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Synthesis and Self Assembling Properties of Rod-Like, 2-Ureido-4-pyrimidinone-Based Main Chain Supramolecular Dendronized Polymers[†]

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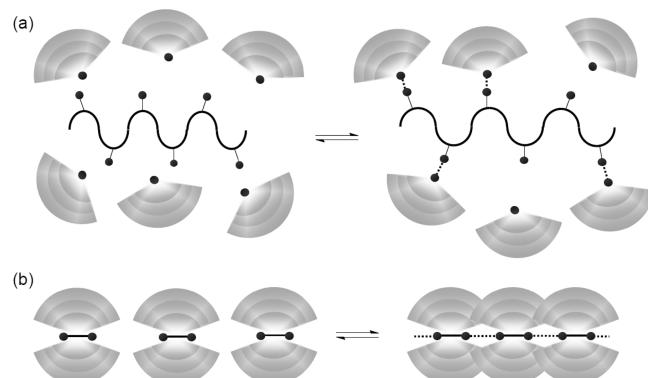
ABSTRACT: A series of G1–G3 supramolecular dendronized polymers **6** bearing dimeric 2-ureido-4-pyrimidinone (UPy) units on the main chain and aliphatic hydrocarbon dendrons as side chain appendages was prepared. Because of the high crystallinity and poor solubility of such rigid rod polymers, only the G3 dendron could confer the resulting polymer **6** ($n = 3$) with enough solubility to enable its characterization and property studies. It was found that the nature of the dendrons play an important role on the UPy binding strength, solubility and self-assembly properties. The reversible nature of the polymerization process was demonstrated in different solvent systems by viscosity studies. A double logarithmic plot of the specific viscosity against concentration revealed a deflection point at 26 mM in CHCl_3 at 26 and 40 °C. Below this critical concentration a straight line with a slope of 1.5 was obtained, while a slope of 4.0–4.2 was secured above this concentration. The data suggested that the associative interaction between the di-UPy monomer **5** ($n = 3$) increased nonlinearly with increasing monomer concentration. While the above investigations confirmed that these were main chain supramolecular dendronized polymers, UV-vis spectroscopic study revealed a large bathochromic shift (32 nm) with increasing polymer concentration in CHCl_3 . This finding was consistent with the formation of J-type aggregates via stair-case stacking between interchain UPy rings. SEM morphological study also confirmed that the resulting polymers appeared as fibrous superbundles with a very high aspect ratio. A model was purposed to rationalize how such bundles could be assembled from the di-UPy dendritic macromonomer **5** via intrachain hydrogen bonding and interchain stacking interactions.

Introduction

Dendronized polymers represent an interesting class of macromolecules with unique structural features such as rigidification of the backbone with increasing size of the dendritic side chains. They are generally prepared by graft-in, graft-from, and macromonomer polymerization approaches.¹ Traditionally, preparation of dendronized polymers mainly relies on covalent connection between the dendritic monomers. However, examples of using noncovalent methods, such as metal coordination, hydrogen bonding, and/or host guest complexation to construct self-assembling supramolecular dendronized polymers are rare, despite the fact that these strategies have been successfully applied to the preparation of many supramolecular nondendronized polymers.² One particular interesting attribute of supramolecular polymers lies on their controllable degree of polymerization (DP) through changes in the solvents, temperature, and other external factors. Hence, such polymers are actually self-healing yet degradable systems and could prove extremely useful in materials applications.

The use of noncovalent methods to anchor dendrons to a polymer backbone via the graft-to method has been exemplified. For example, Stoddart employed host guest binding interaction to graft cationic ammonium dendrons to a polystyrene or poly(acetylene) backbone containing crown ether side chain appendages (Chart 1a).³ Similarly, Jiang disclosed that oligoether dendrons bearing a carboxylic acid group at the focal point could

Chart 1. Supramolecular dendronized polymers prepared via (a) graft-to and (b) macromonomer polymerizations.

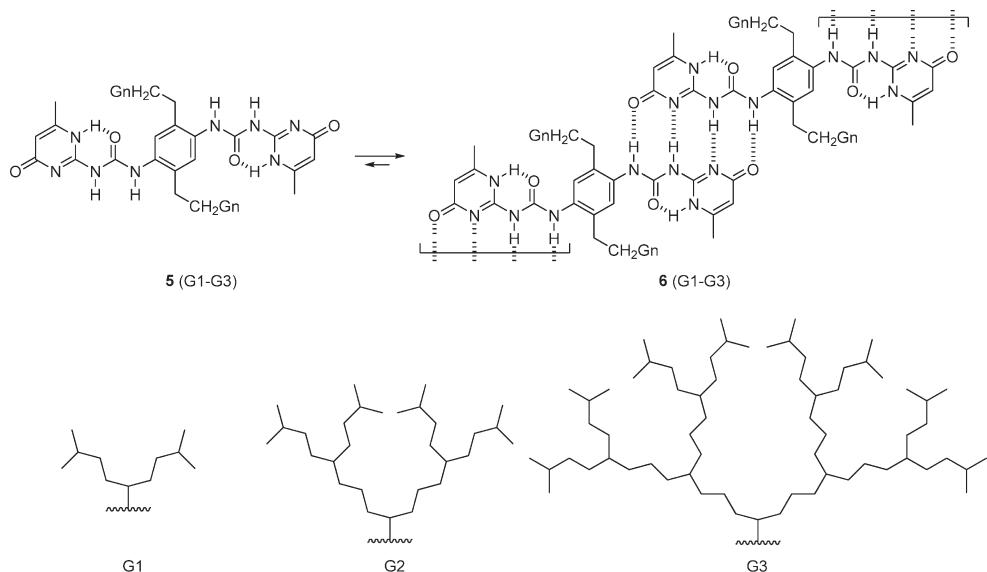


be grafted to a poly(4-vinylpyridine) chain through hydrogen bonding interaction in chloroform.⁴ Main chain supramolecular dendronized polymers based on macromonomer polymerization had also been reported (Chart 1b). For example, Zimmerman disclosed that dendronized Sn^{4+} –porphyrin macromonomers could be linked together through metal–ligand interaction via succinic acid linkers.⁵ Würthner also reported a Ag^+ -promoted polymerization of dendronized bi(pyridine) macromonomers which led to the synthesis of rigid rod dendronized metallopolymers.⁶ However, as metal–ligand interaction is relatively strong among the many supramolecular interactions, in both cases, the reversibility

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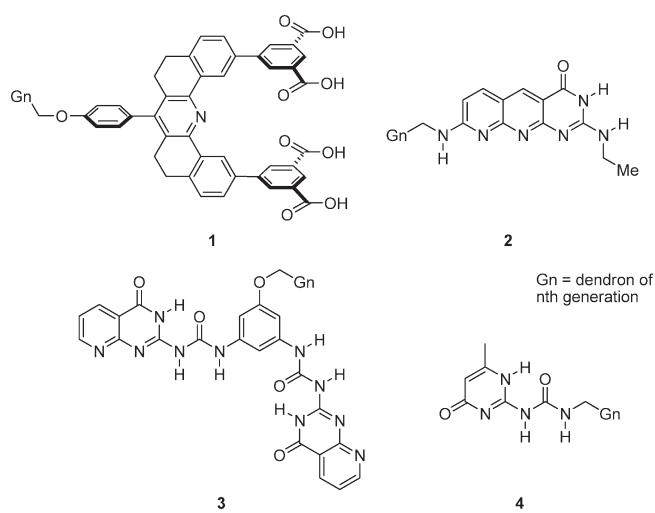
[†]This paper is dedicated to Prof. Henry N. C. Wong on the occasion of his 60th birthday.

Chart 2



of the self-assembly process, *i.e.*, depolymerization, was therefore not demonstrated.

Instead of metal–ligand coordination, hydrogen bonding can also be used as the driving force for self-assembly. The advantage of using hydrogen bonding is that the self-assembly process is readily reversible by change the solvent and temperature. However, despite many successes in using multiple hydrogen bonding systems to prepare supramolecular nondendronized polymers,⁷ only a few examples were disclosed on applying this strategy to prepare supramolecular dendronized polymers. For examples, Zimmerman demonstrated that dendronized monomers bearing different multiple hydrogen bonding motifs, such as bis(isophthalic acid) (**1**)⁸ heterocyclic DDA·AAD (**2**)⁹ and bis(ureidodeazapterin) (**3**)¹⁰ could be used as linkages to construct supramolecular dendronized polymers. However, due to preorganization of the various hydrogen bonding moieties, the predominant species formed were cyclic oligomers, and only a small amount of linear oligomers/polymers was found. Percec also reported that amphiphilic dendronized dipeptides could also self-assemble into helical pores in highly nonpolar cyclohexane solutions.¹¹ Hence, linear supramolecular dendronized polymers were not deliberately prepared as the target molecules in these studies.



