tokyo, Japan). The concentration of nanotubes was determined using extinction coefficient A_{650} = 0.036 $L.mg^{-1}.cm^{-1}$. Near-infrared photoluminescence excitation/emission measurements were performed on a home-built instrument consisting of an IsoPlane SCT 320 spectrograph and PioNIR InGaAs detector (Princeton Instruments) connected to an Olympus IX71 inverted microscope. A 20×objective was used. Samples were excited using a SuperK Extreme supercontinuum laser connected to a Varia variable bandpass filter (NKT Photonics). The excitation wavelength was varied from 491 to 824 nm, and the emission was recorded from 915 to 1354 nm. Data were collected using a custom Labview (National Instruments) automation program. These data were then analyzed and plotted using Matlab (The MathWorks) code. Zeta potential (surface charge) measurements were conducted by suspending polymer-nanotube complexes (~ 3 mg/L) in ultrapure water (18.2 mΩ) in a 1 mL folded capillary cell (Malvern). Measurements were conducted at room temperature using a Zetasizer Nano-ZS instrument (Malvern).

PEG copolymers tested by AFM

(***S***)**-70-TRZ-PEG2K-30-Ph-PCD**, C = 10 mg/mL, 5.0 mg/mL, 2.5 mg/mL, 1.25 mg/mL, 0.625 mg/mL, 0.313 mg/mL, 0.156 mg/mL, $CHCl_3$ stock solutions; (***S***)**-85-TRZ-PEG2K-15-Ph-PCD**, C = 10 mg/mL, 5.0 mg/mL, 2.5 mg/mL, 1.25 mg/mL, 0.625 mg/mL, $CHCl_3$ stock solutions; (***S***)**-30-TRZ-PEG2K-70-Ph-PCD**, C = 10 mg/mL, 5.0 mg/mL, 2.5 mg/mL, 1.25 mg/mL, 0.625 mg/mL, 0.313 mg/mL, 0.156 mg/mL, $CHCl_3$ stock solutions.



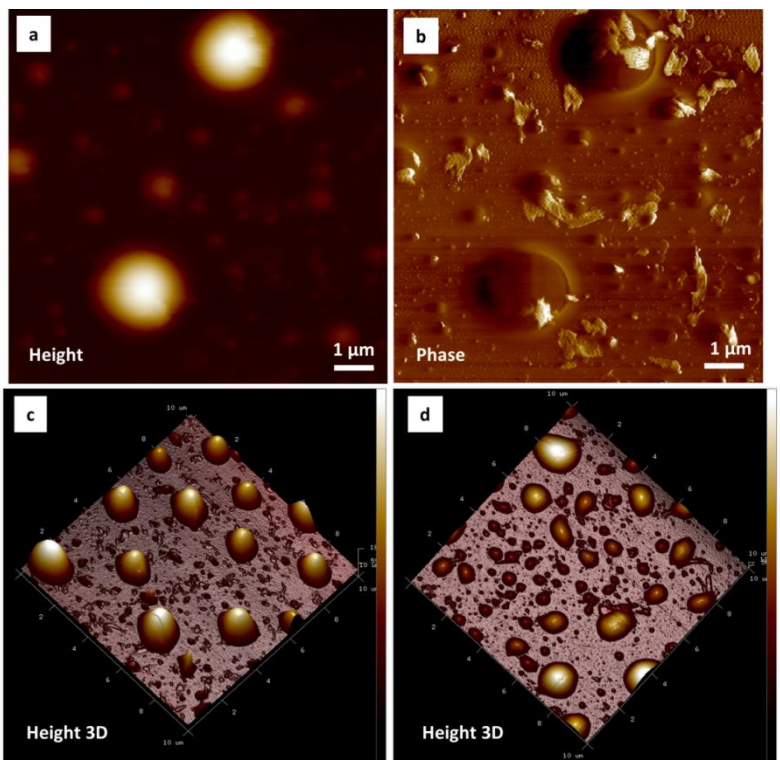
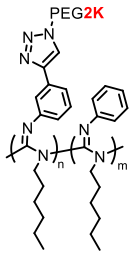


Figure 2S1. Selected phase and height AFM micrographs of **(*S*)-70-TRZ-PEG2K-30-Ph** spin-coated from $CHCl_3$ onto Si-wafer, C = 10 mg/mL (panels a, b); 2.5 mg/mL (panel c); 1.25 mg/mL (panel d). Scan size = 10 x 10 µm (panels a-d)



(*S*)-70-TRZ-PEG2K-30-Ph (n/m, 70:30)

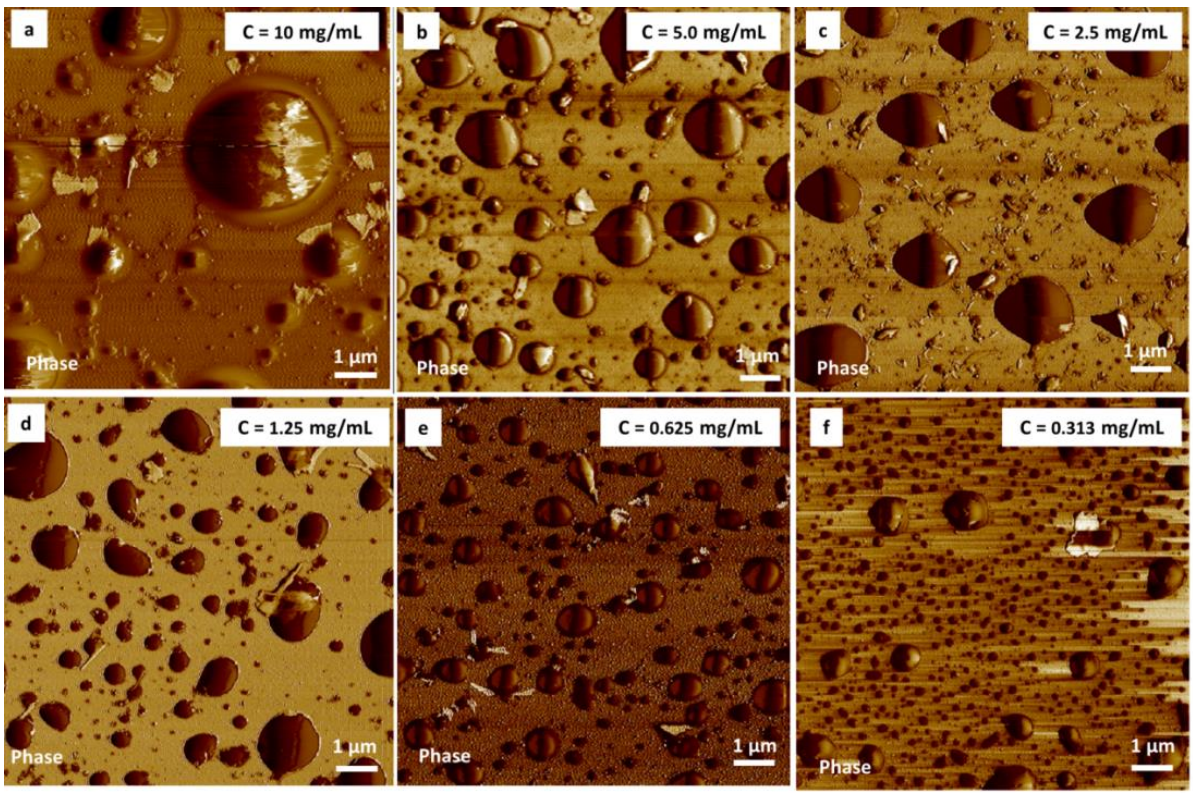
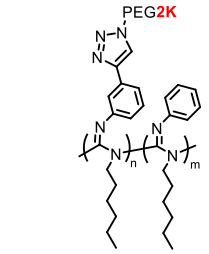


Figure 2S2. AFM micrographs of **(*S*)-70-TRZ-PEG2K-30-Ph** spin-coated from $CHCl_3$ stock on Si-wafer at 10.0 mg/mL (panel a), 5.0 mg/mL (panel b), 2.5 mg/mL (panel c), 1.25 mg/mL (panel d), 0.625 mg/mL (panel e), 0.313 mg/mL (panel f), Scan size = 10 x 10 µm (panels a-f)



(*S*)-85-TRZ-PEG2K-15-Ph (n/m, 85:15)

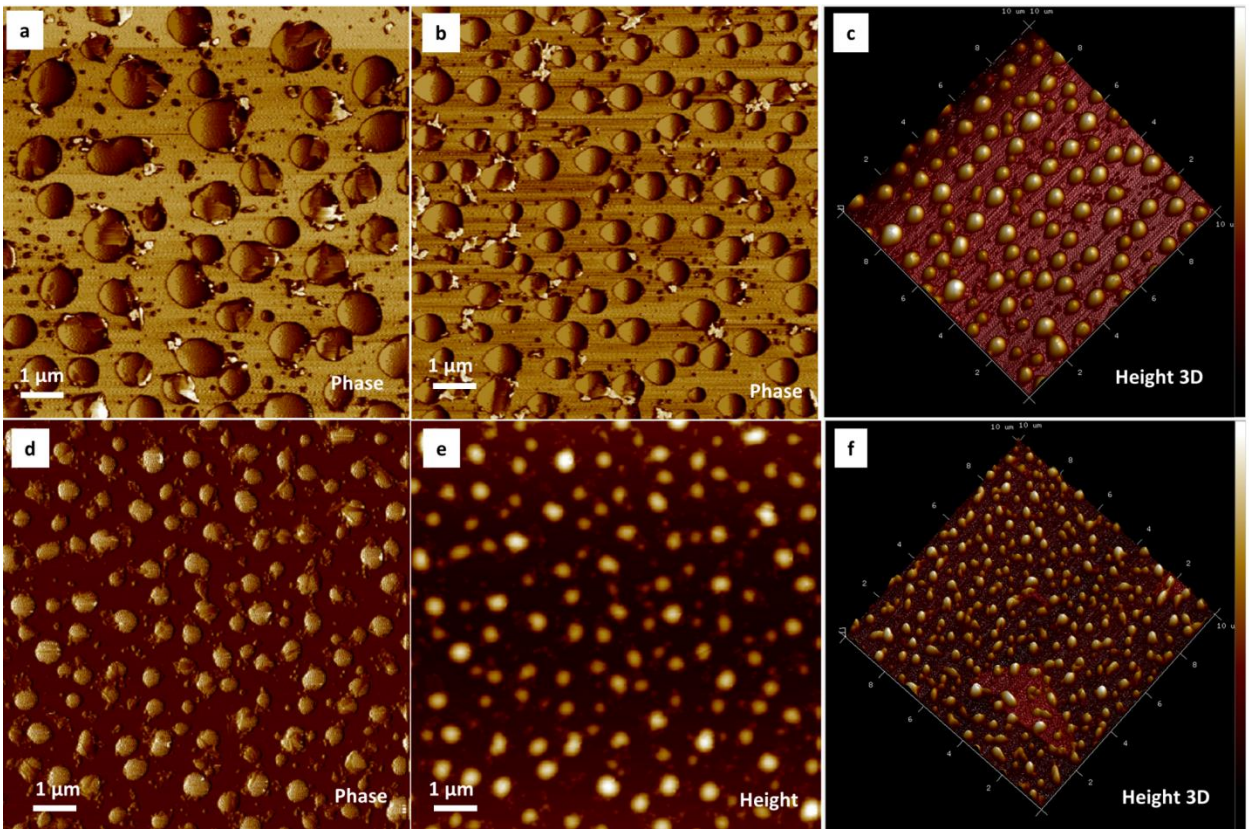


Figure 2S3. Selected phase and height AFM micrographs of **(*S*)-85-TRZ-PEG2K-15-Ph** spin-coated from $CHCl_3$ onto Si-wafer, C = 5.0 mg/mL (panel a); 2.5 mg/mL (panels b, c); 1.25 mg/mL (panels d, e); 0.625 mg/mL (panel f). Scan size = 10 x 10 µm (panels a-f).

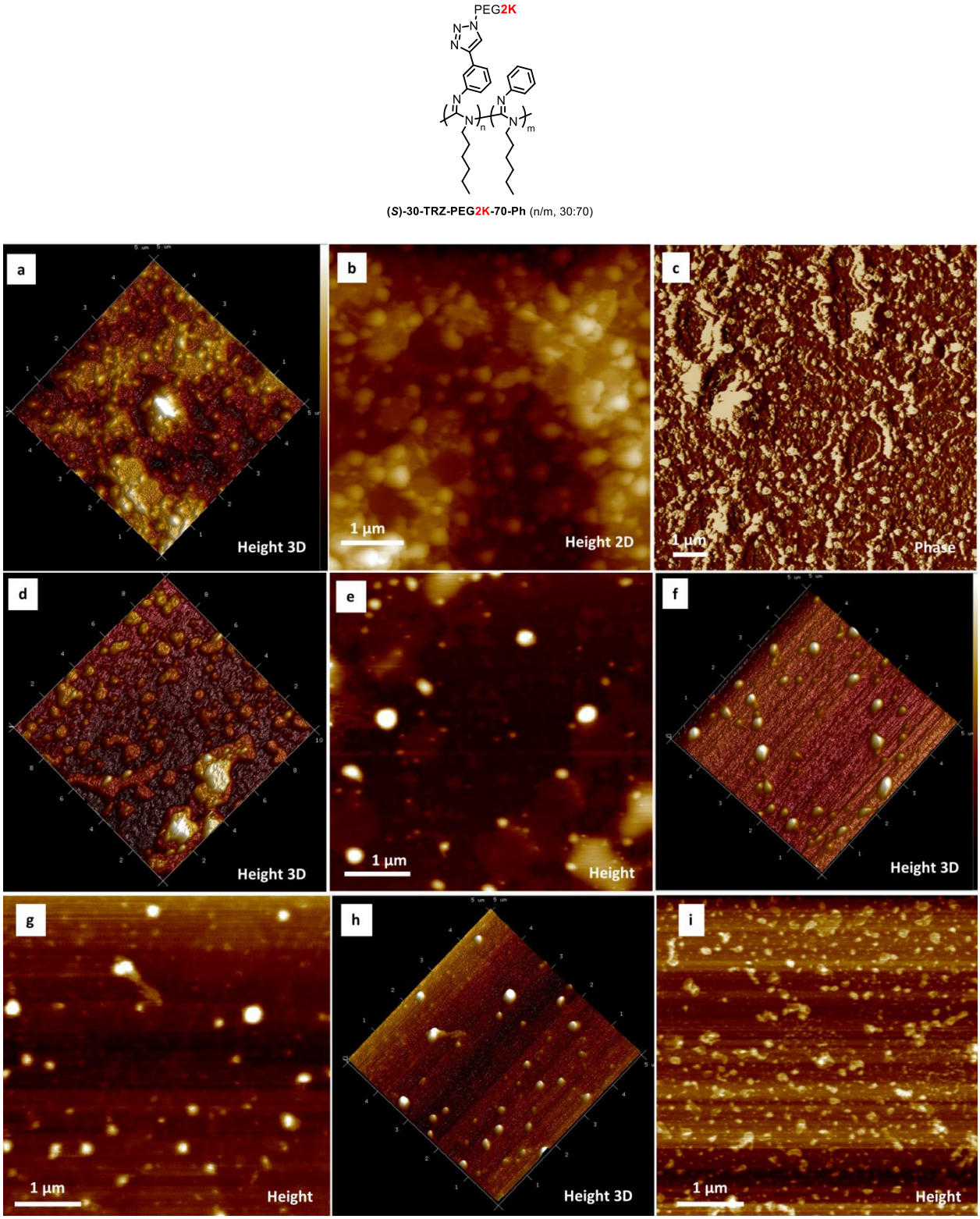


Figure 2S4. Selected phase and height AFM micrographs of **(*S*)-30-TRZ-PEG2K-70-Ph** spin-coated from $CHCl_3$ onto Si-wafer, 64-x dilution series: C = 10 mg/mL (panels a, b); 5.0 mg/mL (panel c); 2.5 mg/mL (panel d); 1.25 mg/mL (panel e), 0.625 mg/mL (panel f), 0.313 mg/mL (panels g, h), 0.156 mg/mL (panel i). Scan size = 10 x 10 µm (panels c, d); 5 x 5 µm (panels a, b, e-i).

