

Supporting information for

**New Self-Assembled Supramolecular Polymers Formed by Self-
Complementary Sextuple Hydrogen Bond Motifs**

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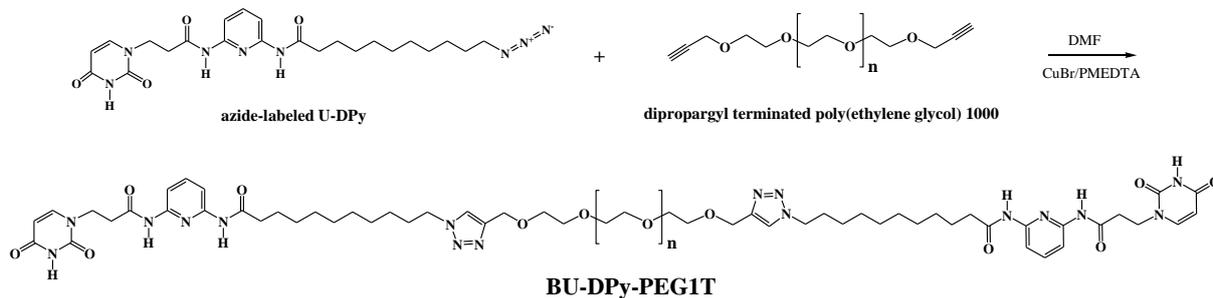
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	Pages
Index	S1
Syntheses	S2
Variable Temperature ¹H NMR Experiments	S8
Isothermal Crystallization Kinetics	S10
Diffusion NMR Experiments	S12
FT-IR Spectra	S13
Polarized Optical Microscopy	S14
Dynamic Light Scattering Analysis	S15
References	S16

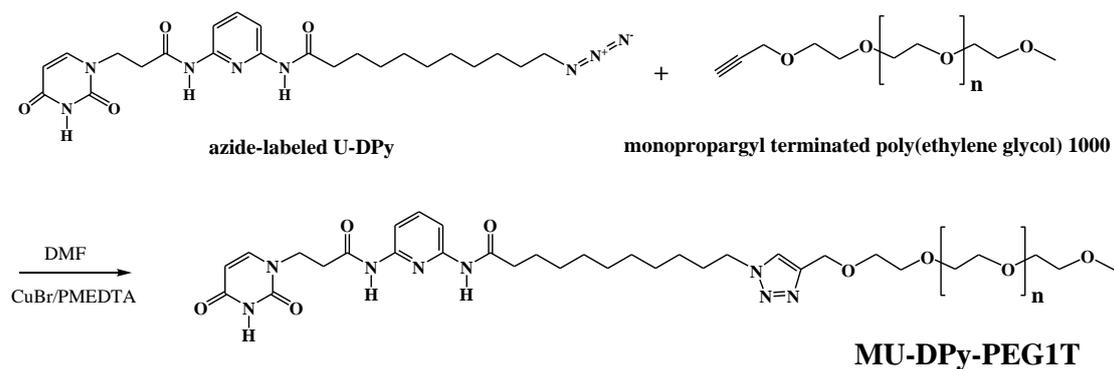
Syntheses

Synthesis of BU-DPy-PEG1T



Dipropargyl terminated poly(ethylene glycol) 1000, Dipropargyl PEG 1000 was synthesized from commercial PEG 1000 according to the procedures described previously.^{S1} Dipropargyl PEG 1000 (2.00 g, 1.82 mmol) and azide-based U-DPy⁴ (0.97 g, 2.00 mmol) were dissolved in DMF (20 mL) and then the resulted solution was purged with a dry argon atmosphere for 10 min. N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA; 35.3 μ L, 0.014 mmol) was added via syringe, leading the mixture to becoming homogeneous and then the solution was degassed through three freeze/thaw evacuation cycles. Upon the addition of CuBr (0.002 mg, 0.02 mmol), the color of the solution was gradually changed from light blue to light green. The reaction mixture was heated to 60 °C and the reaction was allowed to proceed for 36 h. After cooling to 25 °C, the reaction mixture was passed through an aluminum oxide column to remove the Cu(II) catalyst. Finally, the solvent was evaporated, and the residue was purified by column chromatography using silica gel and 30% tetrahydrofuran/methanol as eluents to give as a slightly gray powder of 2.59 g and yield = 90%. Elemental analysis: (The average number of ethylene glycol repeat units for 1000 Da PEG is 23.) found (%): C, 55.52; H, 7.78; N, 10.69; O, 26.01.

Synthesis of MU-DPy-PEG1T



This compound was prepared as described in BU-DPy-PEG1T except the use of replacing by monopropargyl PEG 1000 (2.00 g, 1.82 mmol). The product was isolated by column chromatography using silica gel and 30% tetrahydrofuran/methanol as eluents to give a yellow viscous oil of 2.22 g and yield = 88%. Elemental analysis: (The average number of ethylene glycol repeat units for 1000 Da PEG is 23.) found (%): C, 54.38; H, 7.30; N, 6.68; O, 31.64.