At first glance, synthesis of rigid-rod, main-chain hydrogen bond-mediated dendronized polymers from the self-assembly of

bifunctional dendritic macromonomers should be relatively straightforward. However, this construction process has several inherent problems that are originated from the presence of the dendritic appendage. First, the relatively larger size of the dendron, especially the higher generation ones, can lower the DP value of the polymer due to steric inhibition.⁶ Second, the dendron itself can create a significant different microenvironment polarity in comparison to that of an alkyl substituent normally used in a model compound. This change of polarity can result in an abrupt drop of binding constant and hence decreasing the DP value. For example, Kaifer demonstrated that putting a G3 oligoamide-oligoester dendron at the urea end of a 2-ureido-4-pyrimidinone (UPy) unit (**4**) lowered the dimerization constant from 10^7 to 3 M^{-1} .¹² Meijer and Sijbesma also reported that an appropriately placed oligo(ethylene oxide) chain could lead to a 10^2 – 10^3 -fold drop of the strength of UPy binding.¹³ Third, the dendron itself may induce a switch of the tautomeric equilibrium of the heterocycle, which can again modify the binding constant as well as the binding geometry. We recently demonstrated that subtle changes of the steric congestion around the vicinity of the UPy unit increased the % amount of the weaker binding DADA 4-pyrimidinol tautomer.¹⁴ Fourth, there is always the possibility of forming cyclic oligomers when the dendritic monomer possesses a flexible backbone. In the case of using UPy as the binding unit, Meijer again had reported many interesting findings in the ring–chain equilibrium involving nondendritic di-UPy monomers.¹⁵ Generally, this cyclization problem is a minor issue if the monomer concentration is well above the ring–chain transition critical concentration and if the binding strength between the monomer is very strong.¹⁶ Fifth, polymers with a rigid rod structure generally possess poor solubility, and this can pose problems in their synthesis, structural characterizations and property studies. Last but not least, one should also ensure that the bifunctional UPy dendritic monomer can be prepared in high structural homogeneity, and the sample should be devoid of any mono-functional UPy macromonomer, which can act as a chain stopper and lower the polymerization efficiency. Herein we wish to report our synthetic endeavor to tackle these problems, and to disclose the first synthesis and self-assembling properties of rigid-rod supramolecular dendronized polymers **6** based on the quadruple hydrogen bonding between bifunctional UPy monomers **5** (see Chart 2). Specifically, we noted that the size of the dendron had a dramatic effect on the property of the resulting dendronized polymers. Hence the lower generation dendronized polymers **5**

($n = 1$ and 2) are solids that are poorly soluble in most solvent systems. On the other hand, the corresponding G3 analogue possesses excellent solubility property in most organic solvents, and allowed us to investigate its viscosity property even in highly nonpolar solvents such as hexane. Based on UV spectroscopic and SEM studies, it was found that the polymer chains further self-assembled to form rod-like bundles due to stacking of the UPy moieties in the form of *J*-type aggregates. This paper also reveals that this self-assembling synthetic approach is a viable method to generate new types of sterically congested dendronized polymers with fascinating properties.

Experimental Section

Materials. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was freshly distilled prior to use from sodium/benzophenone ketyl under N_2 . Dimethyl sulfoxide (DMSO) and CH_2Cl_2 were freshly distilled from CaH_2 . *N,N*-Dimethylformamide (DMF) was freshly distilled from $CaSO_4$.

Instrumentation. 1H NMR (300 MHz unless otherwise stated) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Bruker Avance DPX 300 nuclear magnetic resonance spectrometer. All measurements were carried out at 25 °C in $CDCl_3$ unless otherwise stated. Mass spectra analyses using electron spray ionization (ESI) technique or electron impact (EI) technique were obtained on a ThermoFinnigan MAT 95 XL double focusing sector mass spectrometer, and MALDI-TOF analyses on a MALDI Autoflex mass spectrometer. The reported molecular mass (m/z) values, unless otherwise specified, were monoisotopic mass. Elemental analyses were carried out at MEDAC Ltd., Brunel Science Center, Cooper's Hill Lane, Egham, Surrey TW20 0JZ, U.K. SEC measurements were performed on Waters Styragel columns (HR1, HR2, HR3, and HR4 7.8 × 300 mm in serial) at 40 °C using THF as eluent (flow rate = 1.0 mL/min) on a Waters HPLC 515 pump equipped with a Waters 2489 tunable UV absorbance detector or Viscotek LR40 laser refractometer. The retention time (R_t) was reported in minute. Solution viscosity was measured in $CHCl_3$ solution (spectrophotometric grade, stabilized with amylene) or hexane solution (distilled) at a specified temperature in an Ubbelohde or a Zeitzfuchs cross-arm viscometer. Solutions were filtered over 5 mm filters before use. For scanning electron microscopy measurements, the samples were spin-dried with a CHEMAT Technology KW-4A spin-coater at either low (300 rpm) or high spin rate (1500 rpm) at 25 °C on a silicon wafer, coated with Au particles using a Fisons Instruments Polaron SC502 Stutter Coater with a spin rate of 6000 rpm and subsequently studied by a Leo 1450 VP scanning electron microscope at 20 kV and a 3.2 nA probe current.

Synthesis. All reactions were carried out under N_2 unless otherwise stated. The progress of the reactions was monitored by thin layer chromatography (TLC) performed on Merck precoated silica gel 60F₂₅₄ plates, and compounds were visualized with a spray of 5% (w/v) dodecamolybdophosphoric acid in EtOH and subsequent heating. Flash chromatography was carried out on columns of Merck Keiselgel 60 (230–400 mesh).

2-Amino-4-benzylxyloxy-6-methylpyrimidine (18). 2-Amino-4-chloro-6-methylpyrimidine (17) (0.50 g, 3.48 mmol) was added to a suspension of benzyl alcohol (0.54 mL, 5.22 mmol) and NaH (0.21 g, 60% oil suspension, 5.22 mmol) in DMF (5 mL), and the resulting mixture was heated to 50 °C. After 24 h, the suspension was filtered through a pad of Celite. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 1/2) to give the target compound (0.52 g, 72%) as a white solid. Mp: 110–112 °C (hexane/EtOAc). R_f : 0.39 (hexane/EtOAc = 1/2). δ_H : 2.26 (3 H, s, CH_3), 5.11 (2 H, s, NH_2), 5.31 (2 H, s, CH_2Ph), 6.01 (1 H, s, pyrimidyl-H), 7.28–7.45 (5 H, m, Ph). δ_C : 23.6, 67.4, 96.9, 128.0, 128.5, 136.7, 162.9, 168.3, 170.5. HRMS (MALDI-TOF): calcd for $C_{13}H_{17}N_3O + H^+$, 216.1131; found, 216.1130.

General Procedure for the Synthesis of Gn -Dibromides 10 ($n = 1$ –3). To a mixture of Ph_3P (6 mol equiv) and anhydrous K_2CO_3 (1 mol equiv) in CH_2Cl_2 was added CBr_4 (3 mol equiv) at 0 °C. After stirring for 15 min at 25 °C, a solution of Gn -aldehyde 9 (1 mol equiv) in CH_2Cl_2 was added and the resulting suspension was stirred at 25 °C for 3 h. The reaction mixture was concentrated under reduced pressure and hexane was added. The suspension was filtered through a plug of silica gel to obtain the crude product which was further purified by flash chromatography (eluent: hexane) to give the target compound.

G1-Dibromide 10 ($n = 1$). Starting from G1-aldehyde 9 ($n = 1$) (9.89 g, 0.054 mol), Ph_3P (84.46 g, 0.32 mol), anhydrous K_2CO_3 (7.42 g, 0.054 mol), and CBr_4 (53.39 g, 0.16 mol) in CH_2Cl_2 (300 mL), the target compound (11.80 g, 64%) was obtained as a colorless liquid. R_f : 0.79 (hexane). δ_H : 0.88 (6 H, d, $J = 6.6, CH_3$), 0.89 (6 H, d, $J = 6.7, CH_3$), 1.05–1.34 (6 H, m), 1.34–1.61 (4 H, m), 2.21–2.40 (1 H, m, $CHC=CH$), 6.11 (1 H, d, $J = 9.8, CH=CH_2$). δ_C : 22.7, 22.9, 28.3, 32.5, 36.4, 44.3, 87.9, 143.9. m/z (EI): 340 (M^+). HRMS (EI): calcd for $C_{13}H_{24}Br_2^+$, 340.0219; found, 340.0216. SEC (RI): R_t 37.01.