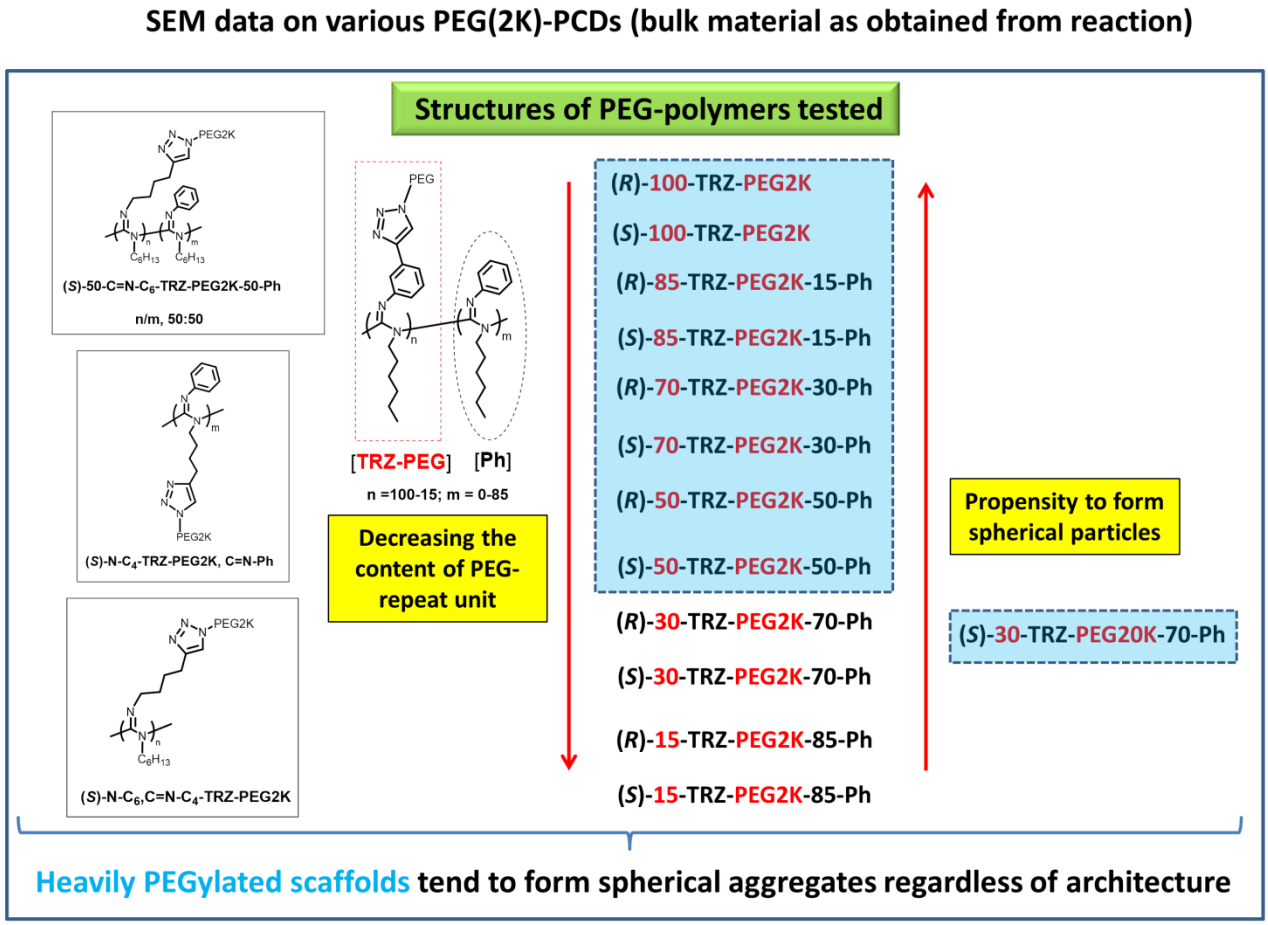
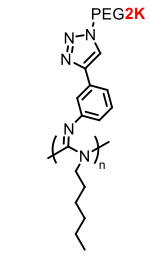


Chart 2S1. SEM data overview



(*R*)-100-TRZ-PEG2K

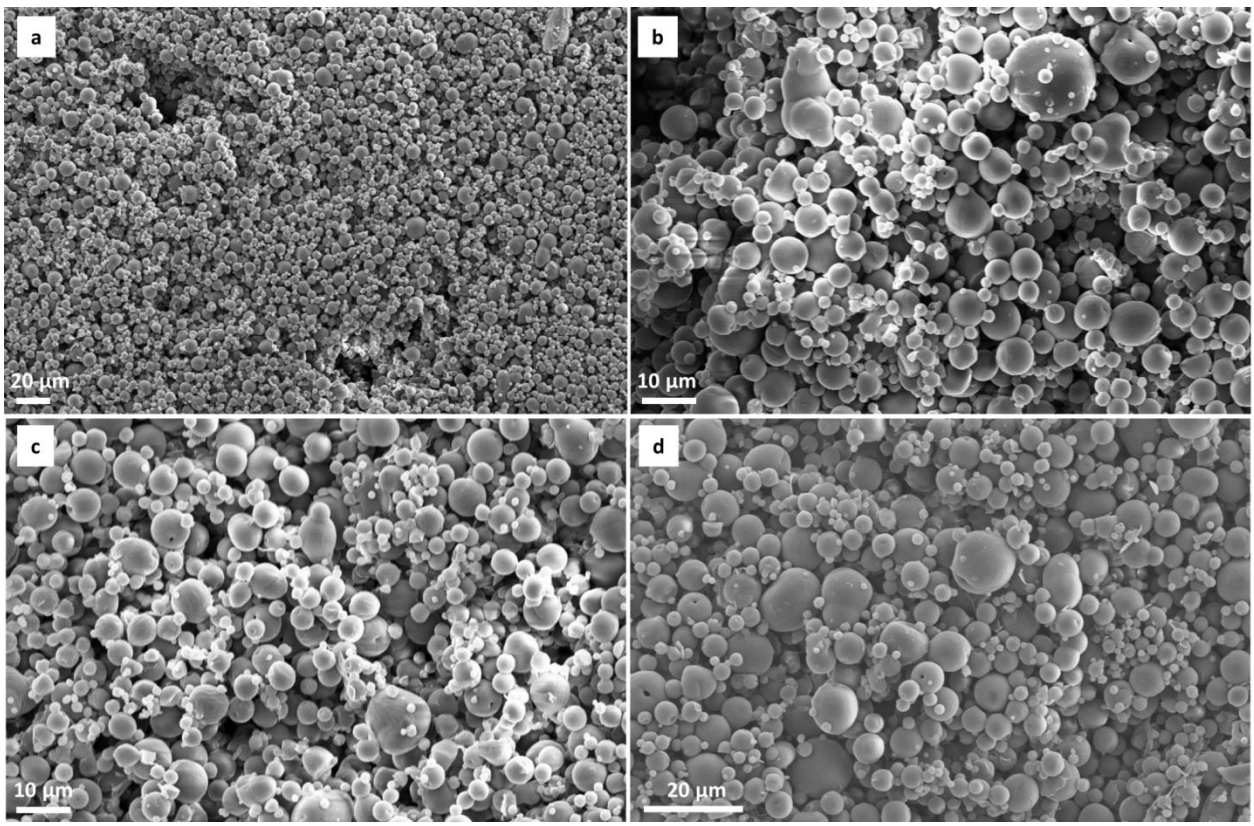


Figure 2S5. SEM micrographs of **(*R*)-100-TRZ-PEG2K**. Scale bar = 20 µm (panels a, d); 10 µm (panels b, c)

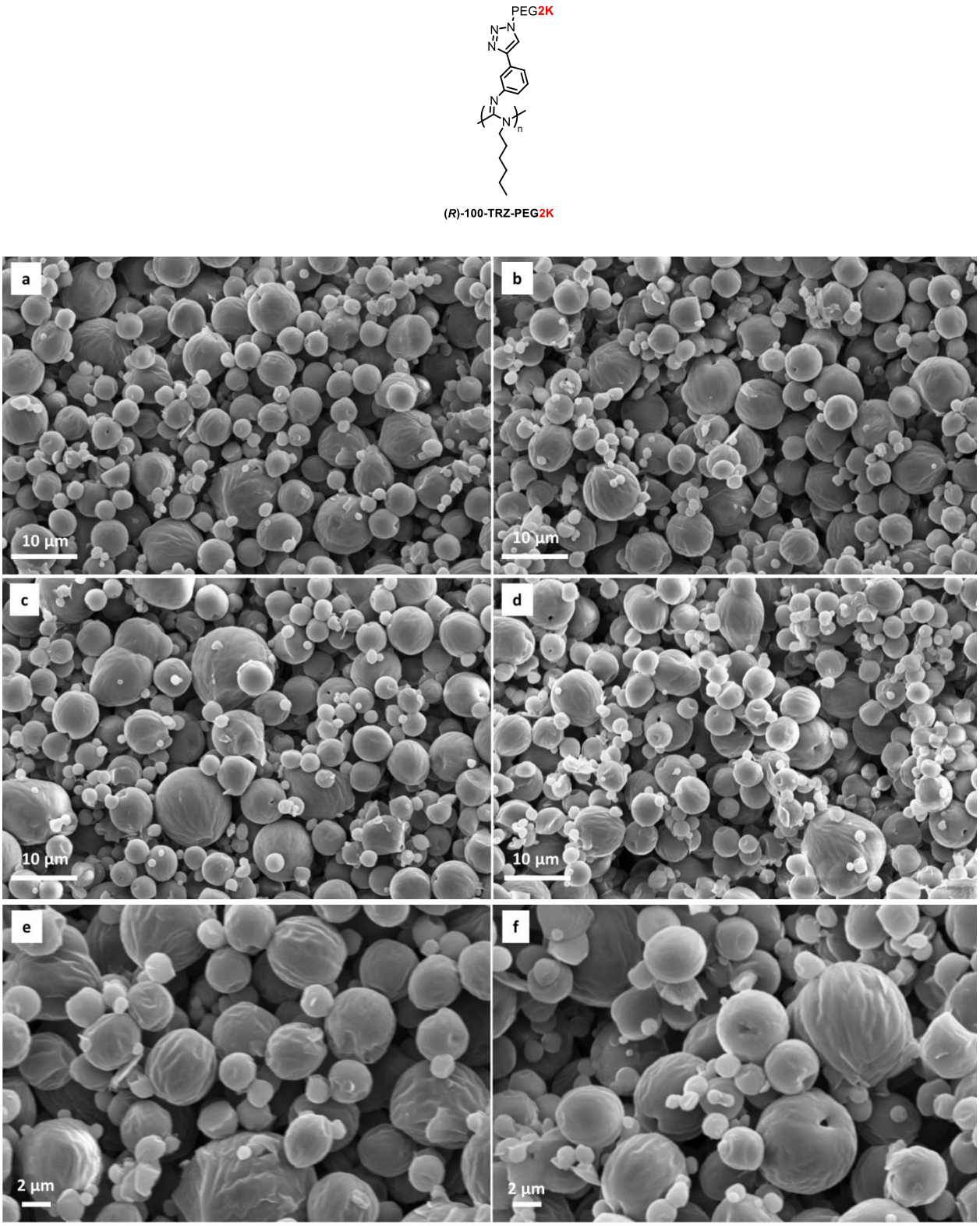


Figure 2S6. SEM micrographs of **(*R*)-100-TRZ-PEG2K**. Scale bar = 10 µm (panels a-d); 2.0 µm (panels e, f)

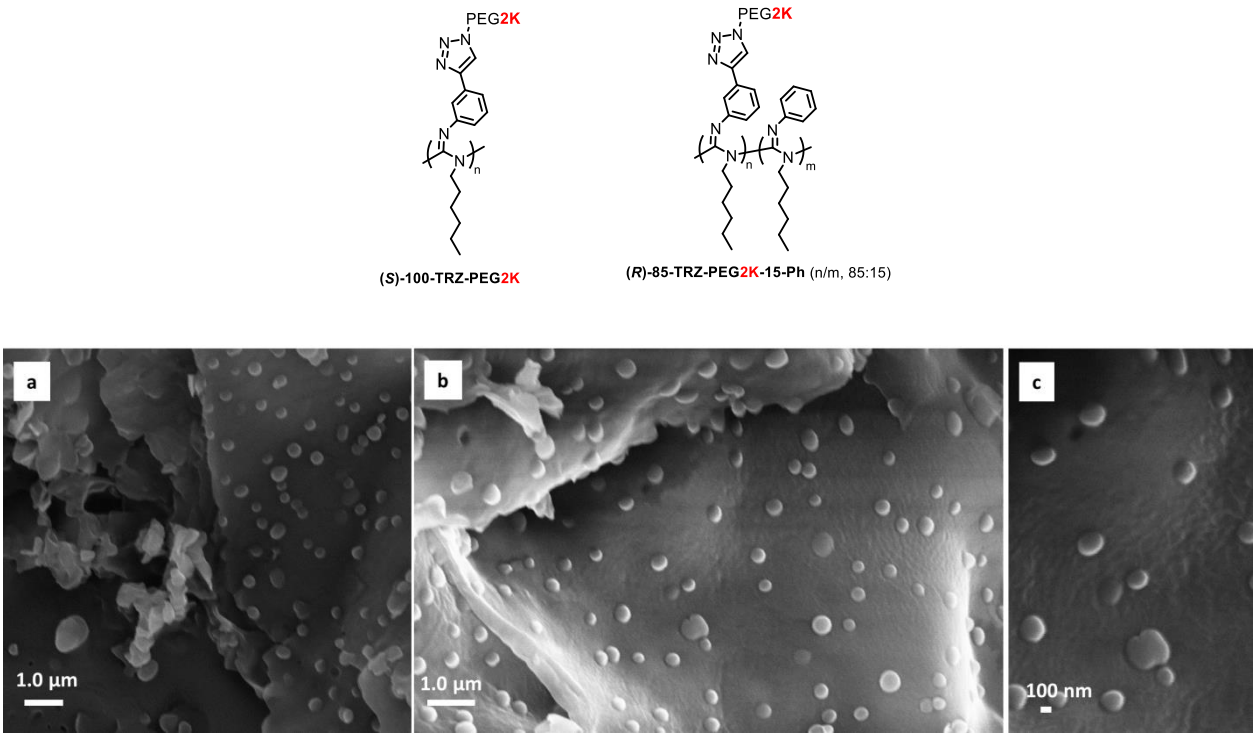


Figure 2S7. SEM micrographs of **(*S*)-100-TRZ-PEG2K**. Scale bar = 1.0 µm (panels a, b); 100 nm (panel c)