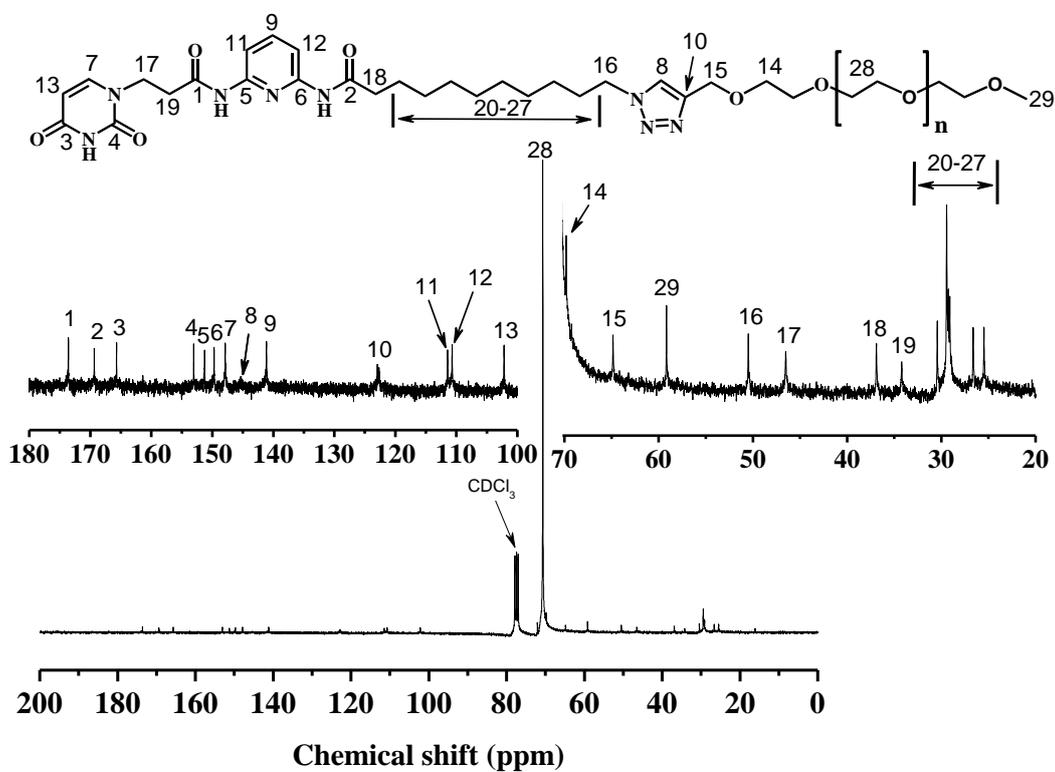
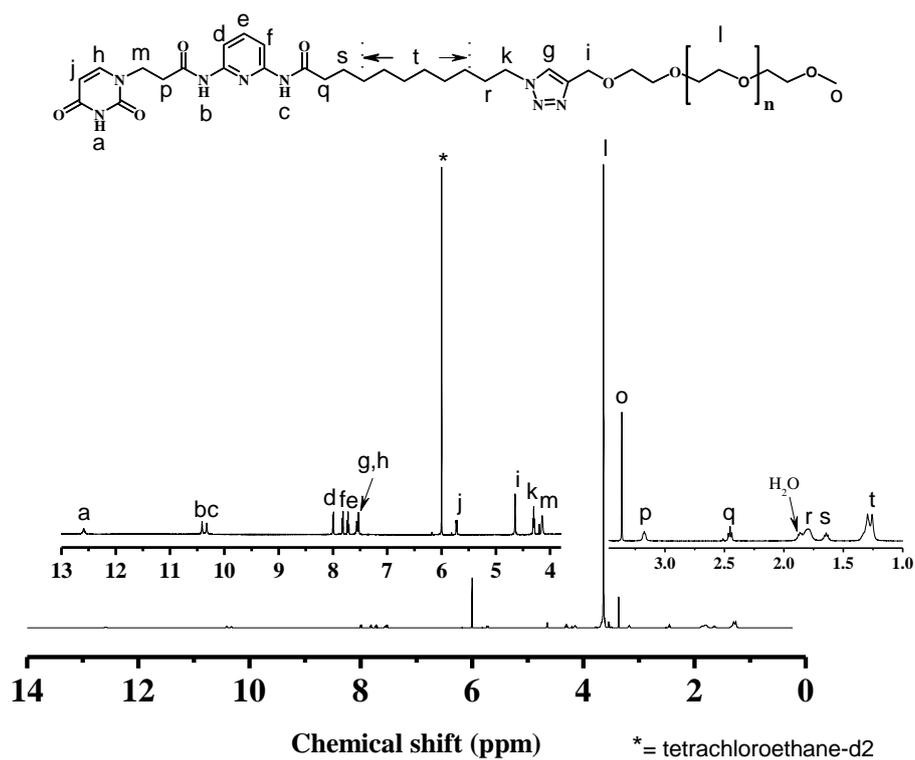


Figure S1. ¹H and ¹³C NMR spectra of MU-DPy-PEG1T.

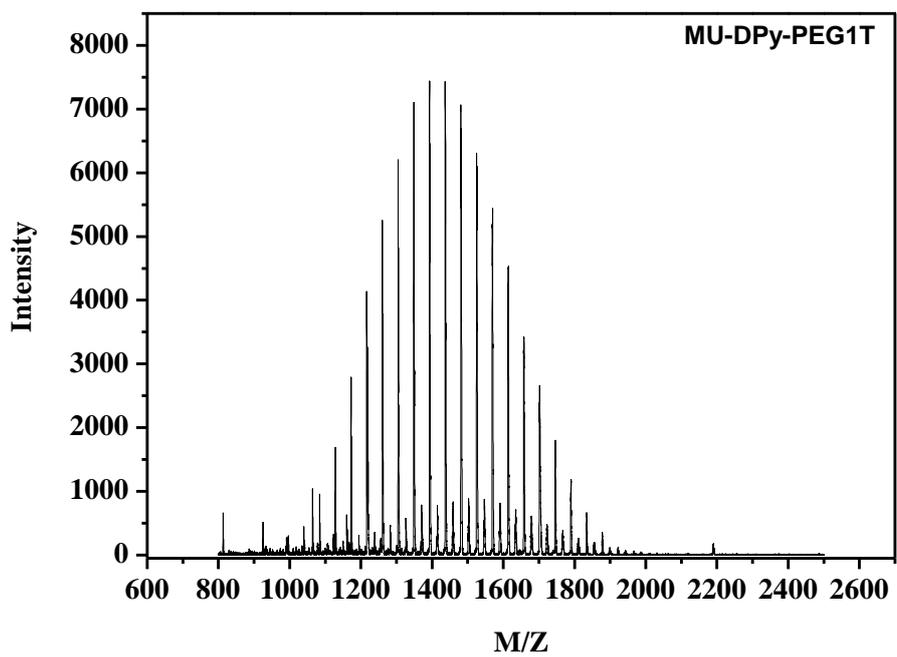


Figure S2. MALDI-TOF mass spectrum of MU-DPy-PEG1T.