G2-Dibromide 10 ($n = 2$). Starting from G2-aldehyde 9 ($n = 2$) (4.95 g, 11.30 mmol), Ph_3P (17.79 g, 67.82 mmol), anhydrous K_2CO_3 (1.56 g, 11.30 mmol), and CBr_4 (11.25 g, 33.91 mmol) in CH_2Cl_2 (30 mL), the target dibromide (5.81 g, 86%) was obtained as a colorless liquid. R_f : 0.84 (hexane). δ_H : 0.88 (24 H, d, $J = 6.6, CH_3$), 1.03–1.58 (34 H, m), 2.30–2.46 (1 H, br s, $CHC=CH$), 6.12 (1 H, d, $J = 9.8, CH=CH_2$). δ_C : 23.0, 24.4, 28.7, 31.4, 31.5, 33.9, 35.2, 36.1, 36.2, 37.9, 43.7, 88.0, 143.8. HRMS (MALDI-TOF): calcd for $C_{31}H_{60}Br_2 + Ag^+$, 699.2094; found, 699.2069. Anal. Calcd for $C_{31}H_{60}Br_2$: C, 62.83; H, 10.20; Br, 26.97. Found: C, 62.93; H, 9.99; Br, 27.07. SEC (RI): R_t 34.45.

G3-Dibromide 10 ($n = 3$). Starting from G3-aldehyde 9 ($n = 3$) (4.95 g, 11.30 mmol), Ph_3P (3.63 g, 13.83 mmol), anhydrous K_2CO_3 (0.32 g, 2.31 mmol), and CBr_4 (2.29 g, 6.92 mmol) in CH_2Cl_2 (5 mL), the target product (2.35 g, 90%) was obtained as a colorless liquid. R_f : 0.87 (hexane). δ_H : 0.90 (48 H, d, $J = 6.6, CH_3$), 1.02–1.43 (74 H, m), 1.51 (8 H, septet, $J = 6.6, CHMe_2$), 2.30–2.50 (1 H, m, $CHC=CH$), 6.12 (1 H, d, $J = 9.9, CH=CH_2$). δ_C : 23.0, 23.87, 23.92, 24.5, 28.7, 31.5, 34.1, 34.3, 35.2, 36.2, 37.5, 38.0, 43.9, 87.9, 143.9. HRMS (MALDI-TOF): calcd for $C_{67}H_{132}Br_2 + Ag^+$, 1205.7730; found, 1205.7761. Anal. Calcd for $C_{67}H_{132}Br_2$: C, 73.32; H, 12.12; Br, 14.56. Found: C, 73.72; H, 12.30; Br, 14.03. SEC (RI): R_t 32.37.

General Method for the Synthesis of Gn -Acetylenes 11 ($n = 1$ –3). *n*-BuLi (1.6 M in hexane, 2.2 mol equiv) was added dropwise to a solution of the Gn -dibromide 10 (1 mol equiv) in THF at –78 °C. After stirring for 30 min at –78 °C and 30 min at 25 °C, the solution was poured into HCl (1 M) and extracted with hexane. The combined extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography (eluent: hexane) to give the target compound.

G1-Acetylene 11 ($n = 1$). Starting from G1-dibromide 10 ($n = 1$) (11.80 g, 0.035 mol) and *n*-BuLi (47.70 mL, 0.076 mol), the target G1-acetylene (5.77 g, 92%) was obtained as a colorless liquid. R_f : 0.62 (hexane). δ_H : 0.89 (12 H, d, $J = 6.5, CH_3$), 1.15–1.64 (10 H, m), 2.04 (1 H, d, $J = 2.4, C\equiv CH$), 2.16–2.32 (1 H, m, $CHC\equiv CH$). δ_C : 22.6, 22.9, 28.1, 32.2, 33.1, 36.7, 69.2, 88.1. m/z (EI): 179 ($M - H^+$). HRMS (EI): calcd for $C_{13}H_{24} - H^+$, 179.1794; found, 179.1789. SEC (RI): R_t 37.20.

G2-Acetylene 11 ($n = 2$). Starting from G2-dibromide 10 ($n = 2$) (4.84 g, 8.17 mmol) and *n*-BuLi (11.23 mL, 17.97 mmol), the target G2-acetylene (3.09 g, 87%) was obtained as a colorless liquid. R_f : 0.71 (hexane). δ_H : 0.88 (24 H, d, $J = 6.6, CH_3$), 1.02–1.31 (22 H, m), 1.31–1.58 (12 H, m), 2.03 (1 H, d, $J = 2.3, C\equiv CH$), 2.25–2.41 (1 H, m, $CHC\equiv CH$). δ_C : 22.9, 24.5, 28.6, 31.3, 31.5, 31.7, 33.6, 35.6, 36.0, 36.1, 37.9, 69.2, 88.3. HRMS

(MALDI-TOF): calcd for $C_{31}H_{60} + Ag^+$, 539.3740; found, 539.3719. Anal. Calcd for $C_{31}H_{60}$: C, 86.03; H, 13.97. Found: C, 85.83; H, 14.25. SEC (RI): R_t 34.52.

G3-Acetylene 11 ($n = 3$). Starting from G3-dibromide **10** ($n = 3$) (2.00 g, 1.82 mmol) and *n*-BuLi (2.51 mL, 4.01 mmol), the target product (1.50 g, 88%) was obtained as a colorless liquid. R_f : 0.80 (hexane). δ_H : 0.87 (48 H, d, $J = 6.6, CH_3$), 1.03–1.55 (82 H, m), 2.03 (1 H, d, $J = 2.3, C\equiv CH$), 2.23–2.40 (1 H, m, $CHC\equiv C$). δ_C : 22.9, 23.75, 23.85, 24.6, 28.6, 31.4, 31.8, 33.8, 34.2, 34.3, 35.7, 36.1, 37.5, 37.9, 69.1, 88.4. HRMS (MALDI-TOF): calcd for $C_{67}H_{132} + Ag^+$, 1045.9387; found, 1045.9374. SEC (RI): R_t 32.32.

General Procedure for the Synthesis of Acetylenic G1-Diesters 14 ($n = 1–3$). A degassed solution of Gn -acetylene **11** (2.5–3 mol equiv), ditriflate **13** (1 mol equiv), NEt_3 (6 mol equiv), $PdCl_2(PPh_3)_2$ (0.15 mol equiv), and CuI (0.15–0.2 mol equiv) in THF/DMF (1/1) was stirred at 25 °C for 15 h. The reaction mixture was taken up in a mixture of saturated NH_4Cl solution, hexane, and EtOAc. After filtration, the organic layer was separated, washed with water and saturated NaCl solution, dried ($MgSO_4$), and filtered. After evaporation of solvent under reduced pressure, the residue was purified as described in the following text.

Acetylenic G1-Diester 14 ($n = 1$). Starting from G1-acetylene **11** ($n = 1$) (5.77 g, 32.00 mmol), ditriflate **13** (6.70 g, 12.93 mmol), NEt_3 (10.80 mL, 77.49 mmol), $PdCl_2(PPh_3)_2$ (1.27 g, 1.81 mmol), and CuI (0.50 g, 2.63 mmol). The crude product was purified by precipitation from EtOH to give the target acetylenic G1-diester (6.38 g, 85%) as a white solid. Mp: 80.5–82 °C. R_f : 0.38 (hexane/EtOAc = 50/1). δ_H : 0.90 (12 H, d, $J = 6.5, CH_3$), 0.91 (12 H, d, $J = 6.5, CH_3$), 1.20–1.65 (26 H, m), 2.52 (2 H, quint, $J = 7.0, CHC\equiv C$), 4.38 (4 H, q, $J = 7.1, OCH_2$), 7.93 (2 H, s, ArH). δ_C : 14.4, 22.6, 22.9, 28.2, 32.9, 33.4, 36.8, 61.6, 79.7, 101.7, 123.0, 134.7, 135.7, 165.7. m/z (ESI): 601 (M + Na^+ , 100%). HRMS (ESI): calcd for $C_{38}H_{58}O_4 + Na^+$, 601.4238; found, 601.4247. Anal. Calcd for $C_{38}H_{58}O_4$: C, 78.85; H, 10.10. Found: C, 79.03; H, 10.34. SEC (UV): R_t 34.00.