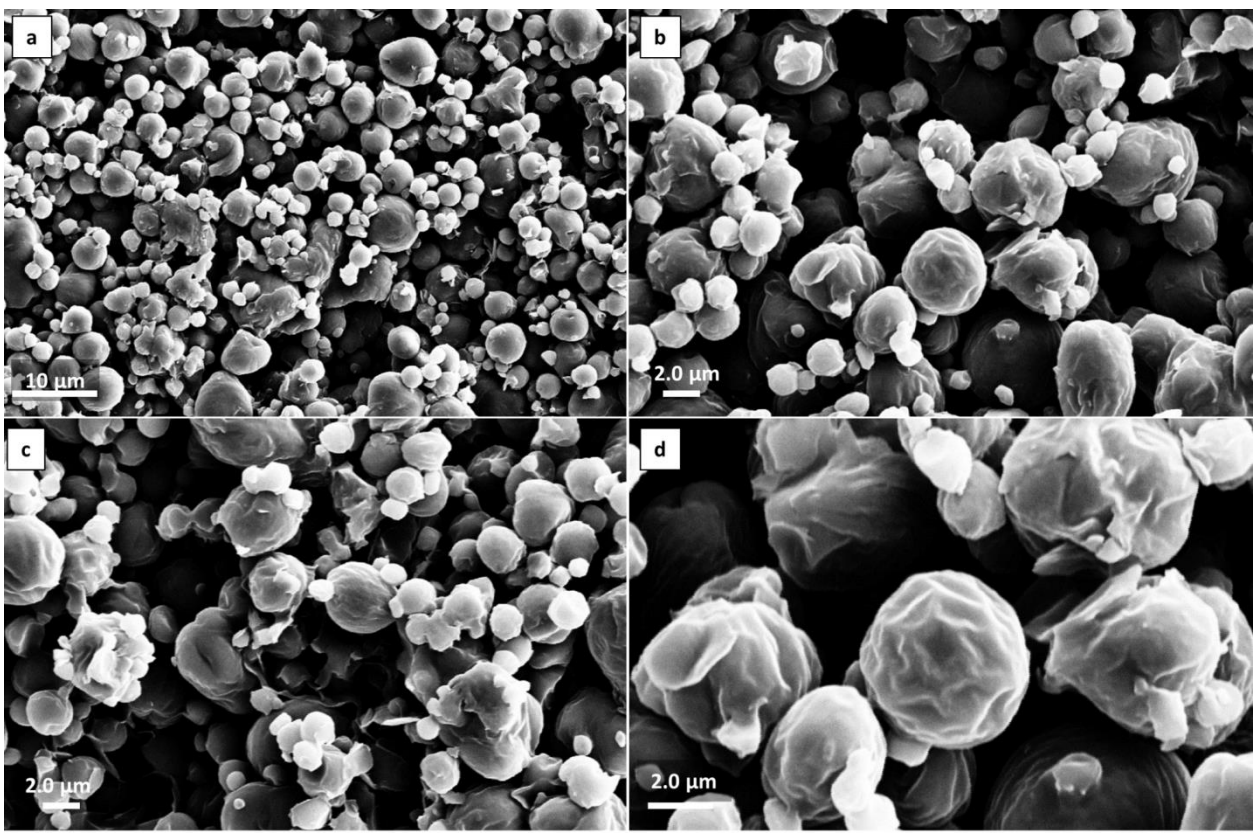


Figure 2S8. SEM micrographs of **(*R*)-85-TRZ-PEG2K-15-Ph**. Scale bar = 10 µm (panel a); 2.0 µm (panels b-d)

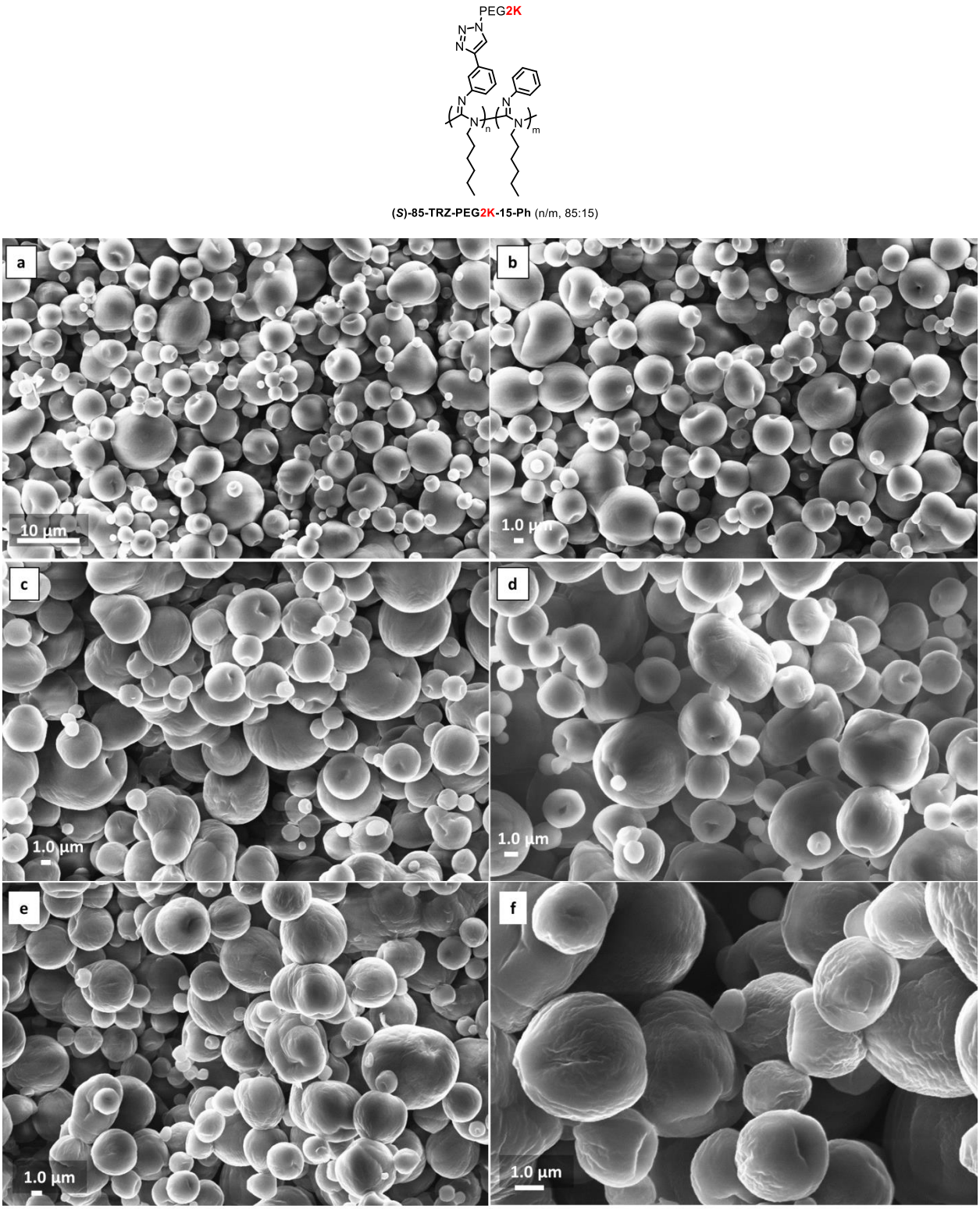
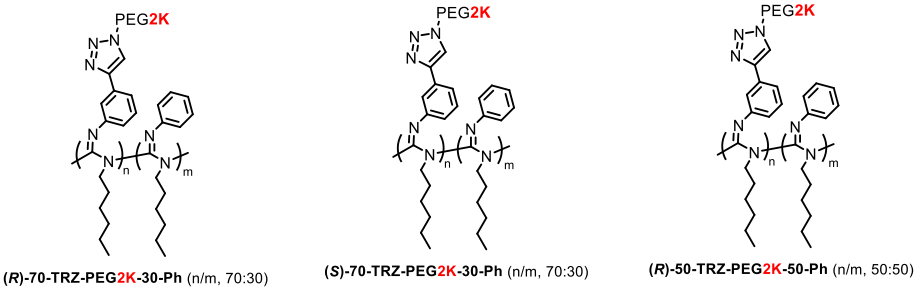


Figure 2S9. SEM micrographs of **(*S*)-85-TRZ-PEG2K-15-Ph**. Scale bar = 10 µm (panel a); 1.0 µm (panels b-f)



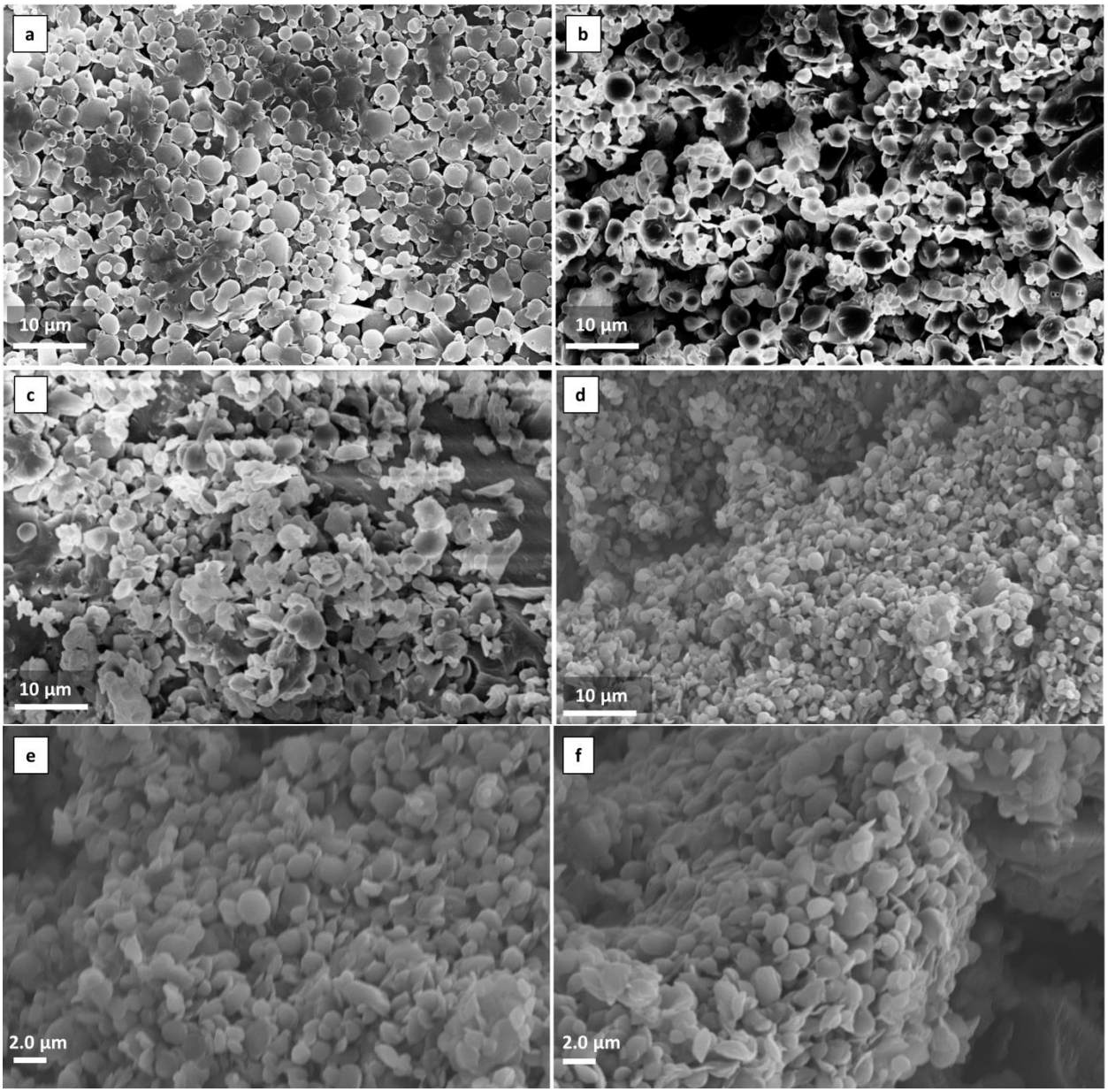
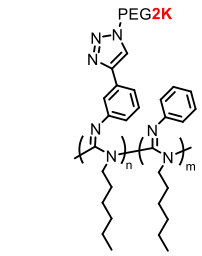
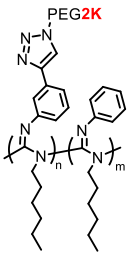


Figure 2S10. SEM micrographs of **(*R*)-70-TRZ-PEG2K-30-Ph** (panels a, b); **(*S*)-70-TRZ-PEG2K-30-Ph** (panel c); **(*R*)-50-TRZ-PEG2K-50Ph** (panels d-f). Scale bar = 10 µm (panels a-d); 2.0 µm (panels e, f)



(*R*)-30-TRZ-PEG2K-70-Ph (n/m, 30:70)



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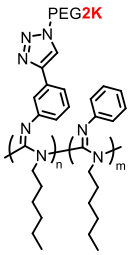


(*S*)-50-TRZ-PEG2K-50-Ph (n/m, 50:50)

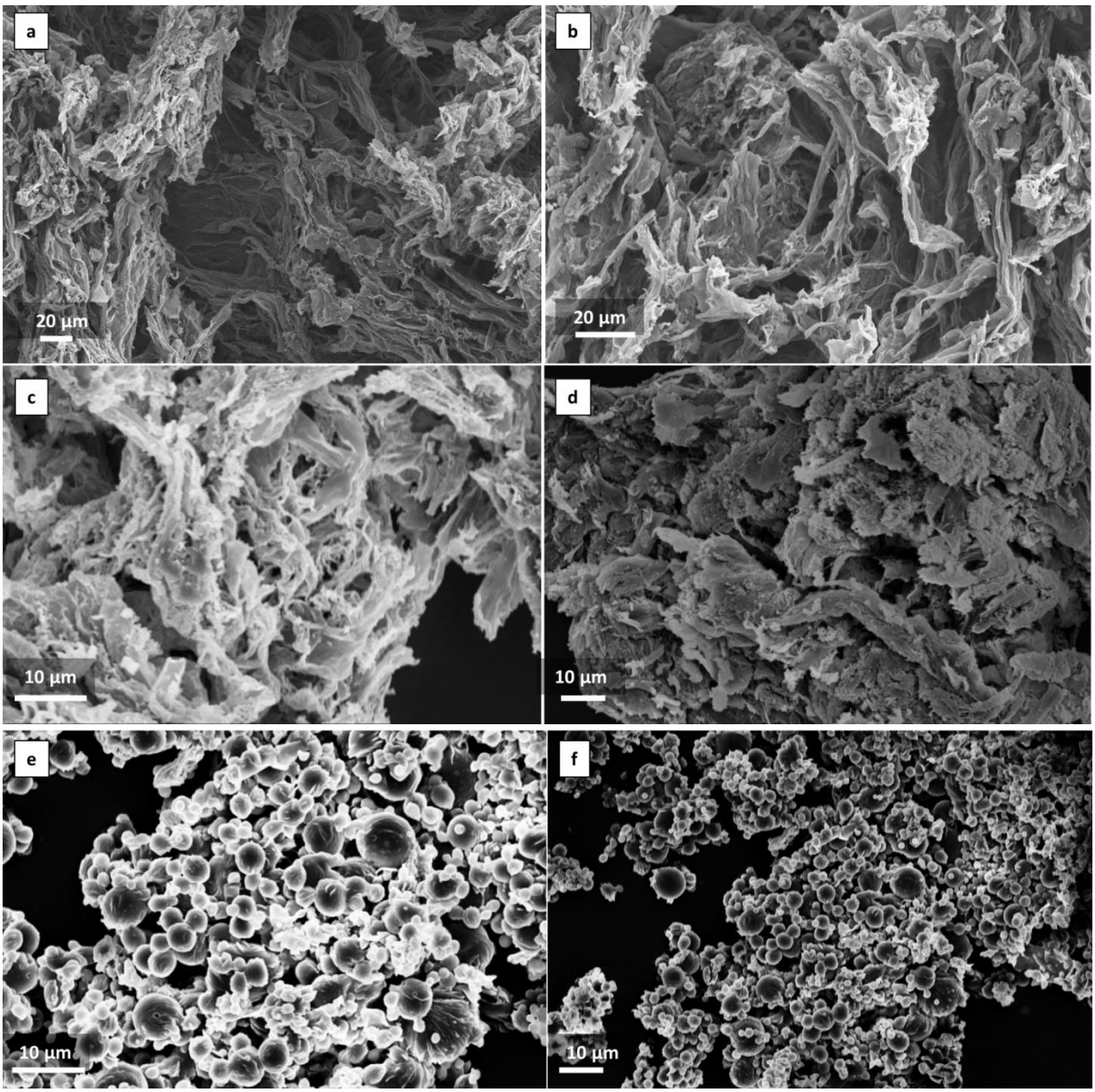


Figure 2S11. SEM micrographs of **(*R*)-30-TRZ-PEG2K-70-Ph** (panels a, b); **(*S*)-30-TRZ-PEG2K-70-Ph** (panels c, d); **(*S*)-50-TRZ-PEG2K-50-Ph** (panels e, f). Scale bar = 20 µm (panels a, b); 10 µm (panels c-f)