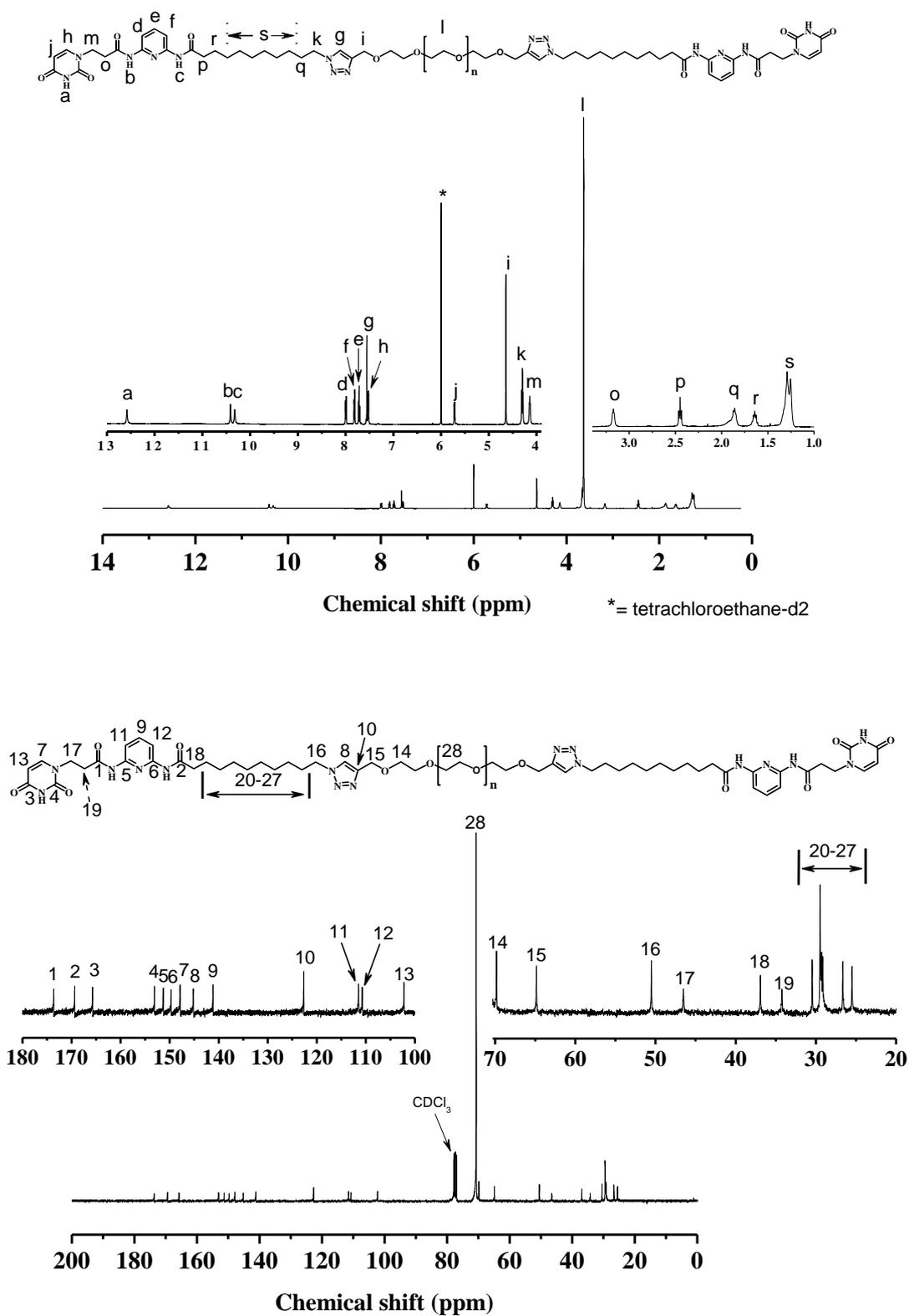


Figure S3. ^1H and ^{13}C NMR spectra of BU-DPy-PEG1T.

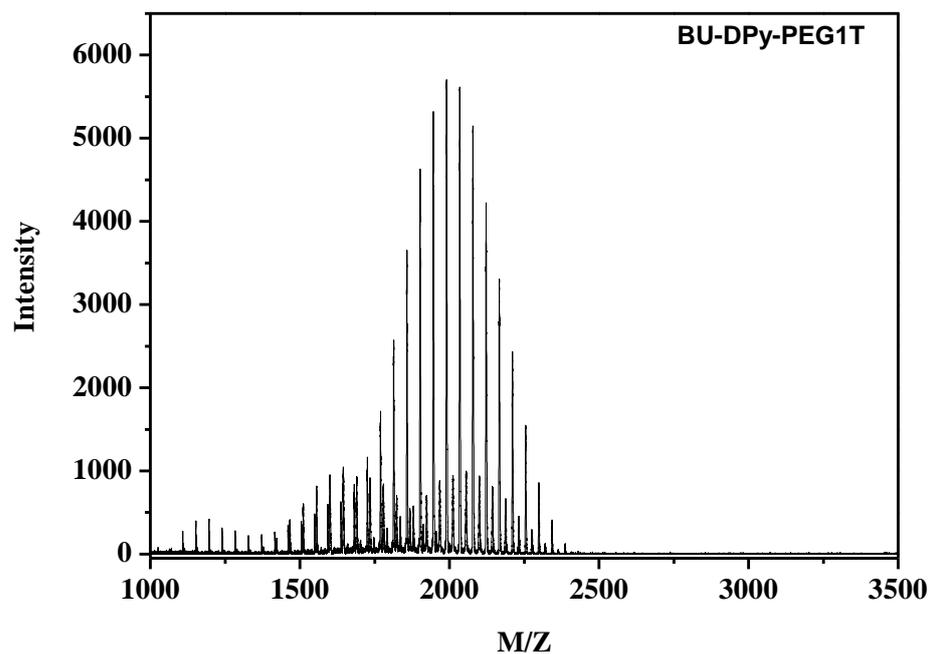


Figure S4. MALDI-TOF mass spectrum of BU-DPy-PEG1T.