Acetylenic G2-Diester 14 ($n = 2$). Starting from G2-acetylene **11** ($n = 2$) (3.09 g, 7.12 mmol), ditriflate **13** (1.23 g, 2.37 mmol), NEt_3 (1.99 mL, 14.24 mmol), $PdCl_2(PPh_3)_2$ (0.23 g, 0.33 mmol) and CuI (0.06 g, 0.33 mmol). The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 50/1) to get the target acetylenic G2-diester (2.31 g, 90%) as a yellow liquid. R_f : 0.66 (hexane/EtOAc = 50/1). δ_H : 0.849 (24 H, d, $J = 6.6, CH_3$), 0.855 (24 H, d, $J = 6.6, CH_3$), 1.03–1.34 (44 H, m), 1.34–1.65 (30 H, m), 2.52–2.69 (2 H, m, $CHC\equiv C$), 4.37 (4 H, q, $J = 7.1, OCH_2$), 7.93 (2 H, s, ArH). δ_C : 14.5, 22.9, 24.7, 28.6, 31.3, 31.4, 33.0, 33.7, 35.6, 36.0, 36.1, 37.9, 61.5, 79.8, 101.6, 123.0, 134.7, 135.7, 165.6. m/z (ESI): 1106 (M + Na^+ , 100%). HRMS (ESI): calcd for $C_{74}H_{130}O_4 + Na^+$, 1105.9861; found, 1105.9866. Anal. Calcd for $C_{74}H_{130}O_4$: C, 82.01; H, 12.09. Found: C, 81.61; H, 12.35. SEC (UV): R_t 31.99.

Acetylenic G3-Diester 14 ($n = 3$). Starting from G3-acetylene **11** ($n = 3$) (1.50 g, 1.60 mmol), ditriflate **13** (0.28 g, 0.53 mmol), NEt_3 (0.45 mL, 3.20 mmol), $PdCl_2(PPh_3)_2$ (0.056 g, 0.080 mmol), and CuI (0.015 g, 0.080 mmol). The crude product was purified by flash column chromatography (eluent: hexane/ CH_2Cl_2 = 20/1) to get the target acetylenic G3-diester (0.56 g, 50%) as a yellow liquid. R_f : 0.16 (hexane). δ_H : 0.87 (96 H, d, $J = 6.6, CH_3$), 1.01–1.64 (170 H, m), 2.50–2.70 (2 H, m, $CHC\equiv C$), 4.38 (4 H, q, $J = 7.1, OCH_2$), 7.95 (2 H, s, ArH). δ_C : 14.5, 22.9, 23.7, 23.8, 24.8, 28.6, 31.4, 33.1, 33.9, 34.16, 34.24, 34.2, 35.7, 36.0, 37.4, 37.9, 61.5, 79.7, 101.7, 123.1, 134.5, 135.9, 165.5. HRMS (MALDI-TOF): calcd for $C_{146}H_{274}O_4 + Na^+$, 2116.1164; found, 2116.1180. Anal. Calcd $C_{146}H_{274}O_4$: C, 83.75; H, 13.19. Found: C, 83.82; H, 13.28. SEC (UV): R_t 30.31.

General Procedure for the Synthesis of Saturated Gn-Diesters 15 ($n = 1–3$). A mixture of the acetylenic Gn -diester **14** and palladium black (3–8% weight of Gn -diester) in absolute EtOH/THF (1/1) was stirred under H_2 (1 atm) at 25 °C. After

20 h, the suspension was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to give the target compound.

Saturated G1-Diester 15 ($n = 1$). Starting from acetylenic G1-diester **14** ($n = 1$) (6.16 g, 10.64 mmol) and palladium black (0.38 g), the target saturated G1-diester (6.25 g, 100%) was obtained as a colorless liquid. R_f : 0.50 (hexane/EtOAc = 50/1). δ_H : 0.88 (24 H, d, $J = 6.6, CH_3$), 1.02–1.22 (8 H, m), 1.22–1.35 (10 H, m), 1.40 (6 H, t, $J = 7.1, CH_2CH_3$), 1.44–1.57 (8 H, m), 2.80–2.92 (4 H, m, $ArCH_2$), 4.38 (4 H, q, $J = 7.1, OCH_2$), 7.64 (2 H, s, ArH). δ_C : 14.5, 22.9, 28.5, 31.2, 31.4, 36.0, 36.1, 38.3, 61.2, 132.6, 133.0, 141.7, 167.7. m/z (ESI): 609 (M + Na^+ , 100%). HRMS (ESI): calcd for $C_{38}H_{66}O_4 + Na^+$, 609.4864; found, 609.4860. Anal. Calcd for $C_{38}H_{66}O_4$: C, 77.76; H, 11.33. Found: C, 77.94; H, 11.44. SEC (UV): R_t 33.89.

Saturated G2-Diester 15 ($n = 2$). Starting from acetylenic G2-diester **14** ($n = 2$) (2.31 g, 2.13 mmol) and palladium black (0.20 g), the target saturated G2-diester (2.30 g, 99%) was obtained as a colorless liquid. R_f : 0.67 (hexane/EtOAc = 50/1). δ_H : 0.87 (48 H, d, $J = 6.6, CH_3$), 1.03–1.34 (60 H, m), 1.34–1.58 (20 H, m), 2.77–2.97 (4 H, m, $ArCH_2$), 4.37 (4 H, q, $J = 7.1, OCH_2$), 7.64 (2 H, s, ArH). δ_C : 14.5, 22.9, 23.9, 28.6, 31.4, 31.6, 34.1, 34.4, 36.1, 36.5, 38.0, 38.1, 61.2, 132.6, 133.0, 141.7, 167.7. HRMS (MALDI-TOF): calcd for $C_{74}H_{138}O_4 + Na^+$, 1114.0487; found, 1114.0419. Anal. Calcd for $C_{74}H_{138}O_4$: C, 81.40; H, 12.74. Found: C, 81.27; H, 12.55. SEC (UV): R_t 31.92.

Saturated G3-Diester 15 ($n = 3$). Starting from acetylenic G3-diester **14** ($n = 3$) (0.37 g, 0.18 mmol) and palladium black (0.01 g), the target saturated G3-diester (0.34 g, 92%) was obtained as a colorless oil. R_f : 0.67 (hexane/EtOAc = 50/1). δ_H : 0.87 (96 H, d, $J = 6.6, CH_3$), 1.01–1.35 (146 H, m), 1.35–1.60 (30 H, m), 2.75–2.99 (4 H, m, $ArCH_2$), 4.37 (4 H, q, $J = 7.1, OCH_2$), 7.64 (2 H, s, ArH). δ_C : 14.6, 23.0, 23.9, 24.0, 28.6, 31.5, 31.7, 34.3, 34.6, 36.2, 36.5, 37.6, 38.0, 38.4, 61.1, 132.8, 133.0, 141.9, 167.5. HRMS (MALDI-TOF): calcd for $C_{146}H_{282}O_4 + Na^+$, 2124.1789; found, 2124.1760. SEC (UV): R_t 30.25.

General Procedure for the Synthesis of Gn-Diacids 16 ($n = 1$ and 2). A mixture of saturated Gn -diester **15** ($n = 1$ and 2) (1 mol equiv) and aqueous KOH (1 M in H_2O , 10–20 mol equiv) in THF/CH₃OH (1/1) was heated under reflux for 18 h. The mixture was cooled to 25 °C and acidified with diluted HCl (1 M) to pH = 2. The aqueous phase was extracted with EtOAc and the combined organic layers were washed with water and saturated NaCl solution, dried ($MgSO_4$), and filtered. The filtrate was concentrated under reduced pressure to give the target compound.

G1-Diacid 16 ($n = 1$). Starting from saturated G1-diester **15** ($n = 1$) (6.25 g, 10.64 mmol) and aqueous KOH (110 mL, 0.11 mol), the target G1-diacid (5.49 g, 97%) was obtained as a white solid. mp: 216–218 °C (CH₃OH). R_f : 0.25 (hexane/EtOAc = 10/1). δ_H ($DMSO-d_6$): 0.84 (24 H, d, $J = 6.6, CH_3$), 0.98–1.33 (18 H, m), 1.33–1.56 (8 H, m), 2.75–2.93 (4 H, m, $ArCH_2$), 7.60 (2 H, s, ArH), 13.08 (2 H, s, COOH). δ_C ($DMSO-d_6$): 22.5, 22.6, 27.8, 30.3, 30.5, 35.3, 35.5, 37.3, 132.1, 133.2, 140.8, 168.4. HRMS (MALDI-TOF): calcd for $C_{34}H_{58}O_4 + Na^+$, 1105.9861; found, 1105.9866. Anal. Calcd for $C_{34}H_{58}O_4$: C, 82.01; H, 12.09. Found: C, 81.61; H, 12.35. SEC (UV): R_t 31.99.