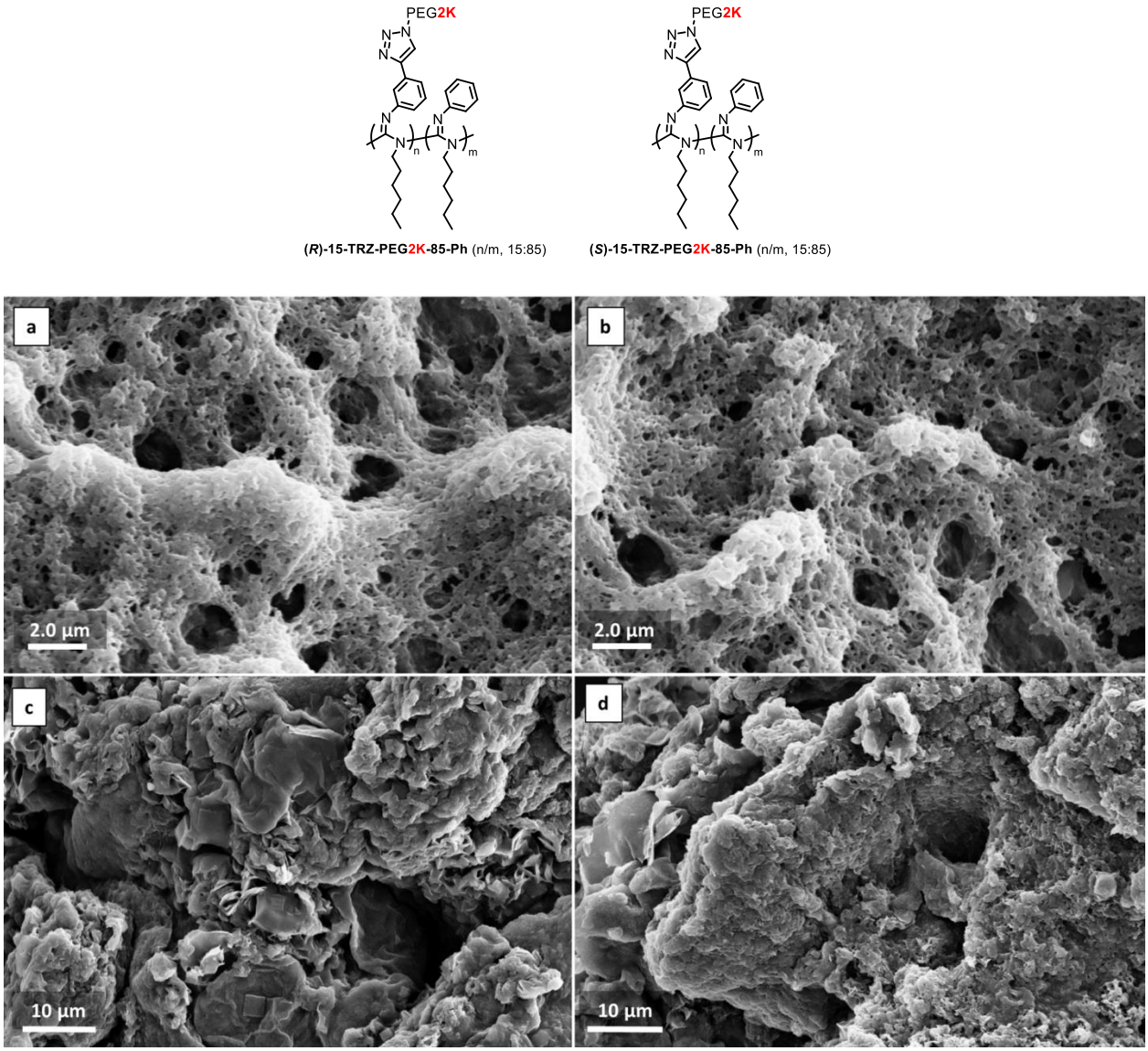


Figure 2S12. SEM micrographs of **(*R*)-15-TRZ-PEG2K-85-Ph** (panels a, b); **(*S*)-15-TRZ-PEG2K-85-Ph** (panels c, d). Scale bar = 2.0 µm (panels a, b); 10 µm (panels c, d)

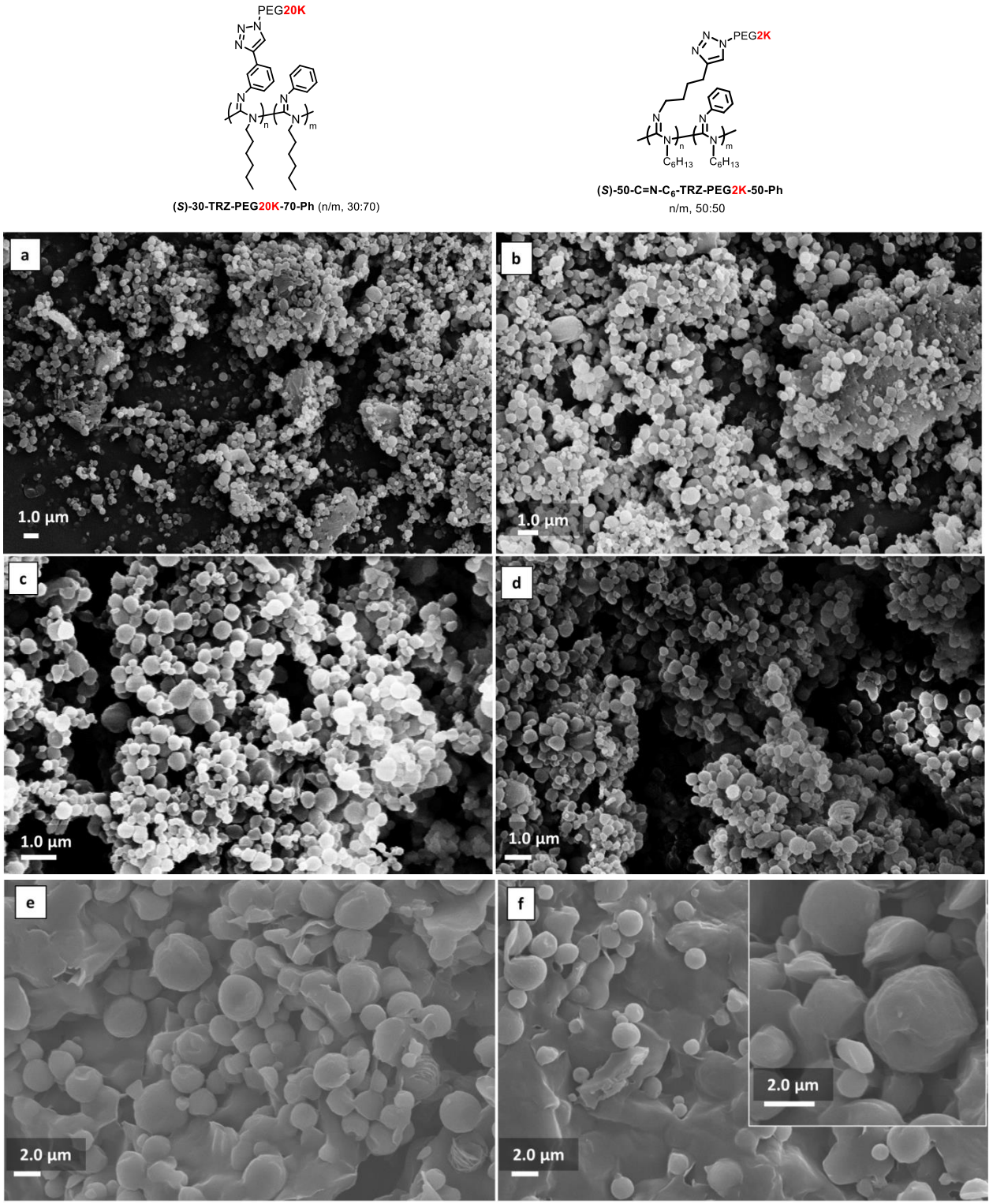


Figure 2S13. SEM micrographs of **(*S*)-30-TRZ-PEG20K-70-Ph** (panels a-d); **(*S*)-50-C=N-C_6-TRZ-PEG2K-50-Ph** (panels e, f). Scale bar = 1.0 µm (panels a-d); 2.0 µm (panels e, f)

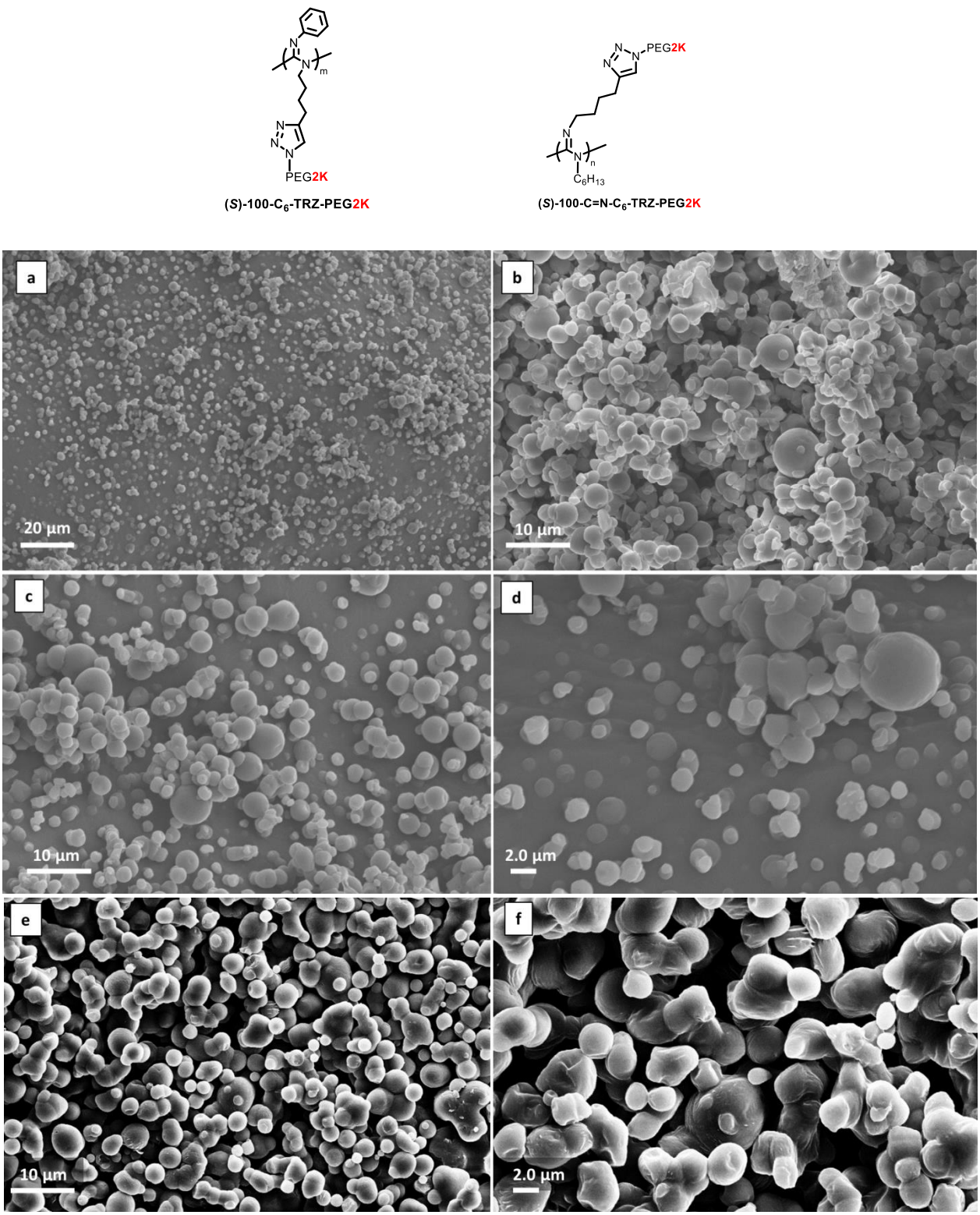


Figure 2S14. SEM micrographs of **(*S*)-100-C_6-TRZ-PEG2K** (panels a-d), **(*S*)-100-C=N-C_6-TRZ-PEG2K** (panels e, f) Scale bar = 20 µm (panel a); 10 µm (panels b, c, e); 2.0 µm (panels d, f)

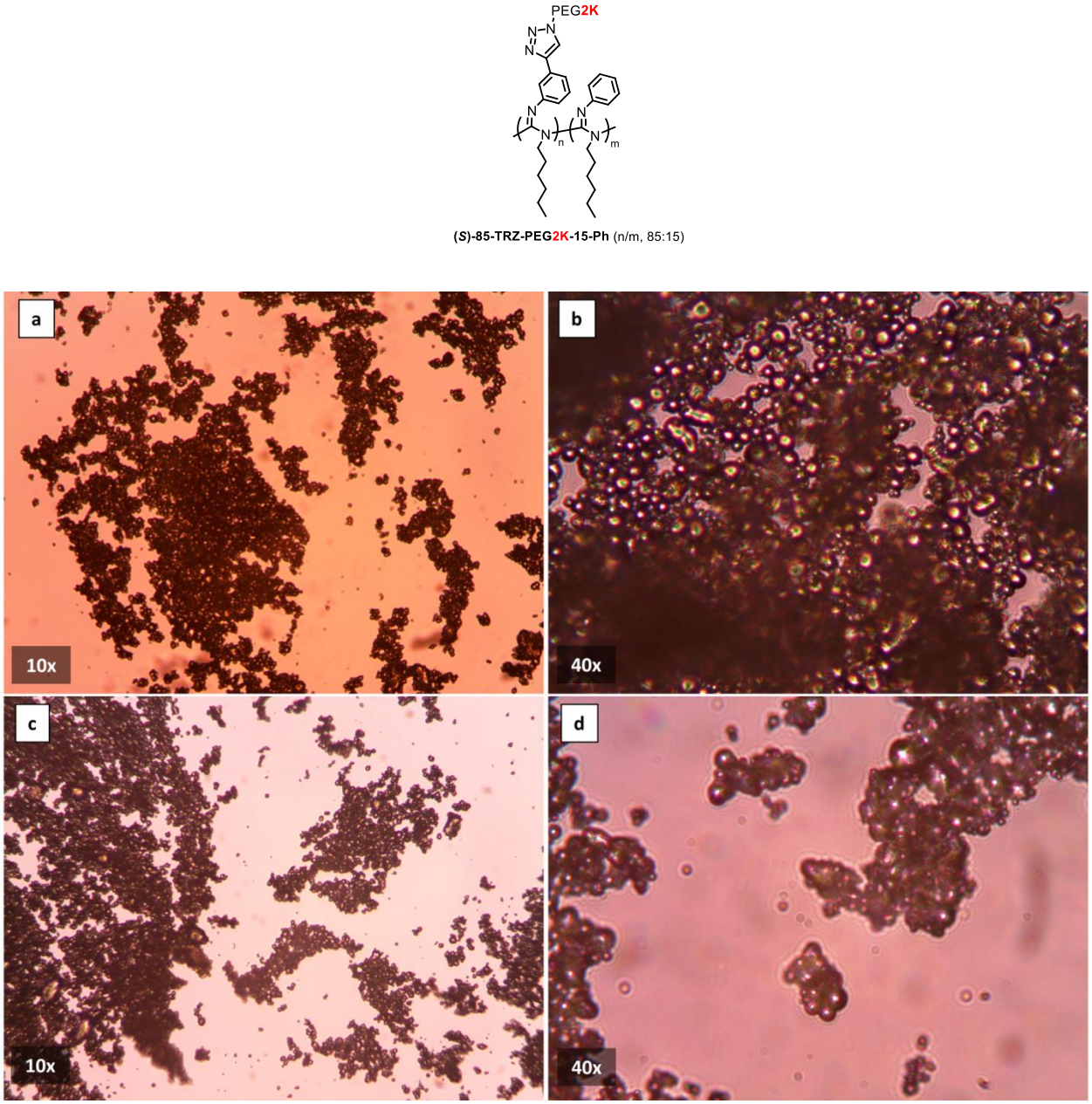
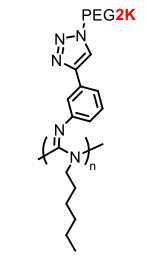


Figure 2S15. Optical micrographs of **(*S*)-85-TRZ-PEG2K-15-Ph** in a form of powder. Magnification = 10x (panels a, c); 40x (panels b, d)