Variable-Temperature NMR Experiments

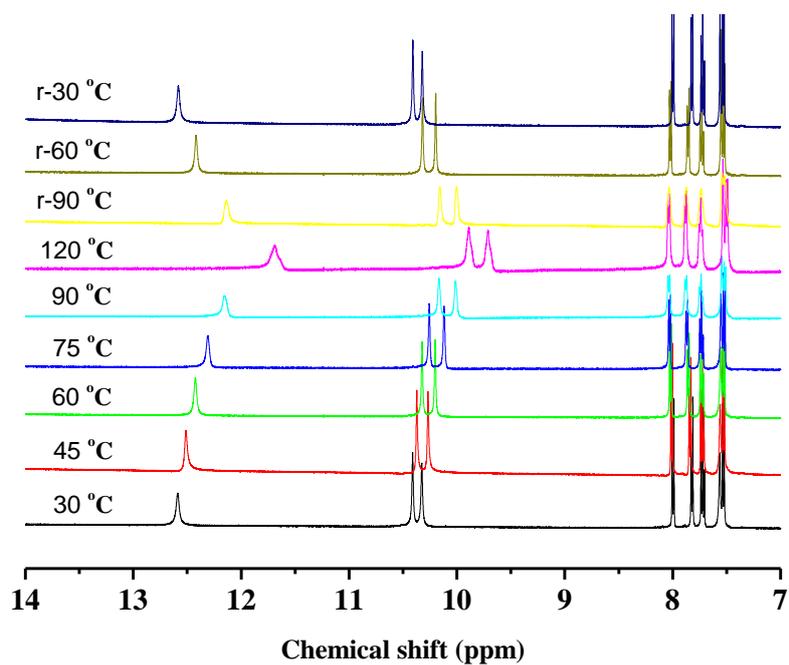


Figure S5a. ^1H NMR spectra at various temperatures for a 40 mM solution of MU-DPy-PEG1T in $\text{tetrachloroethane-}d_2$.

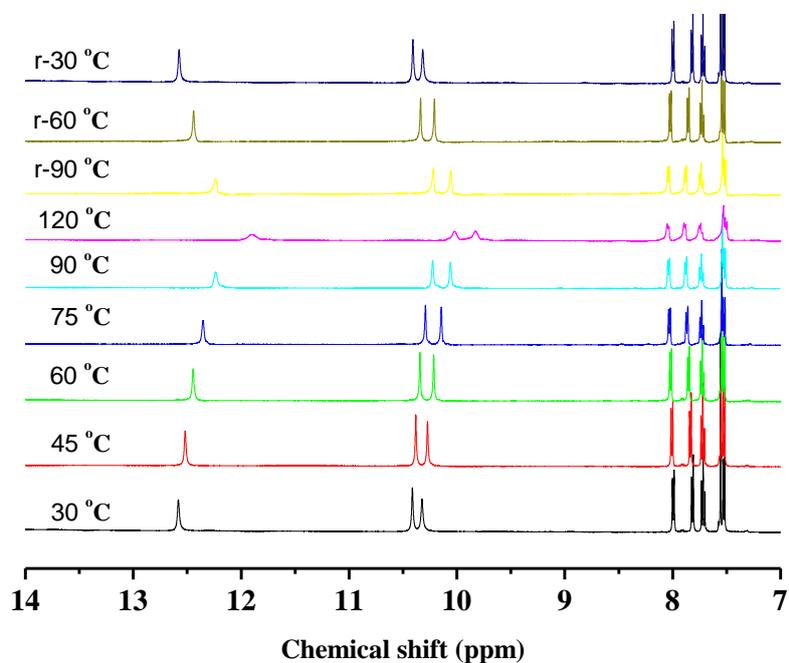


Figure S5b. ^1H NMR spectra at various temperatures for a 40 mM solution of BU-DPy-PEG1T in $\text{tetrachloroethane-}d_2$.

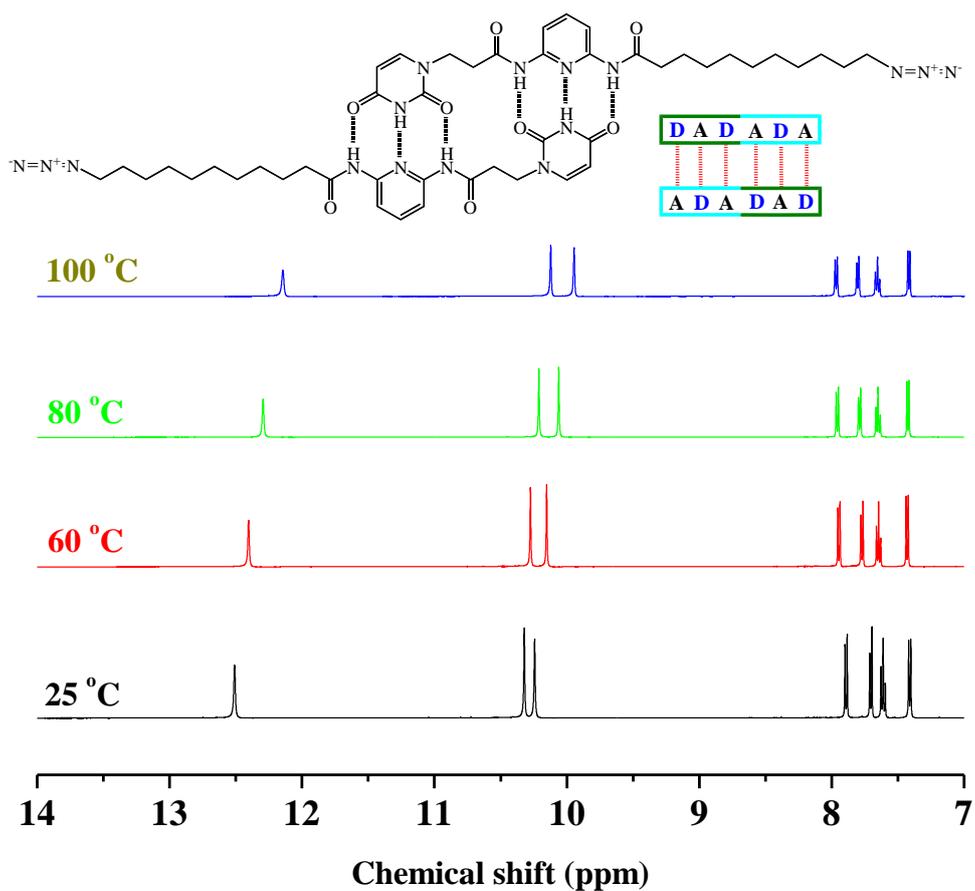


Figure S6. ¹H NMR spectra at various temperatures for a 40 mM solution of N3-U-DPy in tetrachloroethane-*d*₂.