G2-Diacid 16 ($n = 2$). Starting from saturated G2-diester **15** ($n = 2$) (2.30 g, 2.10 mmol) and aqueous KOH (42 mL, 42 mmol), the target G2-diacid (1.96 g, 99%) was obtained as a colorless liquid. R_f : 0.49 (hexane/EtOAc = 30/1). δ_H : 0.85 (48 H, d, $J = 6.6, CH_3$), 1.01–1.70 (74 H, m), 2.84–3.16 (4 H, m, $ArCH_2$), 7.90 (2 H, s, ArH), 10.99–13.25 (2 H, br s, COOH). δ_C : 22.9, 23.9, 28.6, 31.4, 31.8, 34.1, 34.3, 36.1, 36.4, 38.0, 38.1, 132.1, 134.1, 143.5, 173.3. m/z (ESI): 1058 (M + Na^+ , 100%). HRMS (ESI): calcd for $C_{70}H_{130}O_4 + Na^+$, 1057.9861; found, 1057.9866. SEC (UV): R_t 31.99.

G3-Diacid 16 ($n = 3$). A mixture of potassium *tert*-butoxide (0.28 g, 2.49 mmol) and water (0.01 mL, 0.62 mmol) in THF (5 mL) was stirred at 0 °C for 5 min. A solution of the saturated

G3-diester **15** ($n = 3$) (0.33 g, 0.16 mmol) in THF (5 mL) was added and the resulting suspension was stirred 25 °C for 48 h. The mixture was acidified with diluted HCl (1 M) to pH = 2. The aqueous phase was extracted with CH₂Cl₂ (3 × 20 mL) and the combined organic layers were washed with water and saturated NaCl solution, dried (MgSO₄) and filtered. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 50/1) to afford the target G3-diacid (0.31 g, 98%) as a colorless liquid. R_f : 0.76 (hexane/EtOAc = 20/1). δ_H : 0.87 (96 H, d, $J = 6.6$, CH₃), 1.00–1.73 (170 H, m), 2.90–3.10 (4 H, m, ArCH₂), 7.91 (2 H, s, ArH), 9.12–12.36 (2 H, br s, COOH). δ_C : 23.0, 23.8, 24.0, 28.6, 31.4, 31.9, 34.2, 34.3, 34.6, 36.1, 36.6, 37.5, 37.9, 38.4, 131.8, 134.1, 143.5, 171.8. HRMS (MALDI–TOF): calcd for C₁₄₂H₂₇₄O₄ + Na⁺, 2068.1163; found, 2068.1261. Anal. Calcd for C₁₄₂H₂₇₄O₄: C, 83.37; H, 13.50. Found: C, 83.40; H, 13.96. SEC (UV): R_t 30.30.

General Procedure for the Synthesis of Gn-Bifunctional Protected Monomers ($n = 1$ and 2). A solution of Gn-diacid **16** (1 mol equiv), NEt₃ (2.5 mol equiv), and DPPA (2.5–3 mol equiv) in toluene was stirred at 25 °C for 2 h. The amine **18** (2.3 mol equiv) was then added, and the resulting mixture was heated under reflux for 20 h. The reaction mixture was concentrated and purified by precipitation from EtOAc to give the target compound.

G1-Bifunctional Protected Monomer **19 ($n = 1$).** Starting from G1-diacid **16** ($n = 1$) (2.57 g, 4.84 mmol), NEt₃ (1.69 mL, 12.10 mmol), DPPA (4.00 g, 14.52 mmol), and compound **18** (2.40 g, 11.15 mmol), the G1-bifunctional protected monomer (2.81 g, 61%) was obtained as a white solid. Mp: 206–207 °C (toluene). R_f : 0.18 (hexane/EtOAc = 5/1). δ_H : 0.77 (12 H, d, $J = 6.6$, CH₃), 0.78 (12 H, d, $J = 6.6$, CH₃), 0.93–1.45 (22 H, m), 1.47–1.66 (4 H, m), 2.38 (6 H, s, pyrimidyl–CH₃), 2.55–2.76 (4 H, m, ArCH₂), 5.35 (4 H, s, CH₂Ph), 6.27 (2 H, s, pyrimidyl–H), 7.21 (2 H, s, ArNHCONH), 7.29–7.46 (10 H, m, Ph), 7.65 (2 H, s, ArH), 11.18 (2 H, s, ArNH). δ_C : 22.7, 23.8, 28.4, 29.4, 31.2, 34.3, 35.9, 38.3, 68.4, 101.1, 125.3, 128.3, 128.4, 128.7, 132.5, 133.6, 136.0, 152.6, 157.3, 166.9, 170.4. m/z (ESI): 978 (M + Na⁺, 100%). HRMS (ESI): calcd for C₅₈H₈₂N₈O₄ + Na⁺, 977.6362; found, 977.6367. Anal. Calcd for C₅₈H₈₂N₈O₄: C, 72.92; H, 8.65; N, 11.72. Found: C, 73.41; H, 8.88; N, 11.93. SEC (UV): R_t 32.97.

G2-Bifunctional Protected Monomer **19 ($n = 2$).** Starting from G2-diacid **16** ($n = 2$) (1.73 g, 1.67 mmol), NEt₃ (0.58 mL, 4.18 mmol), DPPA (1.15 g, 4.18 mmol), and compound **18** (1.15 g, 4.18 mmol), the G2-bifunctional protected monomer (1.68 g, 69%) was obtained as a white solid. Mp: 145–146 °C (THF/EtOH). R_f : 0.25 (hexane/EtOAc = 10/1). δ_H : 0.85 (48 H, d, $J = 6.5$, CH₃), 0.99–1.28 (60 H, m), 1.28–1.37 (2 H, m), 1.45 (8 H, septet, $J = 6.5$, CHMe₂), 1.53–1.66 (4 H, m), 2.39 (6 H, s, pyrimidyl–CH₃), 2.59–2.75 (4 H, m, ArCH₂), 5.35 (4 H, s, CH₂Ph), 6.26 (2 H, s, pyrimidyl–H), 7.18 (2 H, s, ArNHCONH), 7.30–7.46 (10 H, m, Ph), 7.68 (2 H, s, ArH), 11.15 (2 H, s, ArNH). δ_C : 22.86, 22.88, 23.8, 28.5, 29.3, 31.28, 31.33, 34.0, 34.3, 34.5, 35.98, 36.01, 37.9, 68.4, 101.1, 125.1, 128.3, 128.4, 128.7, 132.5, 133.4, 136.0, 152.5, 157.3, 166.9, 170.4. HRMS (MALDI–TOF): calcd for C₉₄H₁₅₄N₈O₄ + H⁺, 1461.2198; found, 1461.2208. SEC (UV): R_t 31.62.

G3-Bifunctional Protected Monomer **19 ($n = 3$).** A solution of G3-diacid **16** ($n = 3$) (0.61 g, 0.30 mmol) and NEt₃ (0.42 mL, 3.00 mmol) in toluene (5 mL) was stirred at 60 °C for 2 h. The reaction mixture was cooled to 25 °C and DPPA (0.83 g, 3.00 mmol) was added. After the reaction was stirred at 25 °C for 2 h, compound **18** (0.19 g, 0.90 mmol) was then added, and the reaction mixture was heated under reflux for 48 h. The reaction mixture was concentrated and purified by flash column chromatography (eluent: hexane/EtOAc = 30/1) to get the target G3-bifunctional protected monomer (0.36 g, 49%) as a colorless liquid. R_f : 0.46 (hexane/EtOAc = 10/1). δ_H : 0.86 (96 H, d, $J = 6.6$, CH₃), 0.99–1.69 (170 H, m), 2.39 (6 H, s, pyrimidyl–CH₃),

2.52–2.80 (4 H, m, ArCH₂), 5.35 (4 H, s, CH₂Ph), 6.26 (2 H, s, pyrimidyl–H), 7.21 (2 H, s, ArNHCONH), 7.29–7.47 (10 H, m, Ph), 7.69 (2 H, s, ArH), 11.18 (2 H, s, ArNH). δ_C : 22.9, 23.7, 23.9, 24.0, 28.6, 29.3, 31.4, 34.1, 34.3, 34.5, 34.6, 36.0, 37.5, 37.9, 38.2, 68.4, 101.2, 125.1, 128.3, 128.5, 128.7, 132.4, 133.5, 136.0, 152.5, 157.3, 166.9, 170.4. HRMS (MALDI–TOF): calcd for C₁₆₆H₂₉₈N₈O₄ + Na, 2492.3286; found, 2492.3263. Anal. Calcd for C₁₆₆H₂₉₈N₈O₄: C, 80.71; H, 12.16; N, 4.54. Found: C, 81.04; H, 12.31; N, 4.73. SEC (UV): R_t 30.22.