(*S*)-100-TRZ-PEG2K

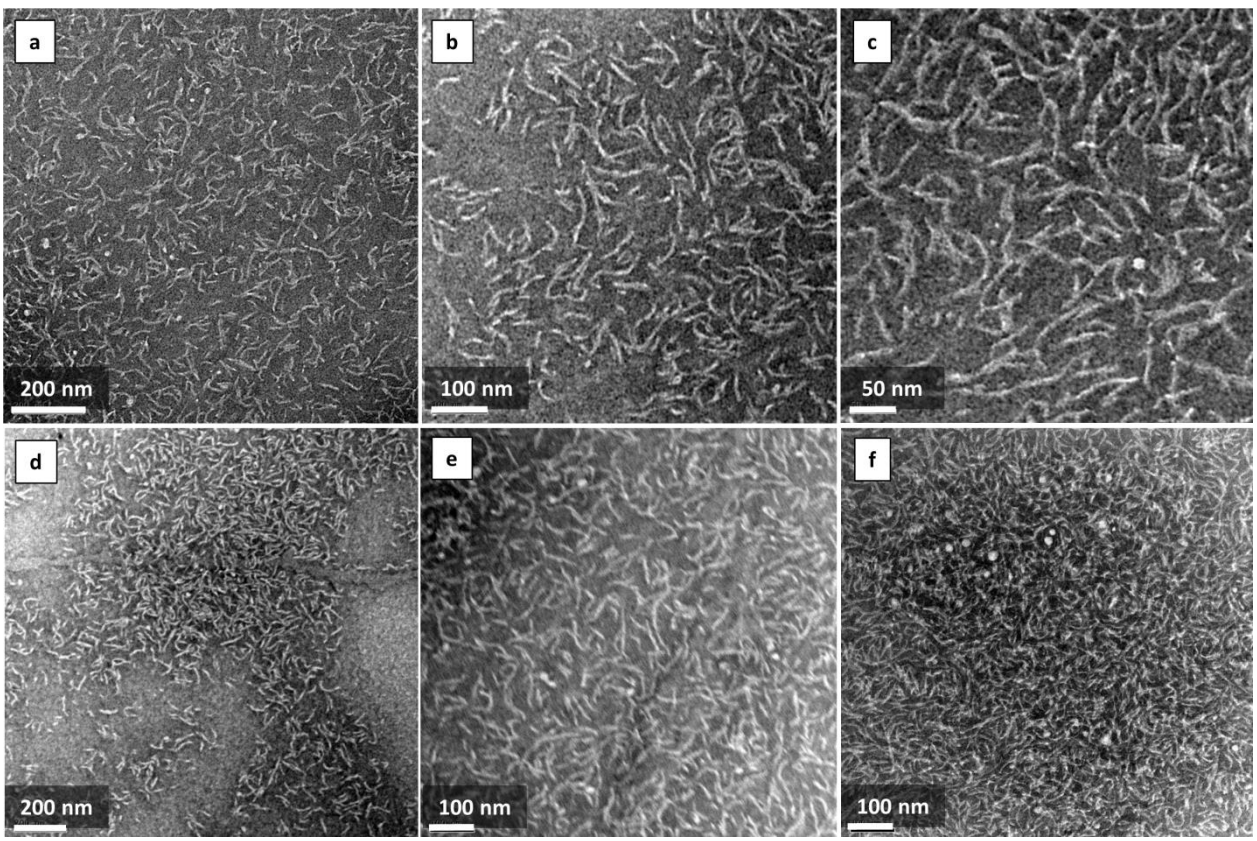


Figure 2S16. TEM micrographs of **(*S*)-100-TRZ-PEG2K** (1.0 mg/mL, panels a-f). Scale bar = 100 nm (panels b, e, f); 200 nm (panels a, d); 50 nm (panel c)

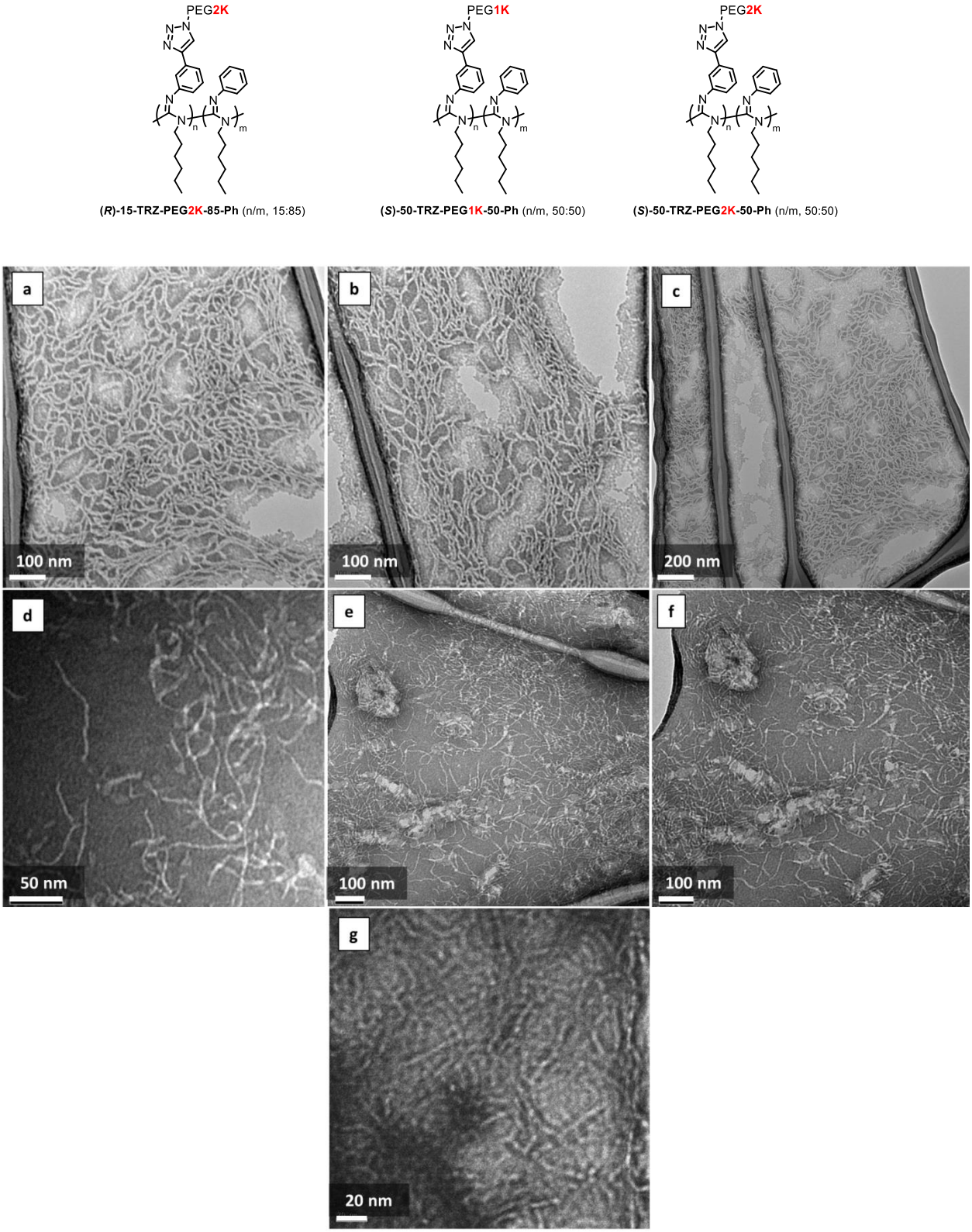
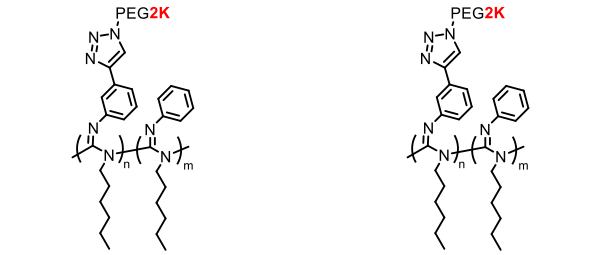


Figure 2S17. TEM micrographs of **(*R*)-15-TRZ-PEG2K-85-Ph** (1.0 mg/mL, panels a-c), **(*S*)-50-TRZ-PEG1K-50-Ph** (0.5 mg/mL, panels d-f), **(*S*)-50-TRZ-PEG2K-50-Ph** (1.0 mg/mL, panel g). Scale bar = 100 nm (panels a, b, e, f); 200 nm (panel c); 50 nm (panel d); 20 nm (panel g)



(*S*)-70-TRZ-PEG2K-30-Ph (n/m, 70:30) (*R*)-70-TRZ-PEG2K-30-Ph (n/m, 70:30)

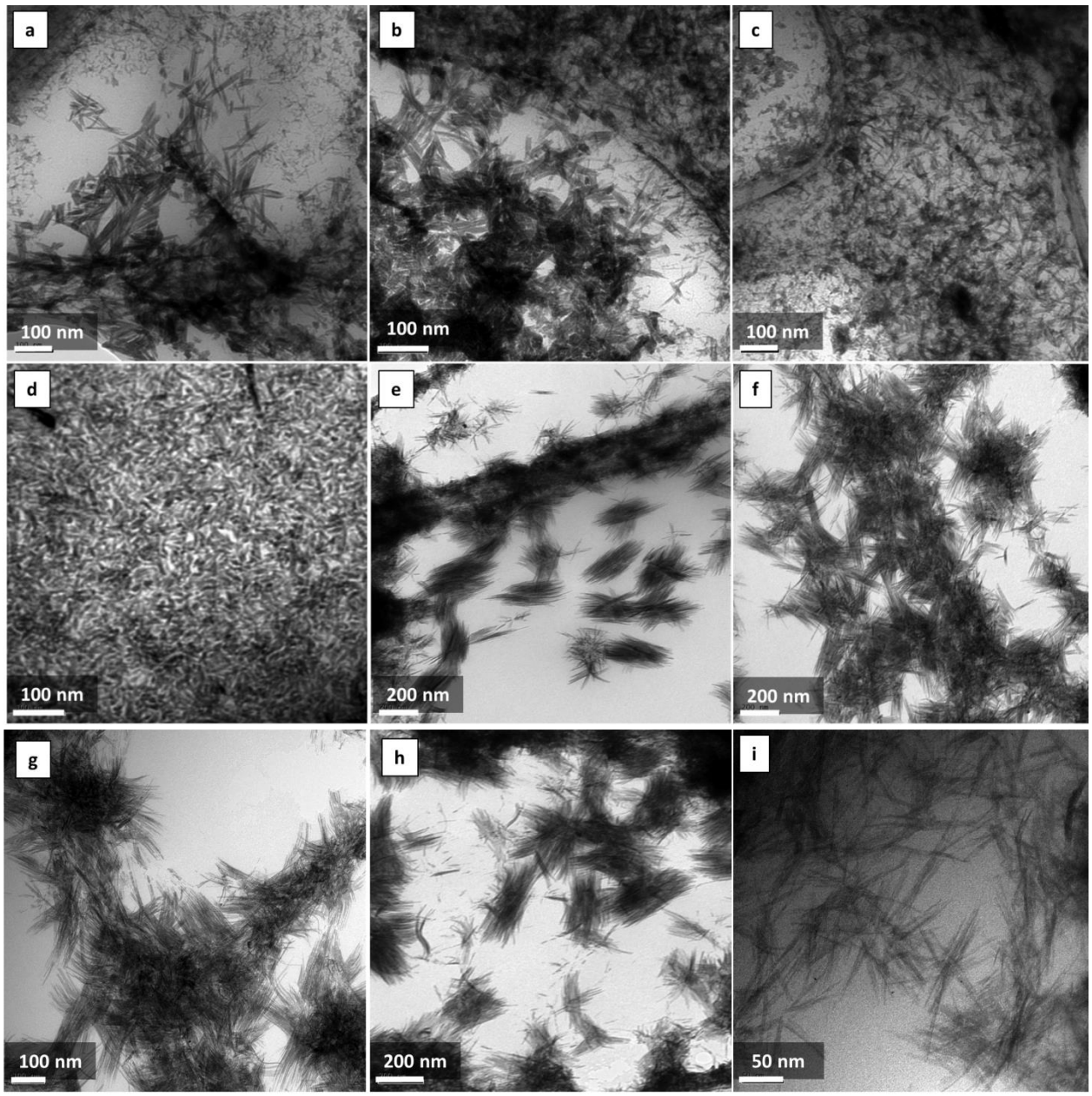
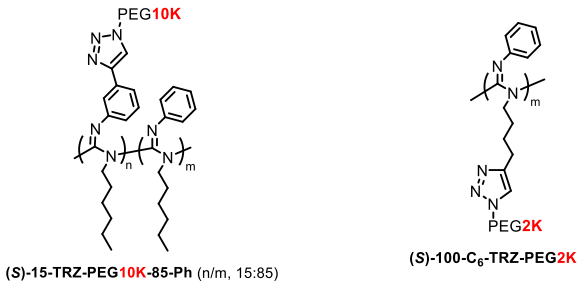


Figure 2S18. TEM micrographs of **(*S*)-70-TRZ-PEG2K-30-Ph** (1.0 mg/mL, panels a-d), **(*R*)-70-TRZ-PEG2K-30-Ph** (1.0 mg/mL, panels e-i). Scale bar = 100 nm (panels a-d, g); 200 nm (panels e, f, h); 50 nm (panel i)



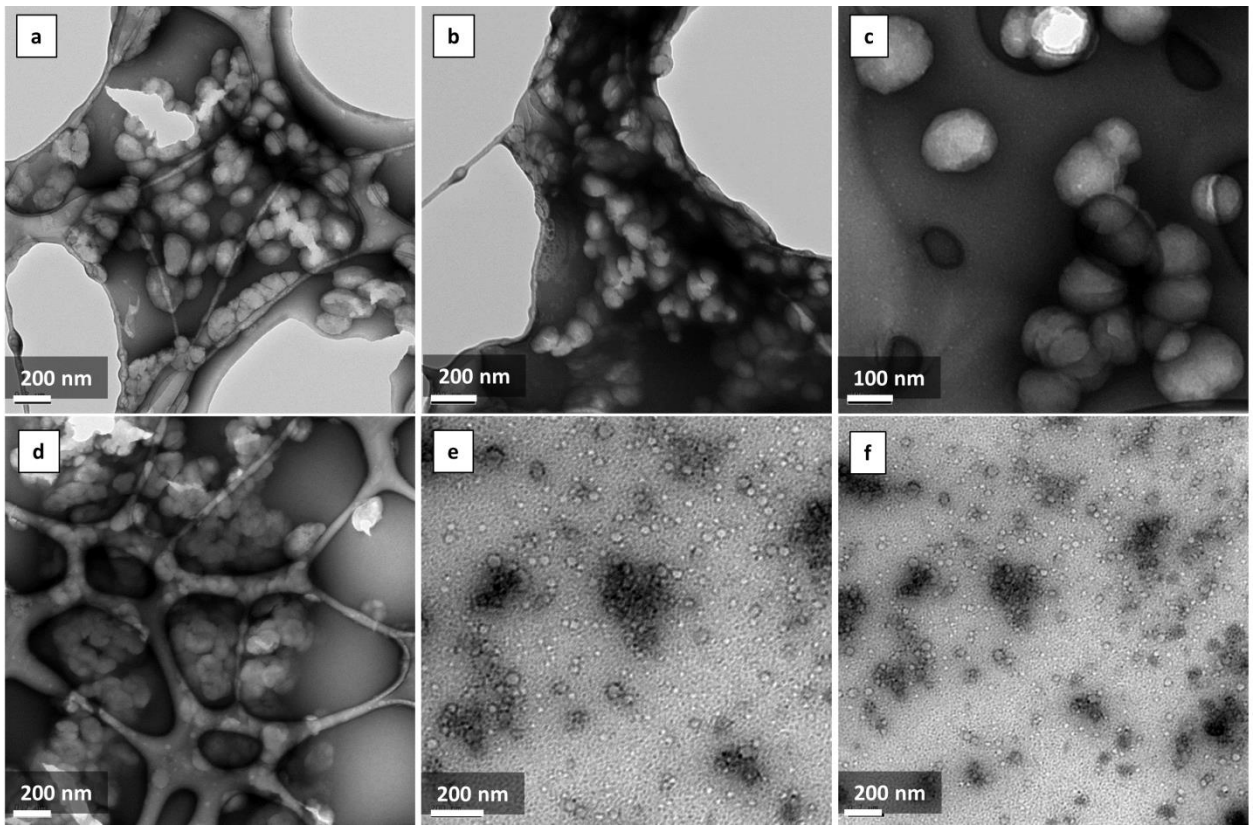
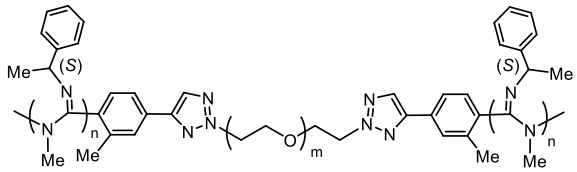