Isothermal Crystallization Kinetics

The conversion of crystallization as functions of time was representatively shown in **Figure S7** and **S8**. The kinetics of isothermal crystallization of the MU-DPy-PEG1T and PEG 1000 was analyzed using Avrami equation (in **Figure S9** and **S10**). The experimental results are well coincident with the linear relation for the early part of transformation.

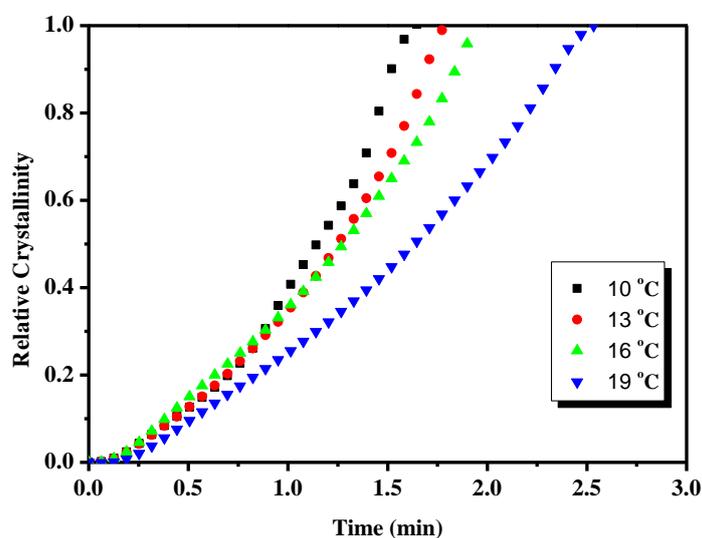


Figure S7. Crystallization isotherms of control PEG 1000 at different temperatures.

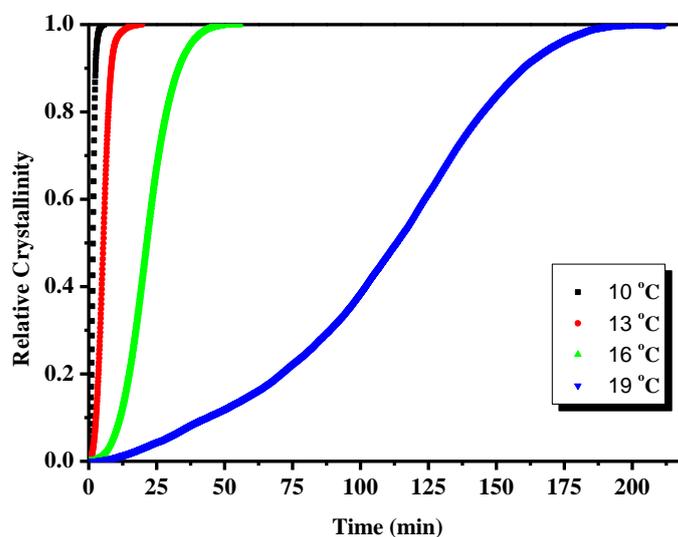


Figure S8. Crystallization isotherms of MU-DPy-PEG1T at different temperatures.

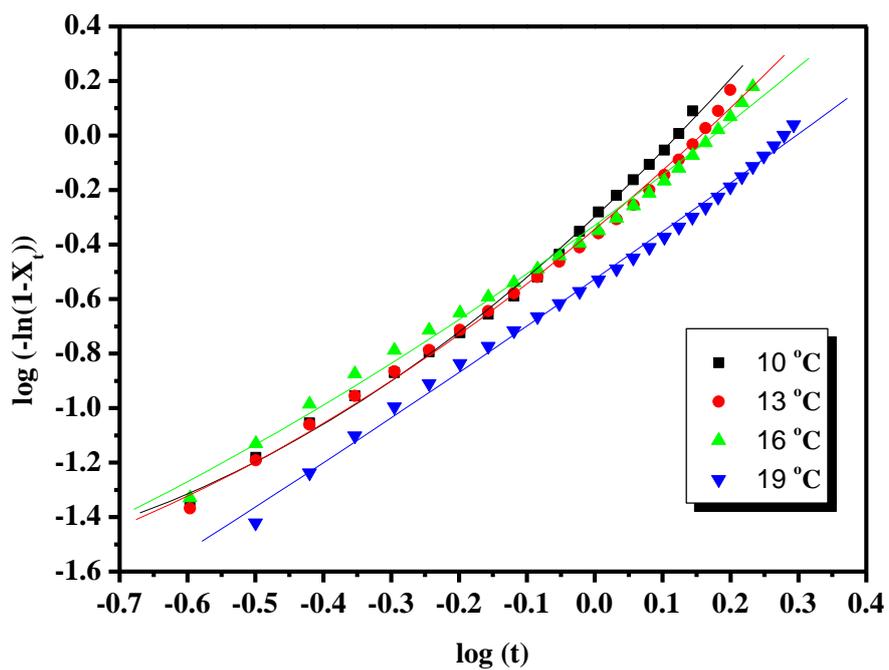


Figure S9. Avrami plot for control PEG 1000 at different temperatures.