G1 Supramolecular Dendronized Polymer **6 ($n = 1$).** A mixture of the G1-bifunctional protected monomer **19** ($n = 1$) (0.20 g, 0.21 mmol) and palladium black (0.06 g) in CH₃OH (12 mL) and CHCl₃ (120 mL) was stirred under H₂ (1 atm) at 25 °C. After 24 h, the suspension was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure and purified by precipitation from CH₃OH to give the target G1-dendronized polymer (0.12 g, 74%) as a white powder. δ_H (400 MHz, DMSO-*d*₆, signal of benzylic Hs were obscured by residue solvent signals): 0.79 (24 H, d, $J = 6.4$, CH₃), 0.98–1.13 (8 H, m), 1.13–1.30 (10 H, m), 1.30–1.55 (8 H, m), 2.17 (6 H, s, pyrimidyl–CH₃), 5.84 (2 H, s, pyrimidyl–H), 7.48 (2 H, s, ArH), 9.48–10.29 (4 H, br s, NHCONH), 11.00–11.72 (2 H, br s, NH in UPy). HRMS (MALDI–TOF): calcd for C₄₄H₈₀N₈O₄ + Na⁺, 797.5412; found, 797.5420. Anal. Calcd for C₄₄H₈₀N₈O₄: C, 68.18; H, 9.10; N, 14.45. Found: C, 68.02; H, 9.63; N, 14.38.

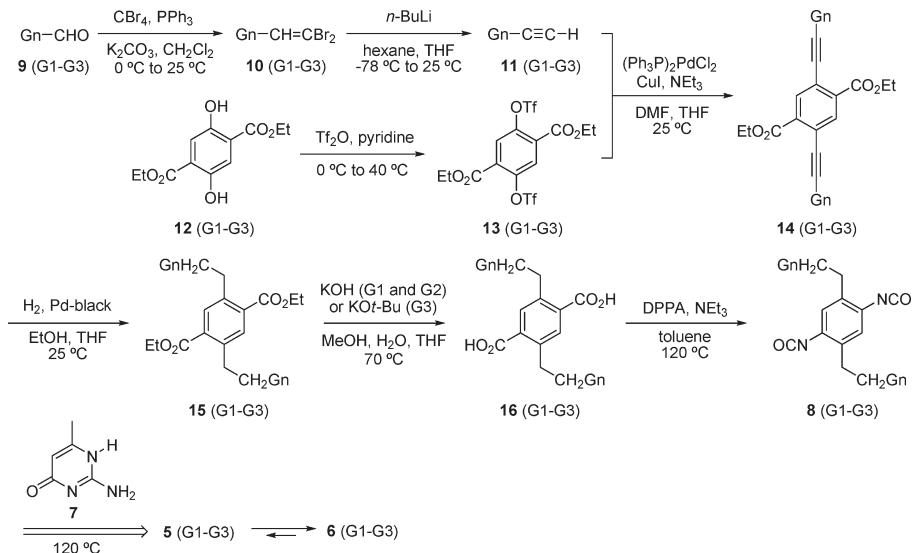
G2 Supramolecular Dendronized Polymer **6 ($n = 2$).** A mixture of the G2-bifunctional protected monomer **19** ($n = 2$) (0.10 g, 0.07 mmol) and Pd(OH)₂–C (0.04 g) in CH₃OH (6 mL) and CHCl₃ (60 mL) was stirred under H₂ (1 atm) at 25 °C. After 24 h, the suspension was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure and purified by precipitation from CH₃OH to give the target G2-dendronized polymer (0.12 g, 80%) as a white powder. Once precipitated, the compound could not be redissolved in any solvents to allow structural characterization. HRMS (MALDI–TOF): calcd for C₈₀H₁₄₂N₈O₄ + H⁺, 1280.1227; found, 1280.1243.

G3 Supramolecular Dendronized Polymer **6 ($n = 3$).** A mixture of the G3-bifunctional protected monomer **19** ($n = 3$) (0.12 g, 0.05 mmol) and Pd(OH)₂–C (0.04 g) in CH₃OH (6 mL) and CHCl₃ (60 mL) was stirred under H₂ (1 atm) at 25 °C. After 24 h, the suspension was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure and purified by precipitation from EtOAc to give the target G3-dendronized polymer (0.09 g, 81%) as a white syrup. δ_H (400 MHz) 4[1H]-pyrimidinone tautomer (76%): 0.86 (96 H, d, $J = 6.3$, CH₃), 0.98–1.73 (170 H, m), 2.20 (6 H, s, pyrimidyl–CH₃), 2.50–3.10 (4 H, s, ArCH₂), 5.80 (2 H, s, pyrimidyl–H), 7.20 (2 H, s, ArH), 11.80 (2 H, br s, NHCONH), 13.28 (1 H, br s, NH in UPy); 4-pyrimidinol tautomer (24%): 0.86 (96 H, d, $J = 6.3$, CH₃), 0.98–1.73 (170 H, m), 2.39 (6 H, s, pyrimidyl–CH₃), 2.50–3.10 (4 H, s, ArCH₂), 6.23 (2 H, s, pyrimidyl–H), 7.71 (2 H, s, ArH), 11.36 (2 H, br s, NHCONH), 13.28 (4 H, br s, NH in UPy). δ_C (100 MHz, some aromatic signals were too weak to be observed): 22.9, 23.0, 23.8, 24.0, 28.6, 31.3, 31.4, 34.1, 34.2, 34.26, 34.31, 148.1, 155.0, 166.8, 172.6. HRMS (MALDI–TOF): calcd for C₁₅₂H₂₈₆N₈O₄ + Na⁺, 2312.2347; found, 2312.2375. SEC (UV): R_t 30.00.

Results and Discussion

1. Design of Di-UPy Macromonomers **5.** The UPy moiety was chosen as the binding unit due to its extremely strong self-dimerization constant ($K_{\text{dim}} = 6 \times 10^7 \text{ M}^{-1}$) in CHCl₃ at 25 °C. This will ensure that the supramolecular dendronized polymer formed will be of high DP values. In principle, any nonpolar dendron could be used as the dendritic component so long as it does not create a highly polar environment or it does not engage in backbiting to the UPy unit. Previously we showed that Fréchet-type oligo(benzyl ether) dendrons could preserve the native binding strength of the UPy unit,

Scheme 1. Synthetic Route To Target Bifunctional Dendritic Monomers **5** ($n = 1-3$)



and they also did not perturb the preferential formation of the DADA tautomer,¹⁷ and therefore were ideal candidates. However, due to synthetic hurdles encountered during the introduction of the two UPy units onto the aromatic core, we needed to anchor the UPy moieties initially as their *O*-benzyl protected derivatives (*vide infra*). Hence, in the final deprotection step of the *O*-benzyl groups, the oligo(benzyl ether) dendrons could not withstand the hydrogenolysis conditions. In the end, our previously reported aliphatic hydrocarbon dendrons¹⁸ were chosen for this job. They are known to possess excellent solubilization properties in nonpolar organic solvents than their linear counterparts, and can also preserve the nonpolar microenvironment around the UPy unit, although they were found to induce more (4–6%) of the weaker binding DADA tautomers.¹⁴ To ensure that the two UPy units were arranged in a linear fashion, they were anchored to a dendronized aromatic ring in a *para* relationship. However, we did notice in a recent report that cyclic species were formed even when the UPy groups were pre-organized in a fixed angle of 180°.¹⁹

2. Synthesis. We initially employed the coupling reaction²⁰ between 6-methylisocytosine (7) and a dendronized diisocyanate **8** to arrive at the target dendronized polymers **6** (Scheme 1). Hence, the known dendritic aldehydes **9**¹⁸ (G1–G3) were converted to the corresponding acetylenes **11** in 59–79% yield via the vinylic dibromides **10** using a Corey–Fuchs reaction sequence.²¹ The terminal acetylenes (2.5–3.0 equiv) **11** were then coupled to a ditriflate **13**, prepared from diethyl 2,5-dihydroxyterephthalate (**12**) employing a literature procedure,²² in the presence of $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, CuI, and NEt₃ to afford the unsaturated diesters **14** in 50–90% yield. The triple bonds were then saturated in the presence of Pd-black to yield the dendronized diesters **15**, followed by alkaline hydrolysis (KOH or KO-*t*-Bu) to produce the diacids **16** in 90–98% overall yield. The diacids **16** were then reacted with diphenyl phosphorazidate (DPPA) and NEt₃ to give the corresponding diacylazides, and immediately subjected to Curtius rearrangement by heating at 120 °C to generate the diisocyanates **8** *in situ*.