Figure 2S19. TEM micrographs of **(*S*)-15-TRZ-PEG10K-85-Ph** (2.5 mg/mL, panels a, b; 1.25 mg/mL, panel c; 0.625 mg/mL, panel d), **(*S*)-100-C_6-TRZ-PEG2K** (0.5 mg/mL, panels e, f). Scale bar = 100 nm (panel c); 200 nm (panels a, b, d-f)



(*S*)-PPMC-*b*-TRZ-PEG20K-TRZ-*b*-(*S*)-PPMS

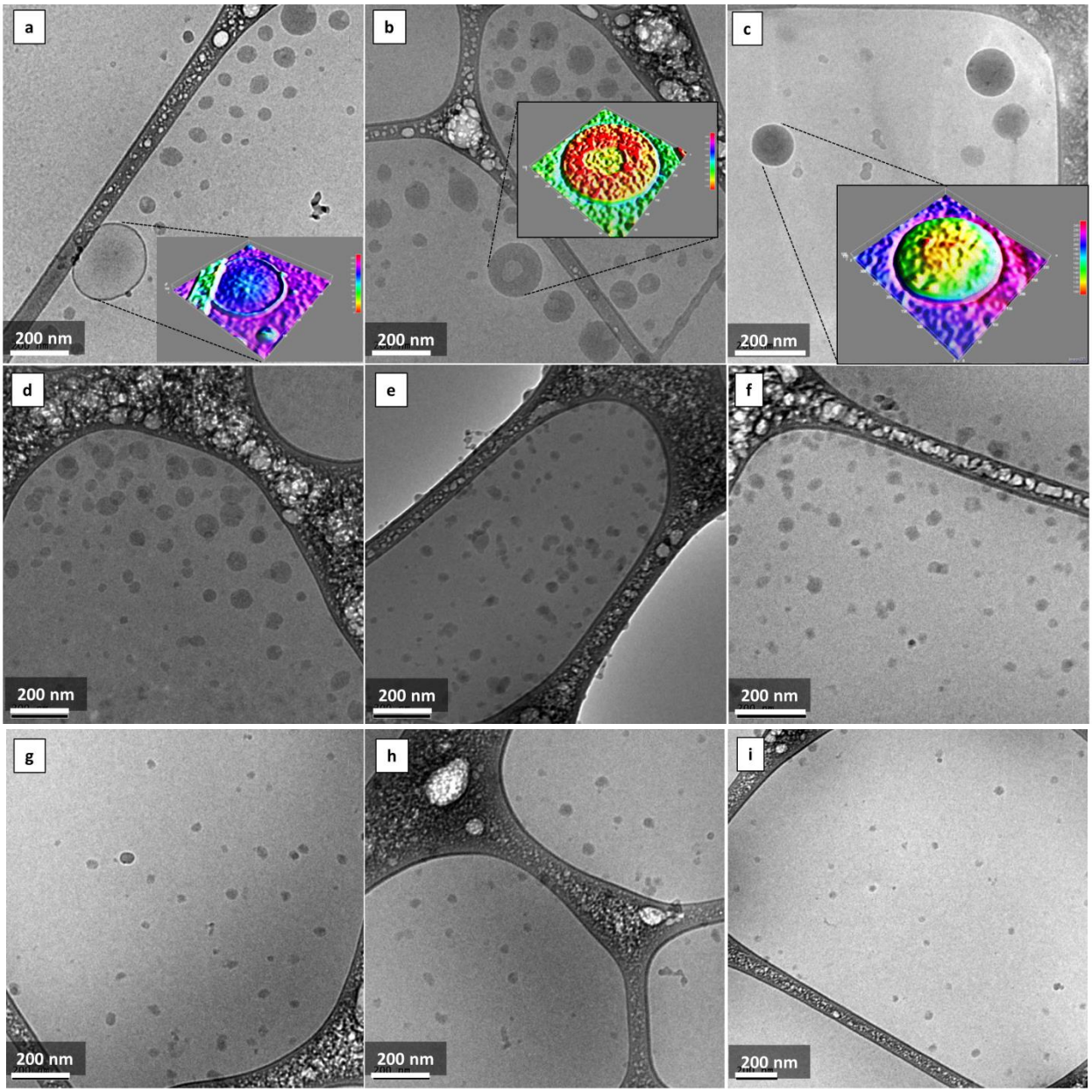
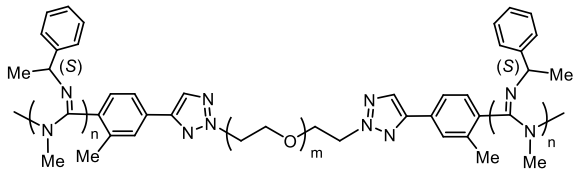


Figure 2S20. TEM micrographs and DLS data for **(*S*)-PPMC-*b*-TRZ-PEG20K-TRZ-*b*-(*S*)-PPMS**[S1] suspension in THF/water (C = 1.0 mg/mL, Z-Average: 215.4 nm, PDI: 0.185, panels a-d; C = 0.5 mg/mL, Z-Average: 97.6 nm, PDI: 0.336, panels e, f; C = 0.25 mg/mL, Z-Average: 76.3 nm, PDI: 0.062, panels g, h; C = 0.125 mg/mL, Z-Average: 75.9 nm, PDI: 0.037, panel i). Scale bar = 200 nm (panels a-i).



(*S*)-PPMC-*b*-TRZ-PEG20K-TRZ-*b*-(*S*)-PPMS

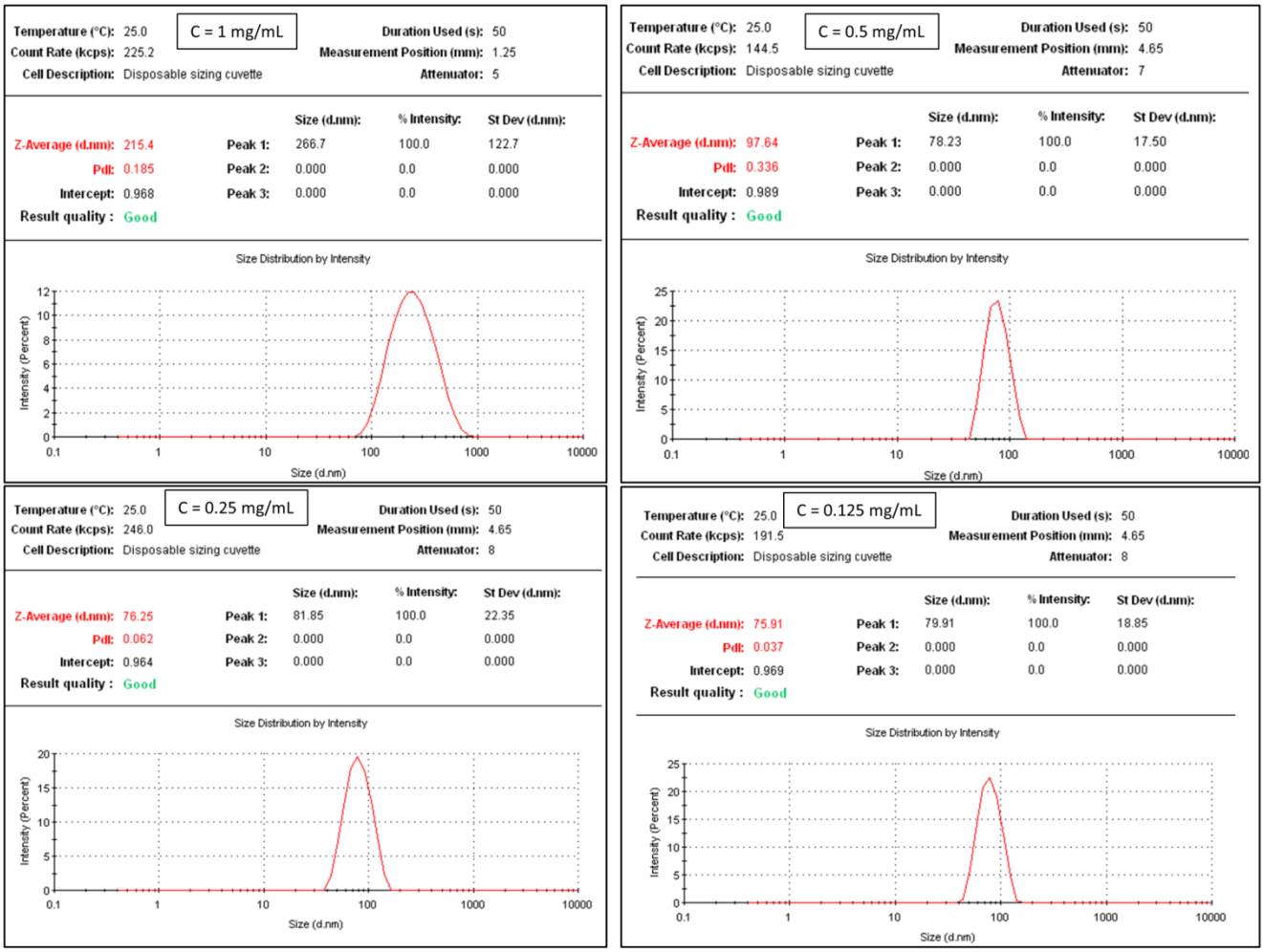


Figure 2S21. DLS plots for **(*S*)-PPMC-*b*-TRZ-PEG20K-TRZ-*b*-(*S*)-PPMS** at different concentrations

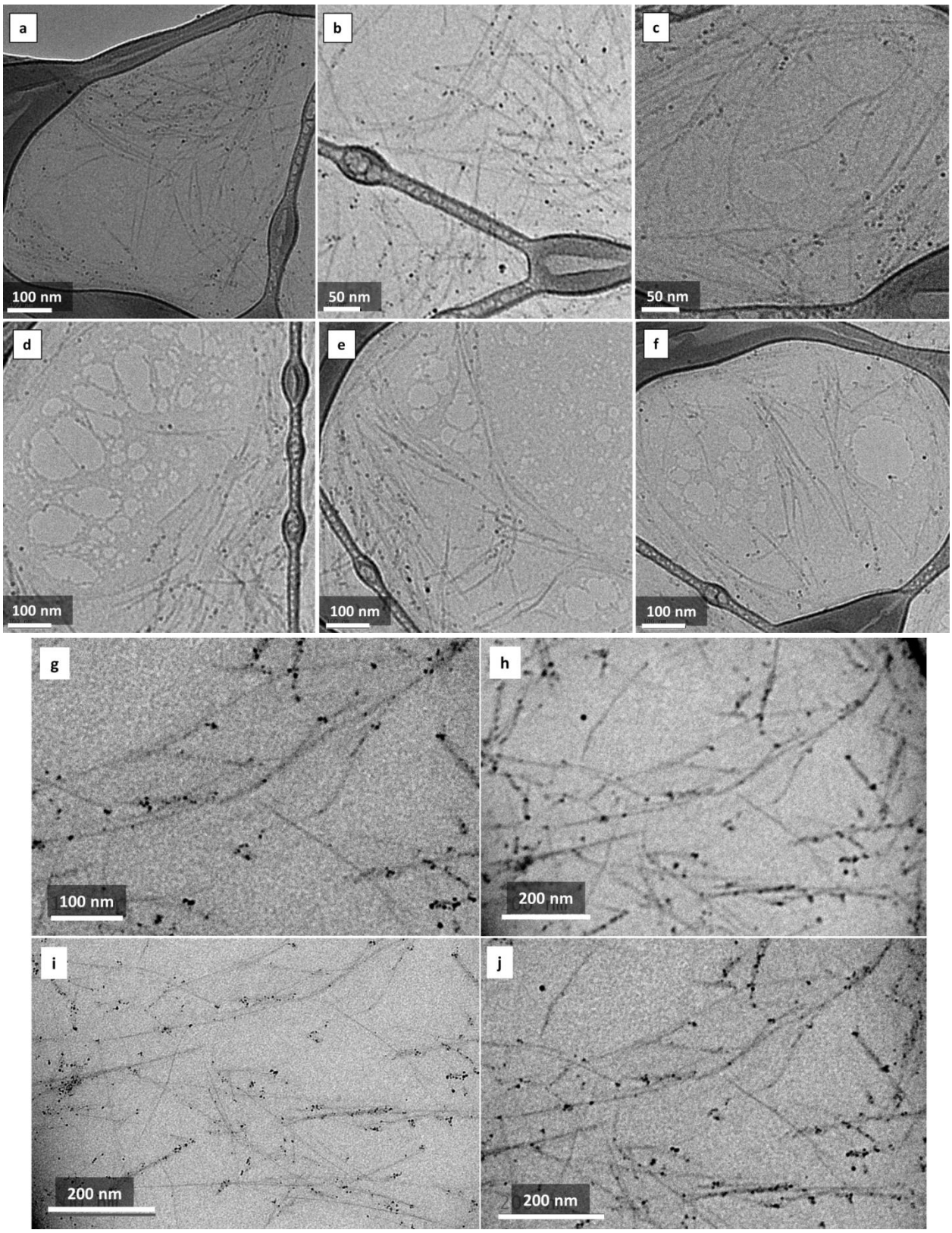


Figure 2S22. TEM micrographs of **(*S*)-50-TRZ-PEG2K-50-Ph@SWCNTs** suspension in water

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): 0.546	Peak 1:	0.546	100.0	4.09
Zeta Deviation (mV): 4.09	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.00251	Peak 3:	0.00	0.0	0.00