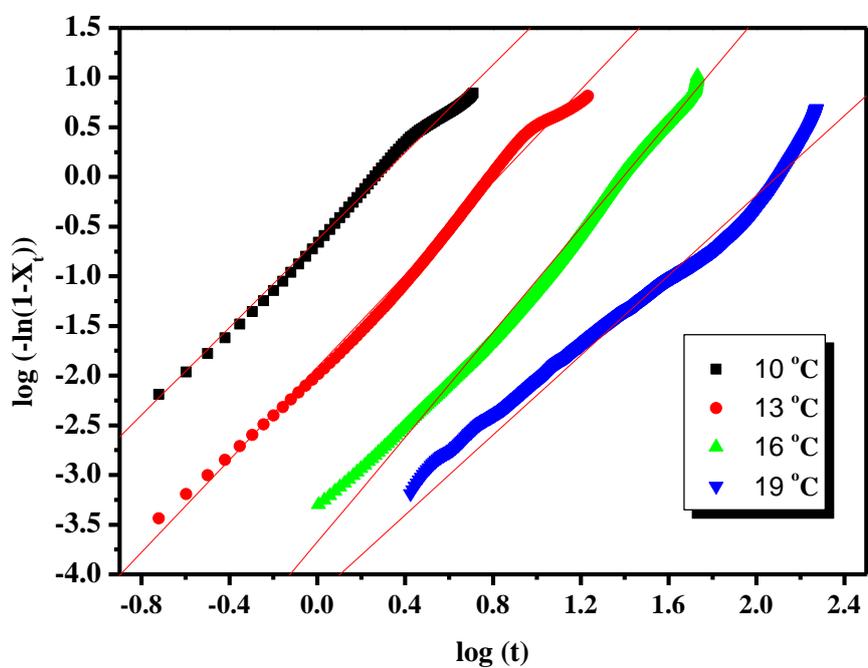


Figure S10. Avrami plot for MU-DPy-PEG1T at different temperatures.

Diffusion NMR Experiments

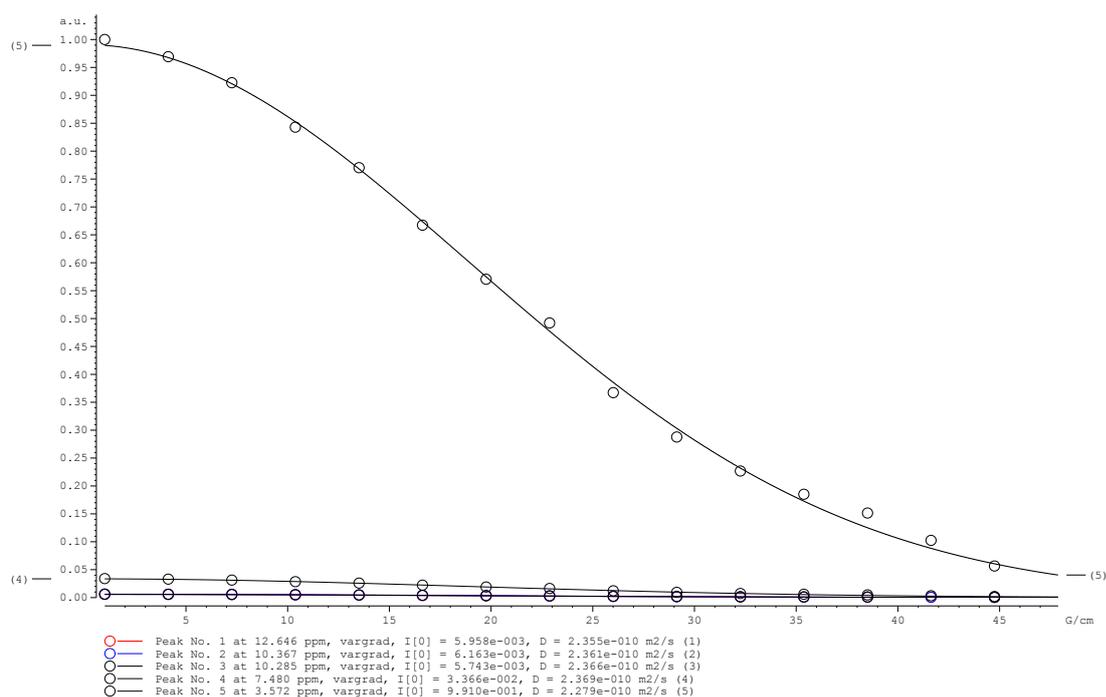


Figure S11. Plot of normalized intensity vs. gradient strength, showing non-linear curve fit and calculated diffusion coefficient (D) for a 16.7 mg/dL solution of BU-DPy-PEG1T. in CDCl₃.