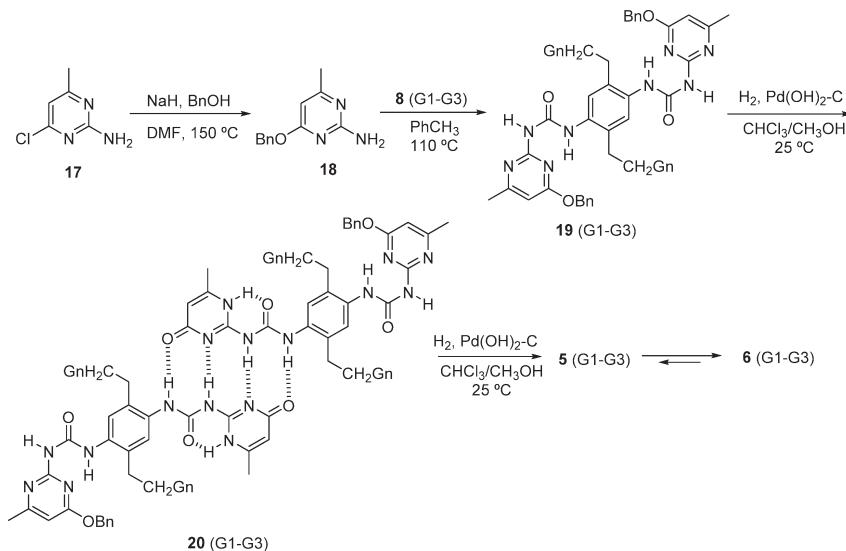
The G1 diisocyanate analogue **8** ($n = 1$) was then allowed to react with 2 equiv of 6-methylisocytosine **7** in an attempt to prepare the G1 di-UPy derivative **5** ($n = 1$), which should then self-assemble to produce the supramolecular G1 dendronized polymer **6** ($n = 1$) in nonpolar solvents. However, problems were encountered during the coupling reaction.

First, compound **7** was only soluble in highly polar solvents while the G1 diacid **16** ($n = 1$)—precursor of the G1 diisocyanate **8** ($n = 1$)—had a relatively poor solubility in these polar solvents, therefore it was difficult to find a suitable solvent to facilitate the reaction. Second, the amino group in isocytosine **7** had a lower nucleophilicity, and hence higher reaction temperature and longer reaction time were required to force the reaction to proceed. Under such harsh conditions the starting materials began to decompose and no desired product could be isolated from the reaction.

To solve the problem stated above, it was decided to use an *O*-benzyl-protected amino compound **18** to react with diisocyanates **8** (Scheme 2). There are several advantages of using this *O*-benzyl-protected compound. First, it has better solubility in many common organic solvents. Second, the nucleophilicity of compound **18** is higher than that of 6-methylisocytosine (**7**). Third, after the reaction, any monocoupled product, if present, can be easily separated from the doubly coupled target compound **19**. Fourth, the benzyl groups in compounds **19** can be cleanly removed by hydrogenolysis in high yield to give the target monomers **5**. Hence, this modified synthetic route was used for the synthesis of our G1–G3 dendronized supramolecular polymers **6**. It should be mentioned here that the use of *O*-benzyl protected group in the synthesis of UPy compounds had already been demonstrated by Meijer.²³

The amino compound **18** was prepared in 72% yield by heating a mixture of benzyl alcohol, NaH, and commercially available 2-amino-4-chloro-6-methylpyrimidine (**17**) in DMF using a literature procedure.²⁴ Reaction of 2 equiv of **18** with the G1–G3 diisocyanates **8** proceeded smoothly to give the doubly protected monomers **19** in 49–69% yield.

The two *O*-benzyl groups had to be removed from the bifunctional protected monomers **19** in order to release the target dendronized di-UPy monomers **5**. However, two critical issues had to be addressed in the final synthetic step. First, hydrogenolysis of the two *O*-benzyl groups must go to 100% completion. If only one of them is removed, the resulting mono-UPy compound will serve as a polymer chain stopper that will inevitably lower the DP value. Second, once the hydrogenolysis has proceeded to a certain extent, there will be the presence of the mono-UPy and di-UPy compounds, together with the supramolecular oligomers formed from these two species. Under this circumstance, it is necessary to maintain the solubility of the many species in the reaction

Scheme 2. Synthetic Route To Target Bifunctional Dendritic Monomers 5 ($n = 1\text{--}3$) via an *O*-Benzyl Protection Strategy

medium. If precipitation occurs during hydrogenolysis, the mono-UPy unit, still carrying one *O*-benzyl moiety, located at the oligomer chain ends will have difficulty to undergo further hydrogenolysis due to phase separation. This will lead to incomplete removal of the *O*-benzyl groups and hence a poor DP value. This precipitation problem is particularly acute for rigid rod supramolecular polymers such as those described here. In principle, the latter problem could be alleviated by adding hydrogen bond donor or acceptor solvents such as acetic acid or alcoholic solvents in the reaction medium, which can reduce the extent of oligomer formation and also keeps the highly polar di-UPy monomer in solution.

Hydrogenolysis of the G1 and G2 protected monomers **19** was first carried out using 10% palladium on charcoal or palladium black in THF as the solvent. Removal of the first *O*-benzyl group was very fast and resulted in the immediate formation of dimers **20**. However, dismantling of the second one proceeded very slowly, and formation of insoluble oligomeric species was noted. At this point, the reaction failed to proceed further and the hydrogenolysis was just partially completed. This was particularly problematic with the G1 and G2 series, as they lacked larger hydrocarbon dendrons to enhance their solubility. We also tried adding EtOH or acetic acid to the reaction mixture in order to break down the UPy quadruple hydrogen bonding interactions but the precipitation problem still persisted. Furthermore, the precipitated G1 and G2 oligomers could not be redissolved in most organic solvents for structural characterization. It was also difficult to monitor the extent of the reaction by thin layer chromatography as significant tailing on the plates was observed.

It was then decided to monitor the reaction by ¹H NMR spectroscopy. Hydrogenolysis of the G1 and G2 compounds **19** was carried out in diluted solutions (~1 mM) using catalytic Pd(OH)₂ on charcoal in a 10/1 mixture of CDCl₃/CD₃OD. Under the reaction conditions, no precipitate was formed during the reaction and complete removal of the *O*-benzyl groups was realized. Hence, compounds **19** could be cleanly converted to the supramolecular dendronized polymers **6** by conducting the hydrogenolysis under the above-mentioned conditions. After that the catalyst was removed by filtration and the products **5** were isolated by precipitation with CH₃OH ($n = 1$ and 2) or EtOAc ($n = 3$). While the precipitated G1 dendronized polymer **5** ($n = 1$, yield = 74%)

could be redissolved in polar solvents such as DMF and DMSO, the G2 analogue (yield = 80%) was devoid of any solubility in any solvents. The G3 analogue (yield = 81%), on the other hand, was highly soluble in nonpolar solvents.

3. Structural Characterizations. The structural identities of the compounds were confirmed by a combination of ¹H and ¹³C NMR spectroscopy, mass spectrometry (MS) and size exclusion chromatography (SEC). The ¹H NMR spectral signals of the various bifunctional compounds **14**–**16** and **19** are well separated into distinctive regions. The first is the set of signals originated from the hydrocarbon dendrons at δ 0.8–1.6 and δ 2.4–3.0. The second is due to the set of signals of the nondendritic substituents attaching to the central aromatic core, and the third is a singlet located at $\sim \delta$ 7.6–7.9 due to the aromatic hydrogens of the central core; its exact position is dependent on the nature of the nondendritic substituents. After coupling of the pyrimidine rings to the central core, the bifunctional *O*-benzyl protected monomers **19** ($n = 1\text{--}3$) are readily diagnosed by the signal (δ 6.25) correspond to the pyrimidine nucleus and that (δ 5.3) of the benzyl protons. Of particular interest is that the two urea N–H protons resonate at very different positions (δ 11.2 and 7.2). The downfield signal is the one that can form an intramolecular hydrogen-bond to the pyrimidyl nitrogen. Incidentally, all the chemical shift values of these signals are independent of the dendrimer generation.

The molecular mass of all compounds were also determined by mass spectrometry. For compounds with higher molecular weight values, the use of MALDI–TOF was needed in order to obtain the molecular ion peak. The obtained experimental values agreed well with the theoretical values.