Result quality : Good

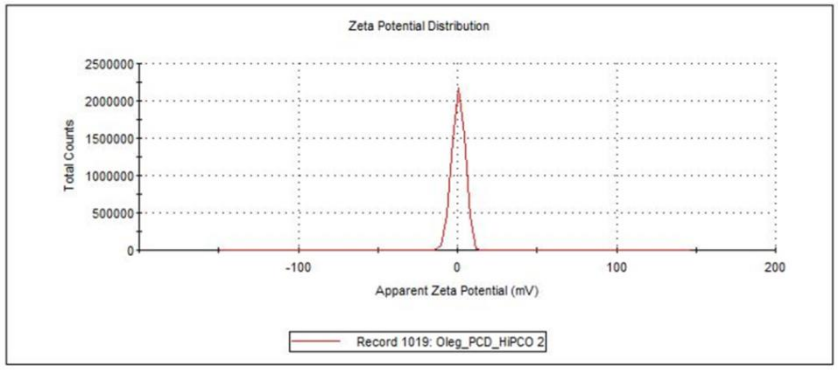


Figure 2S23. DLS plot of **(*S*)-50-TRZ-PEG2K-50-Ph@SWCNTs** suspension in water

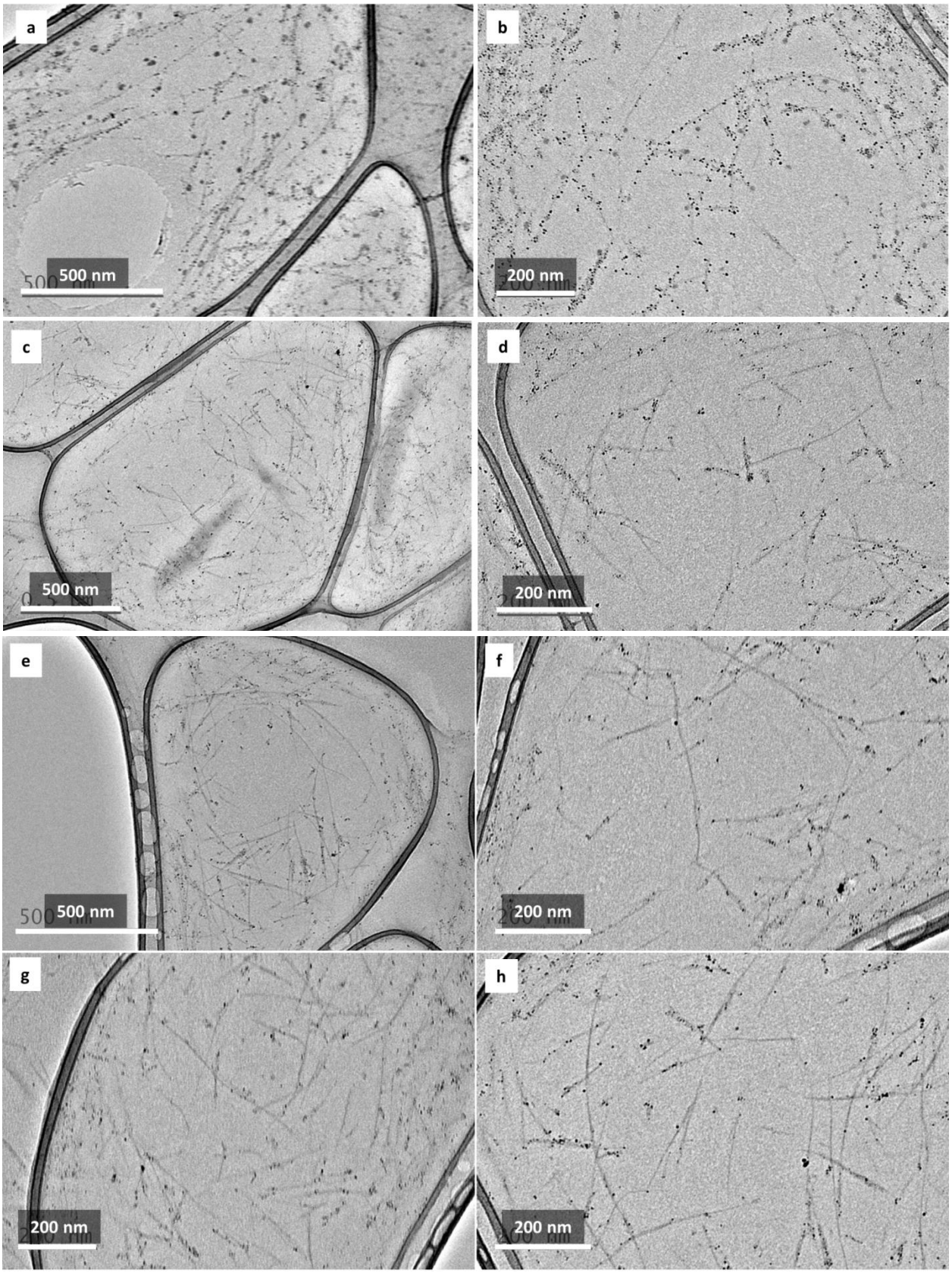


Figure 2S24. TEM micrographs of **(*R*)-85-TRZ-PEG2K-15-Ph@SWCNTs** suspension in water

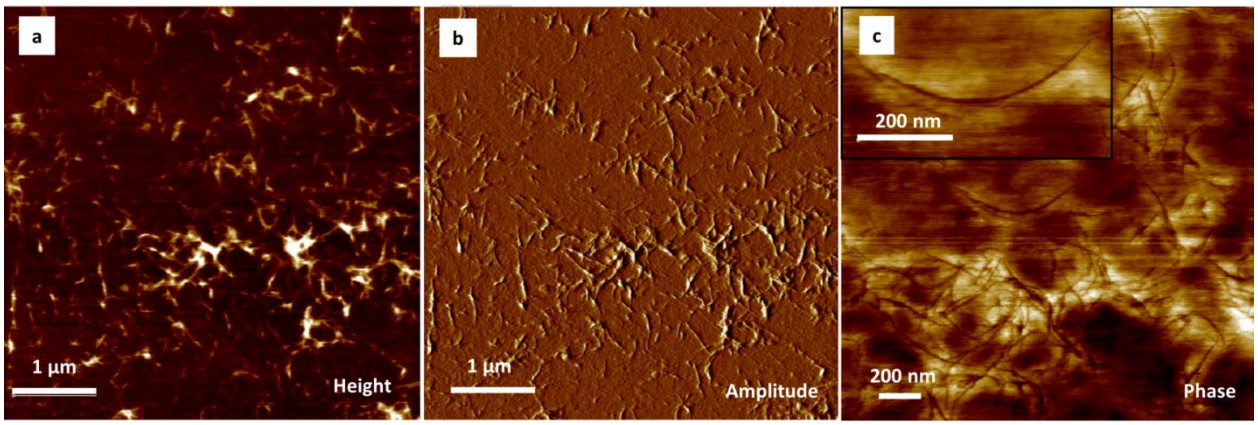


Figure 2S25. Selected height and amplitude AFM micrographs of **(*S*)-50-TRZ-PEG2K-50-Ph@SWCNT** drop-casted from aqueous suspension onto Si-wafer, dried at ambient temperature, and rinsed with DI water; panels a-c. Scale bar = 1 µm (panels a, b), 200 nm (panel c)

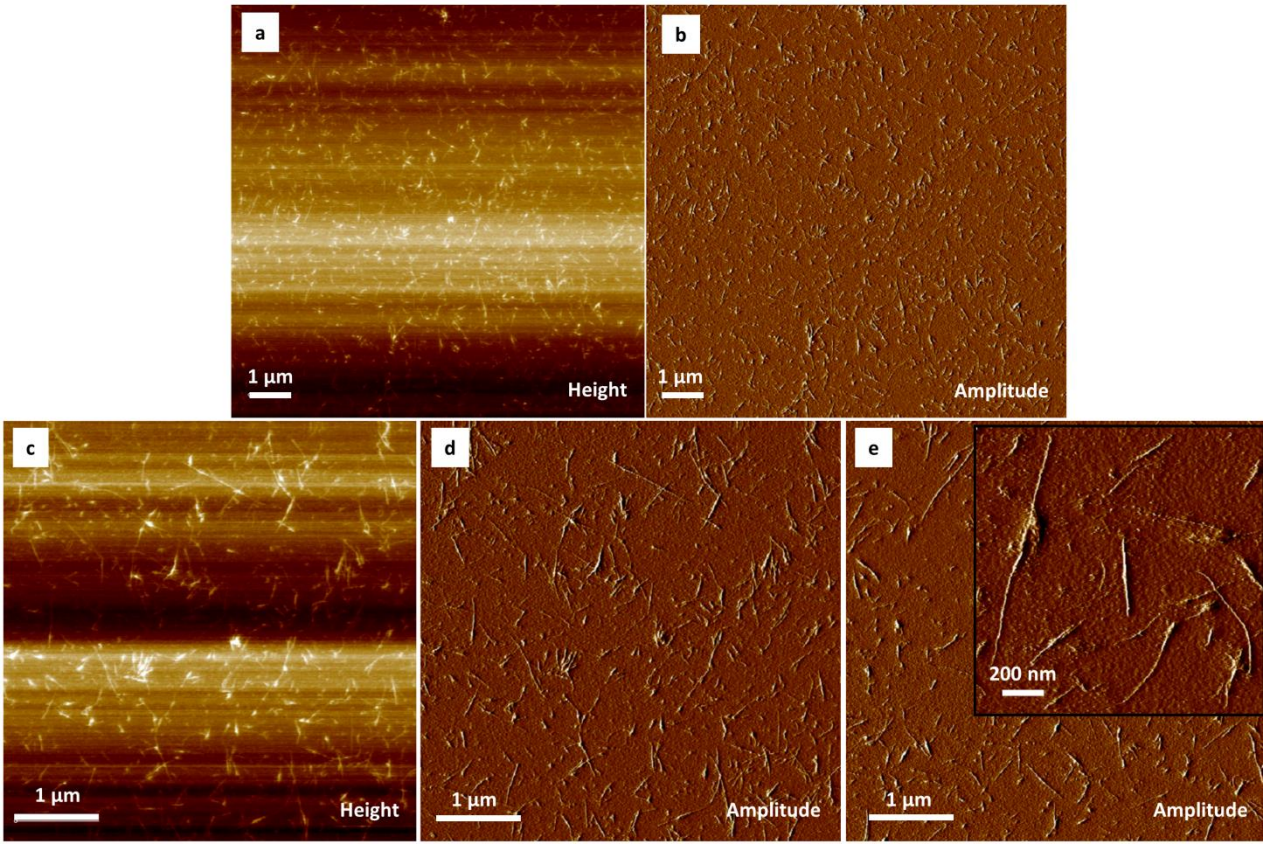


Figure 2S26. Selected height and amplitude AFM micrographs of **(*R*)-85-TRZ-PEG2K-15-Ph@SWCNTs** drop cast from aqueous suspension onto Si-wafer dried at ambient temperature, panels a-e. Scale bar = 1 µm (panels a-e)

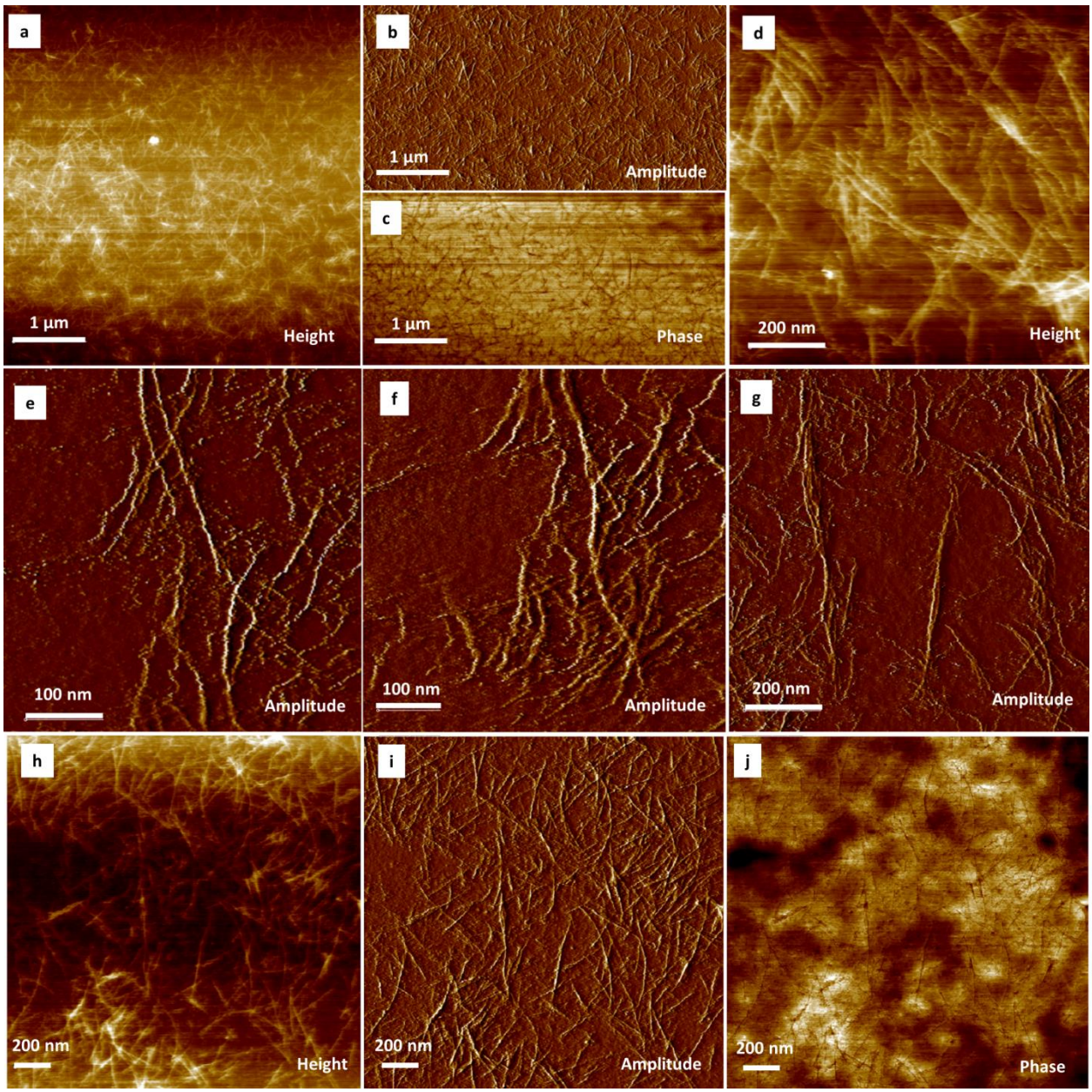


Figure 2S27. Selected height, amplitude, and phase AFM micrographs of **(*R*)-85-TRZ-PEG2K-15-Ph@SWCNTs** drop cast from aqueous suspension onto Si-wafer (after drying at ambient temperature and washing with DI water, panels a-j). Scale bar = 1 µm (panels a-c), 200 nm (panels d, g-j), 100 nm (panels e-f)

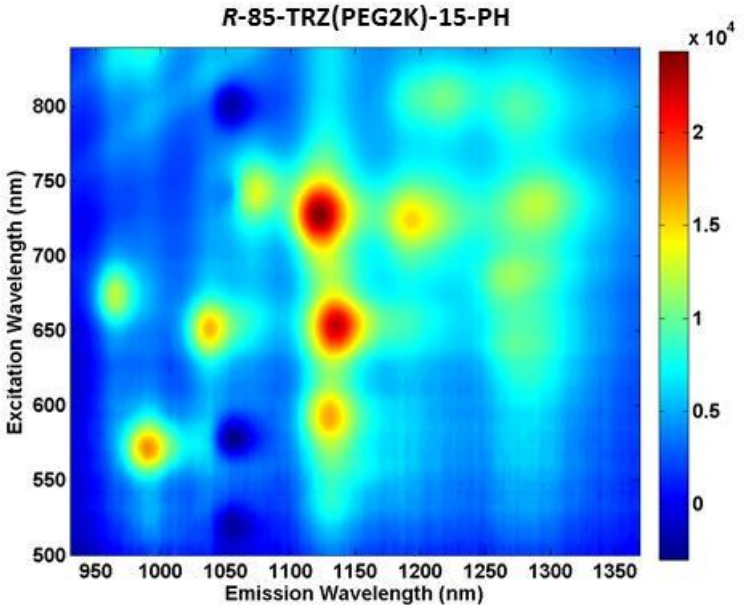


Figure 2S28. Photoluminescence excitation-emission plot of (*R*)-85-TRZ-PEG2K-15-Ph@SWCNTs (C = 7.2 mg/mL)