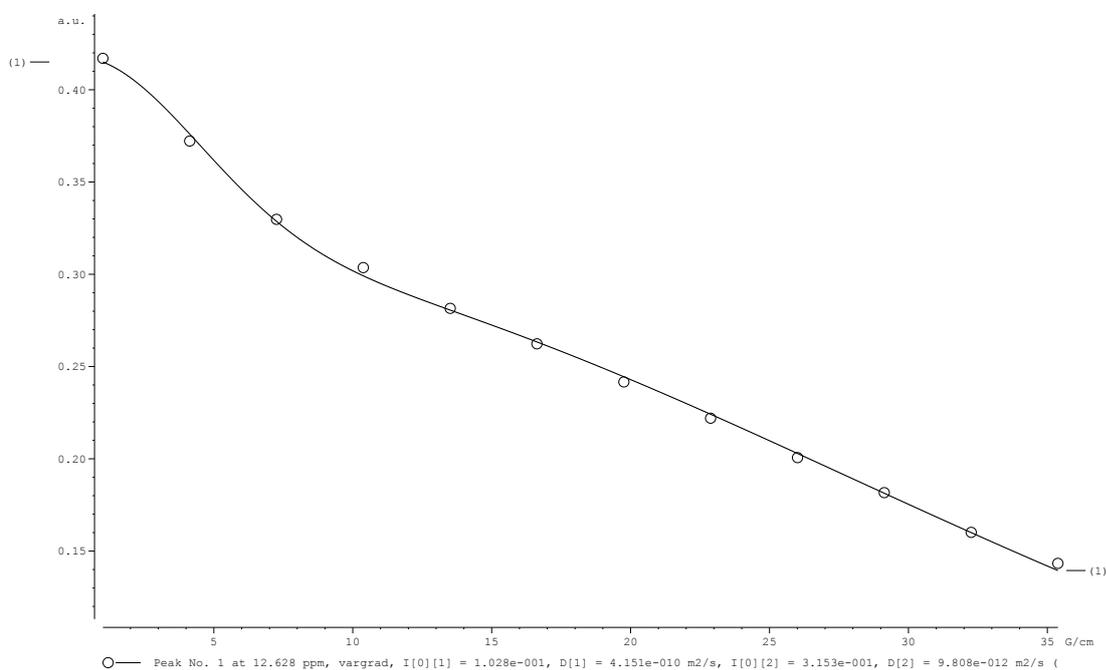


Figure S12. Plot of normalized intensity vs. gradient strength, showing non-linear curve fit and calculated diffusion coefficient (D) for a 167 mg/dL solution of BU-DPy-PEG1T. in CDCl₃.

FT-IR Spectra

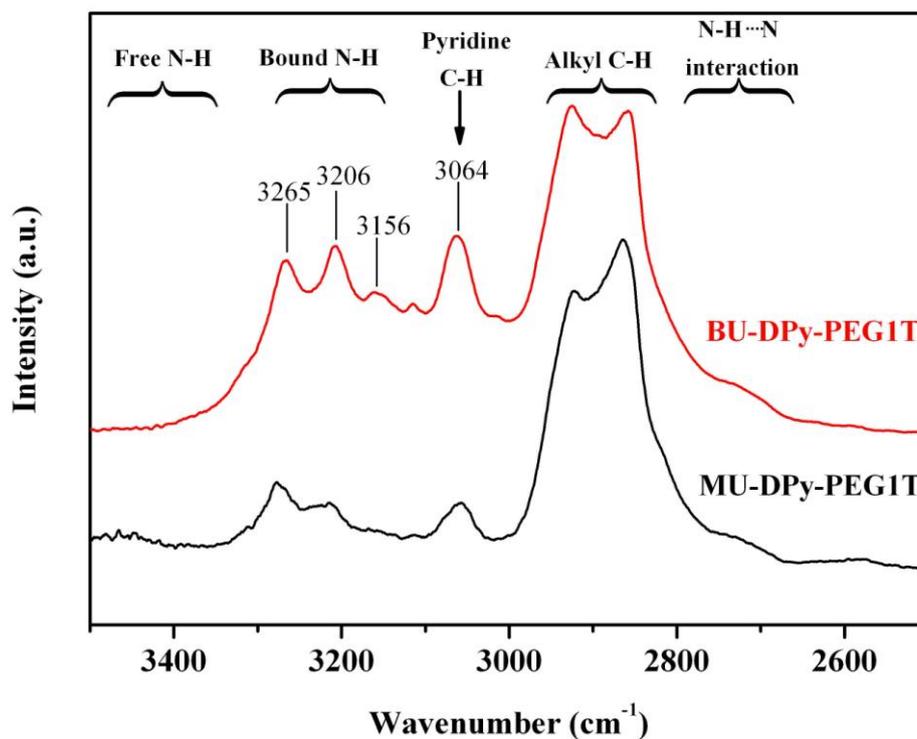


Figure S13. FTIR spectra recorded at room temperature in the range 2500–3500 cm⁻¹ for MU-DPy-PEG1T and BU-DPy-PEG1T in the bulk state.

Figure S13 illustrates FTIR spectra of the N-H stretching region of MU-DPy-PEG1T and BU-DPy-PEG1T. Vibration at 3265 cm⁻¹ corresponds to the stretching of the medium hydrogen-bonded N-H groups, and the characteristic peaks at 3156 and 3206 cm⁻¹ are frequencies generally observed for strongly hydrogen-bonded N-H. Notably, an absorption peak above 2650–2780 cm⁻¹ occurs, indicative for N-H...N inter-association, which implies that uracil groups are highly complementary to the DAP group.

Polarized Optical Microscopy

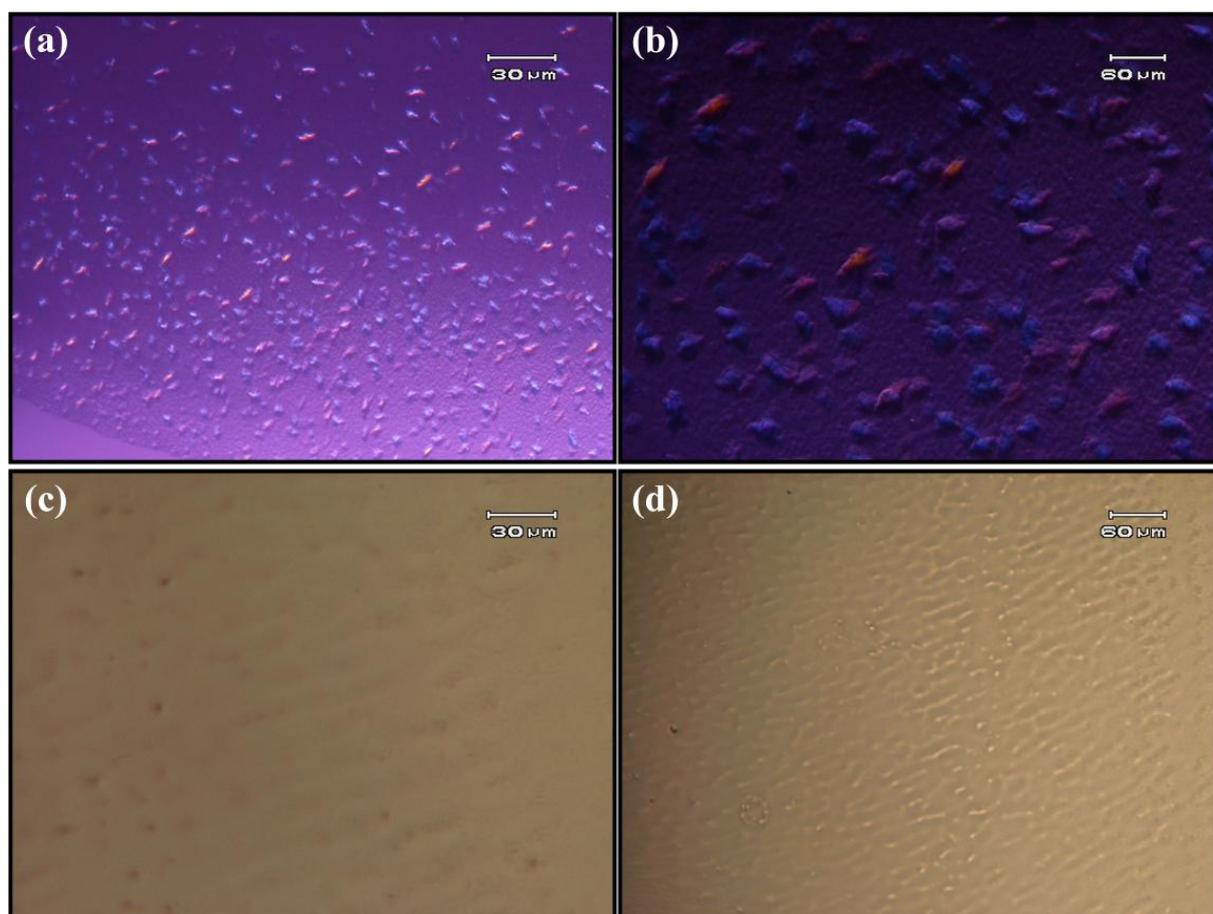


Figure S14. Polarized optical microscopy of (a, b) MU-DPy-PEG1T and (c, d) BU-DPy-PEG1T.

The polarized optical microscope (POM) were undertaken in order to compare the crystallization behaviors of MU-DPy-PEG1T and BU-DPy-PEG1T at room temperature. The results presented in Figure S14 suggest that the crystal morphology formed in MU-DPy-PEG1T thin film. In addition, it is easier to distinguish the crystalline and amorphous phase for polymer crystallization by using a transmission mode with a gypsum plate. This indicates that a pink color is denoted as an amorphous phase whereas crystalline birefringence is blue (Figure S14a and b). In contrast, BU-DPy-PEG1T show no birefringence in POM images (Figure S14c and d). This result also confirms that BU-DPy-PEG1T is amorphous. In other word, the attachment of difunctional U-DPy to PEG1T chain ends led to the disappearance of PEG1T crystallization, suggesting that the U-DPy groups on chain ends possess steric effect to hinder the formation of PEG1T crystalline.

Dynamic Light Scattering analysis

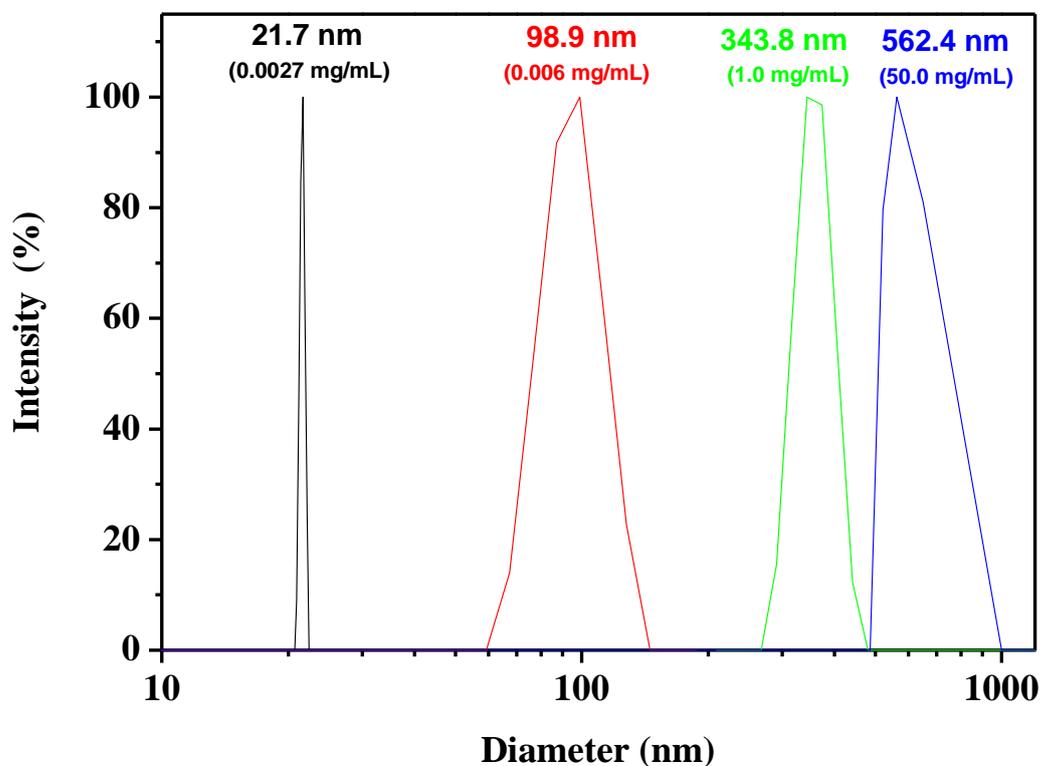


Figure S15. Size distribution analysis (DLS) at differential concentrations of BU-DPy-PEG1T in chloroform.

The DLS data are in good agreement with those of the AFM results: nanoparticles 22 nm in diameter in extremely dilute solutions and aggregates for more concentrated solutions. It should be noted that these larger particles scatter much more broadly than an extremely dilute sample (0.0027 mg/mL); it is therefore likely that linear polymers are present in the more concentrated samples.

References

S1. W. H. Binder and R. Sachsenhofer, *Macromol. Rapid Commun.* 2008, **29**, 1097.