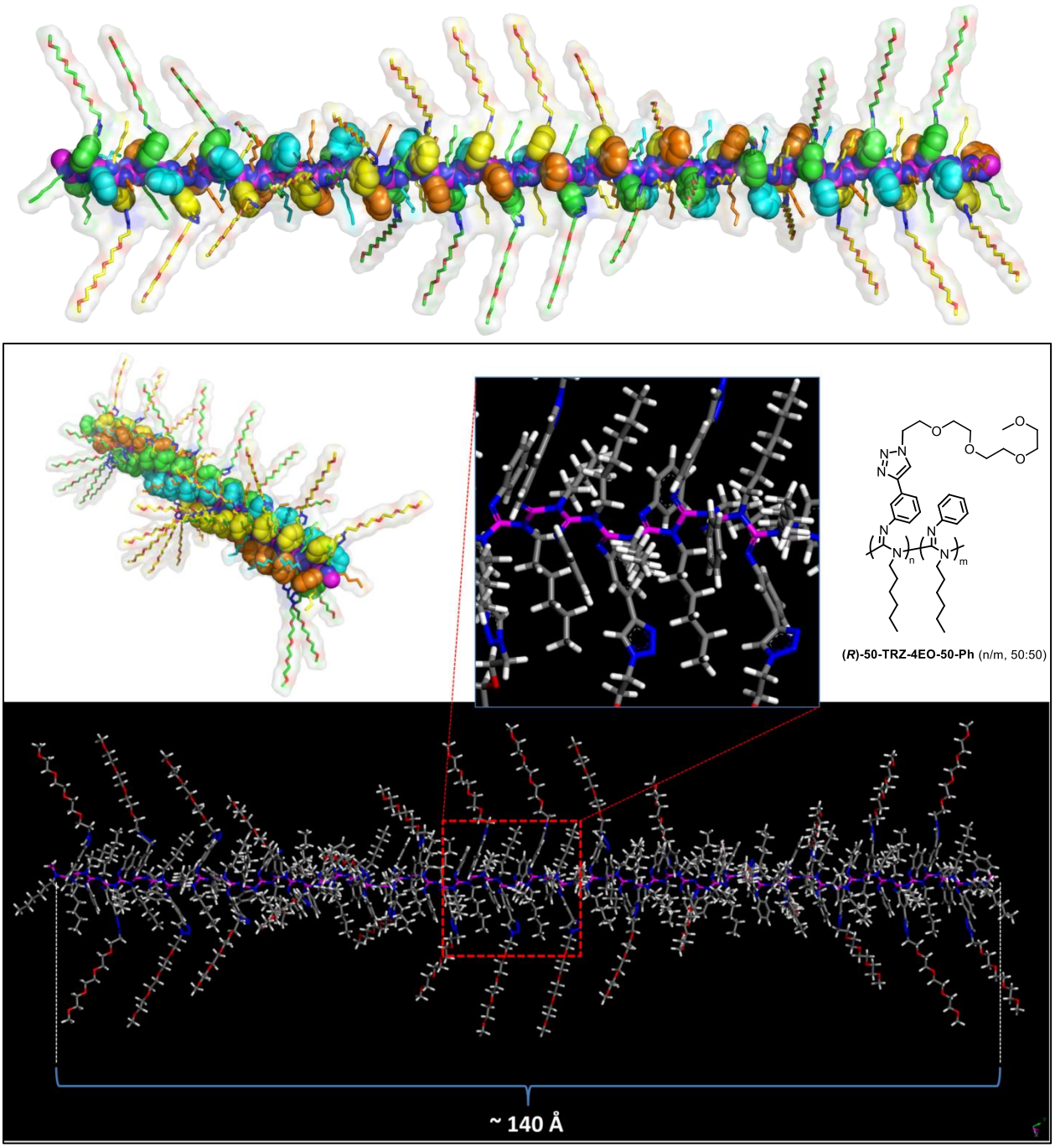


Figure 2S29. Molecular diagram of **(*R*)-50-TRZ-4EO-50-Ph** co-polymer (*P*-helix), **sparsely grafted** scaffold. Shown here is 61-mer segment of the polymeric chain with rows of substituents (each depicted in its own colour, *i.e.*, orange, yellow, cyan, and green, correspondingly) tuned in a helical fashion around a polycarbodiimide scaffold (magenta). Lower panels display all-atom model of the same scaffold featuring its total length (~ 140 Å) as calculated using Molecular Mechanics, Forcite, Universal Force Field, E_{total} = 95307.97 kcal/mol (initial structure), E_{total} = 3875.55 kcal/mol (final structure). Animated version of structure is uploaded as a separate cartoon.

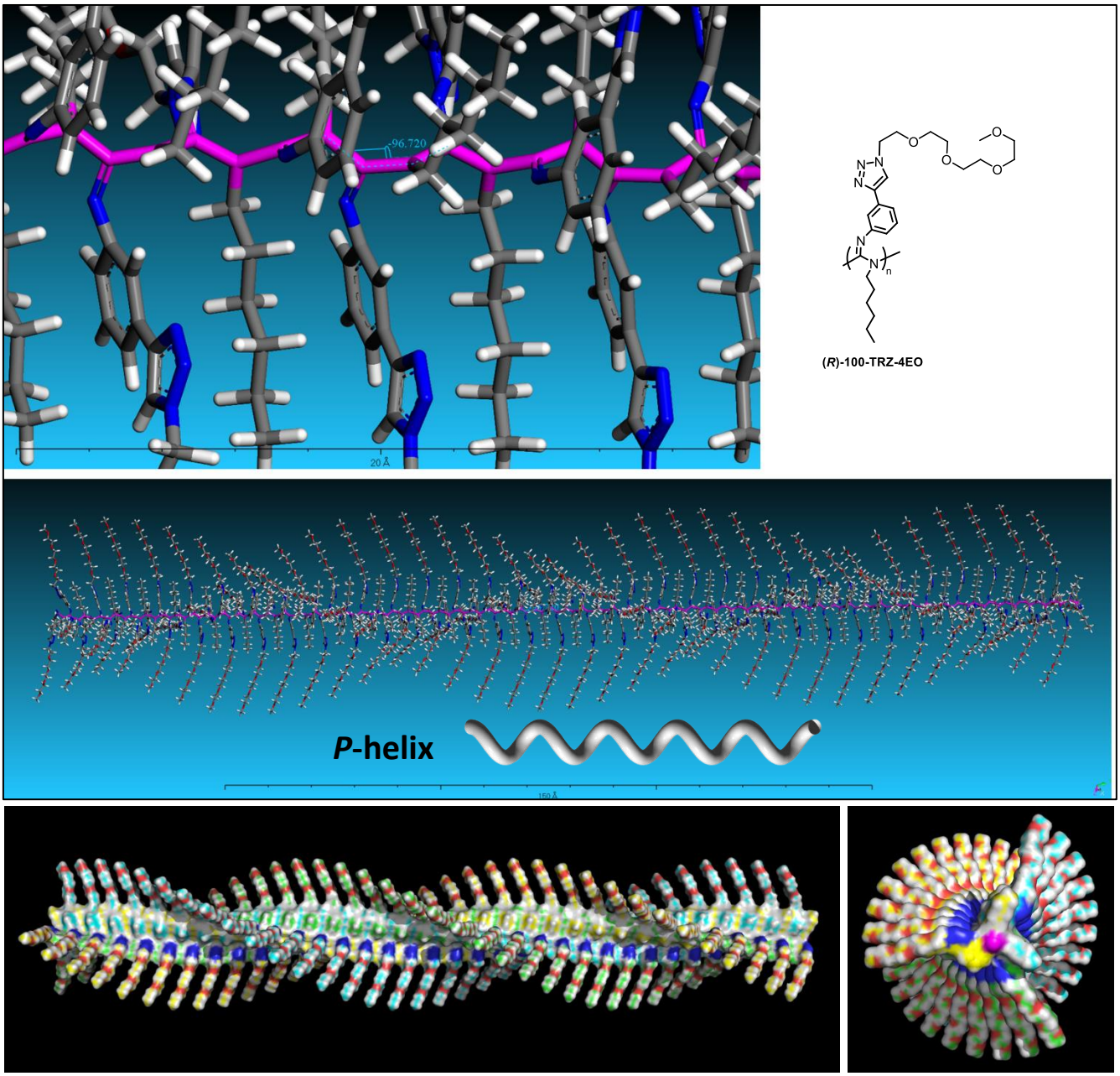
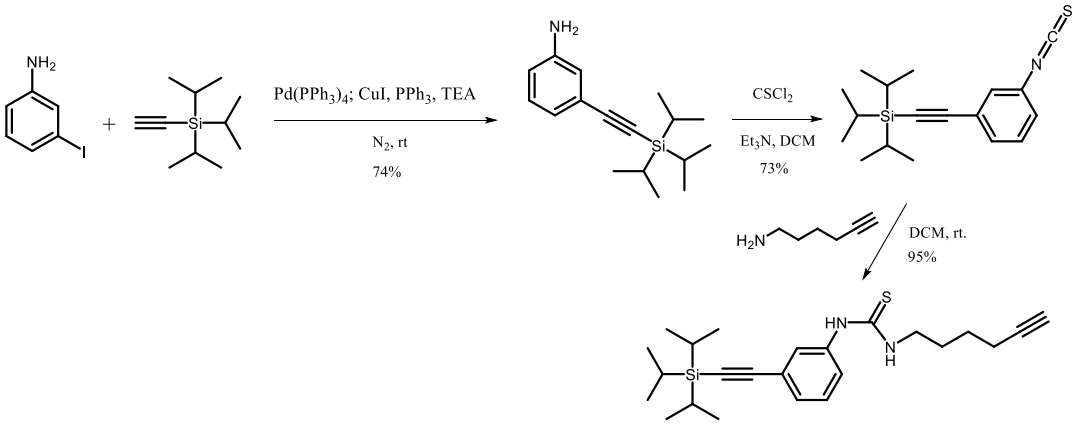
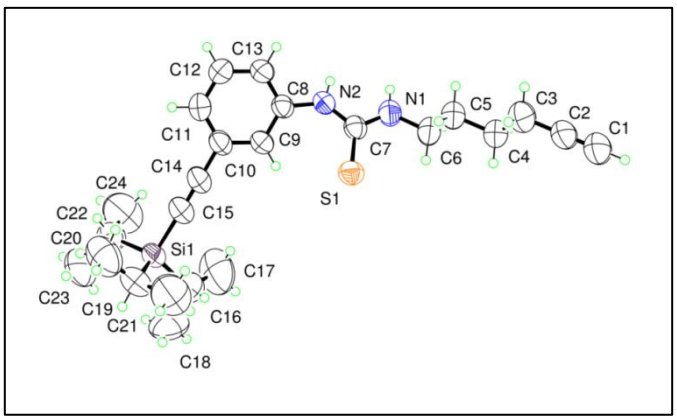


Figure 2S30. Molecular diagram of **(*R*)-100-TRZ-4EO** homopolymer (*P*-helix), **densely grafted** scaffold. Shown here is 100-mer segment of the polymeric chain with 3 rows of substituents (each depicted in its own colour, *i.e.*, yellow, cyan, and green, correspondingly) tuned in a helical fashion around a polycarbodiimide scaffold (magenta). Lower panels display all-atom model of the same scaffold with total length of ~ 238 Å and the torsion angle (-96.7°) as calculated using Molecular Mechanics, Forcite, Dreiding Force Field, E_{total} = 1517937254.53 kcal/mol (initial structure), E_{total} = 12255.03 kcal/mol (final structure).



TIPS-thiourea



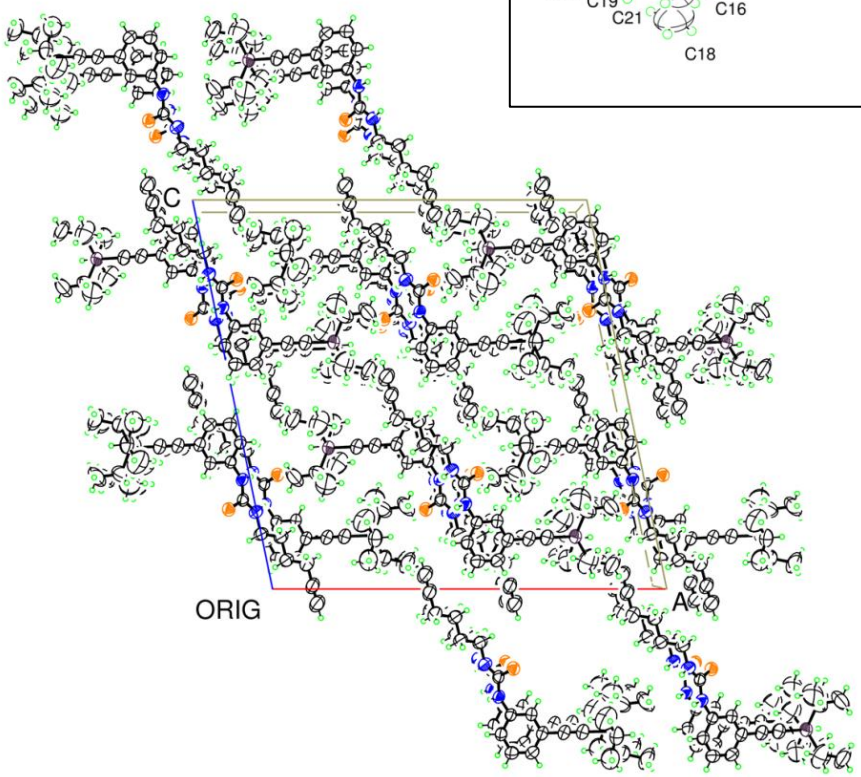


Figure 2S31. Synthesis,[9d] molecular structure, and unit cell diagram of TIPS-protected thiourea

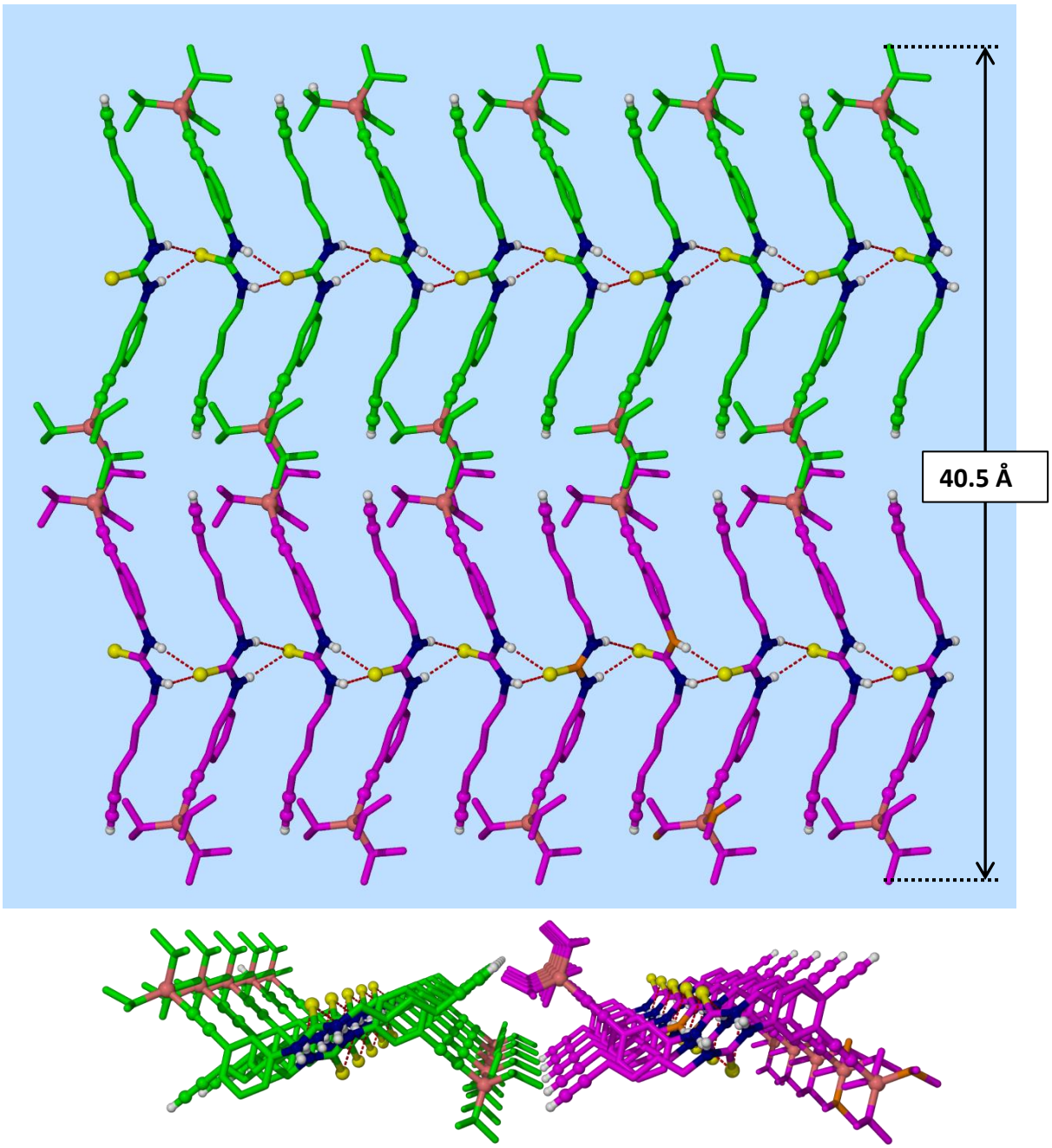


Figure 2S32. NH…S=C contacts in TIPS-protected thiourea, 2.55 and 2.69 Å, correspondingly (front and side views of the two adjacent rows of molecules); Si atoms depicted as light brown balls, sulfur atoms are shown as yellow balls

References

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(S2) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115-119.

(S3) G. M. Sheldrick, *Acta Crystallogr. Sect. C-Struct. Chem.*, 2015, **71**, 3-8.