The purity of the synthesized compounds was also checked by SEC (Styragel HR1, HR2, HR3, and HR4 columns in serial, THF, 40 °C) using polystyrenes as the standards. Because of the significant difference in the nature of our compounds and polystyrenes, the calculated M_w values were slightly different from the theoretical ones. In all cases, a sharp peak with a polydispersity index (PDI) of less than 1.04 was found, confirming the compounds were of high homogeneity.

4. Supramolecular Polymerizations of **5.** The G1 dendronized di-UPy monomer **5** ($n = 1$) is insoluble in nonpolar solvents and has very poor solubility even in polar solvents such as DMSO and DMF. Therefore, NMR spectroscopy could only be conducted in DMSO-*d*₆ in diluted solution

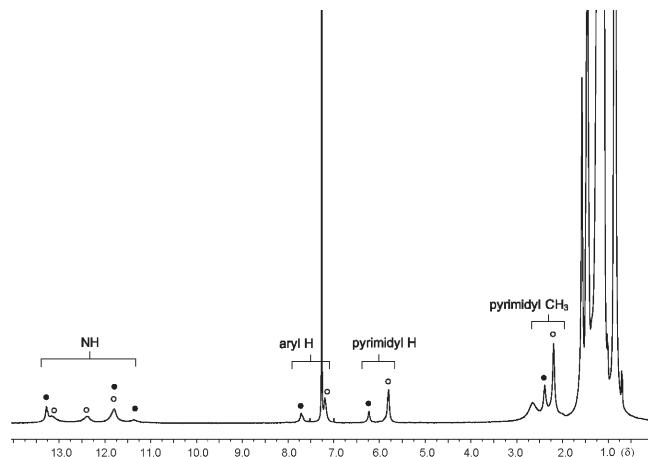


Figure 1. ^1H NMR spectrum (400 MHz, CDCl_3 , 8.7 mM) of G3 supramolecular dendronized polymer **6** ($n = 3$). ○ and ● indicate signal peaks of DDAA and DADA species, respectively.

(0.65 mM). As expected, the UPy unit existed in the monomeric 4[3H]-pyrimidinone form, in which the intramolecular hydrogen-bonded NH resonated at the most downfield region (δ 11.4) and the remaining two urea NH signals appeared at δ 9.5–10.3. The precipitated G1 di-UPy monomer **5** ($n = 1$) could also be characterized by MALDI–TOF mass spectroscopy. The experimental molecular weight ($M + \text{Na}^+$: 797.5420) matched with the theoretical value (797.5412). However, no peaks of oligomeric aggregates were observed. As the compound was only soluble in very polar solvents, in which it existed in monomeric state, and hence its supramolecular properties were not investigated.

The G2 dendronized di-UPy monomer **5** ($n = 2$) was insoluble in any solvents once precipitated from CH_3OH , characterization could only be done during the hydrogenolysis. As mentioned earlier, its ^1H NMR spectrum showed the complete disappearance of the *O*-benzyl proton signal (see Supporting Information for details). An aliquot from the reaction mixture was taken out and subjected to MALDI–TOF analysis and the experimental molecular ion peak ($M + \text{H}^+$: 1280.1243) matched with the theoretical value (1280.1227). On the other hand, the precipitate solid sample failed to produce any mass spectrum. Again, due to its insolubility, no further studies could be done.

In sharp contrast, the G3 di-UPy monomer **5** ($n = 3$) is soluble in most nonpolar solvents such as CHCl_3 , hexane, and toluene, and could be characterized by ^1H NMR spectroscopy in CDCl_3 (Figure 1). Some notable features were observed. First, the downfield signals at δ 11–13.5 corresponding to the three hydrogen-bonded N–Hs were observed. This confirmed that the monomeric units **5** ($n = 3$) were hydrogen-bonded together to form the polymer species **6**. Second, all peak signals were broadened, suggesting they were originated from a polymer structure. Third, two sets of proton signals were observed, which corresponded to the 4[1H]-pyrimidinone DDAA and 4-pyrimidinol DADA tautomeric structures. The dominant species could be assigned to the 4[1H]-pyrimidinone in which the pyrimidyl proton resonated at δ 5.8. The peak with a lower intensity at δ 6.2 was due to the pyrimidyl proton of 4-pyrimidinol.²⁰ From their relative integrations, the amount of DDAA and DADA tautomeric species in CHCl_3 was 3/1. The percentage of DADA tautomer was very large as compared to the analogous mono-UPy compounds bearing the same aliphatic hydrocarbon dendron,¹⁴ in which the ratio was about 20/1. A higher percentage of DADA tautomer also indicated that

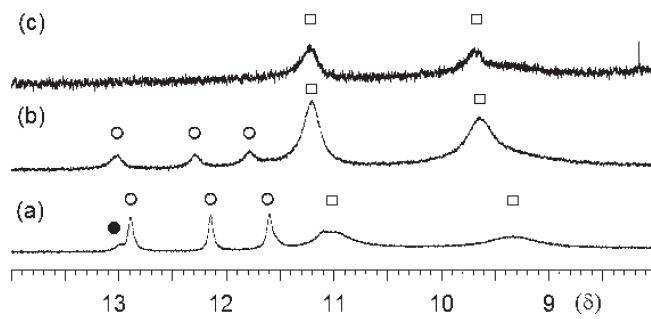


Figure 2. Partial ^1H NMR (400 MHz) spectrum of 8.7 mM solutions of supramolecular dendronized polymer **6** ($n = 3$) in (a) 10%, (b) 25% and (c) 35% $\text{DMSO}-d_6$ in CDCl_3 . ○, ●, and □ indicate signal peaks of the DDAA, DADA, and 4[3H]-pyrimidinone species, respectively.

the binding strength between the UPys should be slightly weakened. Nonetheless, the positions of the NH signals in both the DDAA and DADA forms did not change in the concentration range between 58 mM and 10 μM (see Supporting Information for details). Even at the lowest concentration (10 μM), the polymeric signals were still observed and no monomeric signals were found. Assuming the polymeric species formation was over 90% at the lowest concentration, the binding strength between the UPy units in the DDAA form was estimated to be 10^7 M^{-1} in CDCl_3 at 25 °C.

The self-assembling properties of the G3 supramolecular dendronized polymer **6** ($n = 3$) was further investigated by ^1H NMR spectroscopy in 10%, 25%, and 35% $\text{DMSO}-d_6$ in CDCl_3 (8.7 mM) (Figure 2). It was found that signals (δ 8.8–11.3) corresponding to the monomeric 4[3H]-pyrimidinone appeared in all three solvent systems. In 10% $\text{DMSO}-d_6$, the monomer as well as the polymer signals (δ 11.5–13.2) from both the DDAA and DADA forms were still observable. The intensity ratio of polymer to monomer signals was about 1/1, which indicated that polymer formation was greatly depressed. Incidentally the relative amount of DADA, as compared to DDAA tautomeric form, also decreased. This result was consistent with the literature finding, in which polar solvent systems disfavored the formation of DADA tautomer.²⁰ When the percentage of $\text{DMSO}-d_6$ was increased to 25%, the DADA signals disappeared and the intensities of the monomeric 4[3H]-pyrimidinone signals became higher than those of DDAA. From the signal integrations, only 10% of the UPy groups were in polymeric form. In 35% DMSO , the polymer signals completely vanished and only signals corresponding to the monomeric 4[3H]-pyrimidinone were observed. The ^{13}C NMR spectrum of polymer **6** ($n = 3$) was also recorded in CDCl_3 . Because of its polymeric nature, the peaks were very broad. While the signals due to the aliphatic dendrons could be clearly identified, those of the aromatic and heteroaromatic carbons gave very weak signals.

The G3 supramolecular polymer **6** ($n = 3$) was analyzed by MALDI–TOF mass spectrometry. The molecular ion peak ($M + \text{Na}^+$: 2312.2375) matched well to the theoretical value (2312.2347). However, no peak due to oligomeric species could be observed. The polymer sample was also subjected to SEC analysis in THF at 40 °C. In this case, a sharp peak was found with a PDI value of 1.01. Incidentally, the retention time ($R_t = 30.00 \text{ min}$) was very close to that ($R_t = 30.22 \text{ min}$) of the di-*O*-benzyl derivative **20** ($n = 3$), suggesting the polymer dissociated into individual monomer unit **5** ($n = 3$) under the column conditions.

Attempts were also made to obtain the molecular weight (MW) and size distribution of the G3 supramolecular dendronized polymer **6** by dynamic laser light scattering (DLLS) experiments. At low polymer concentrations (1–5 mg/mL),

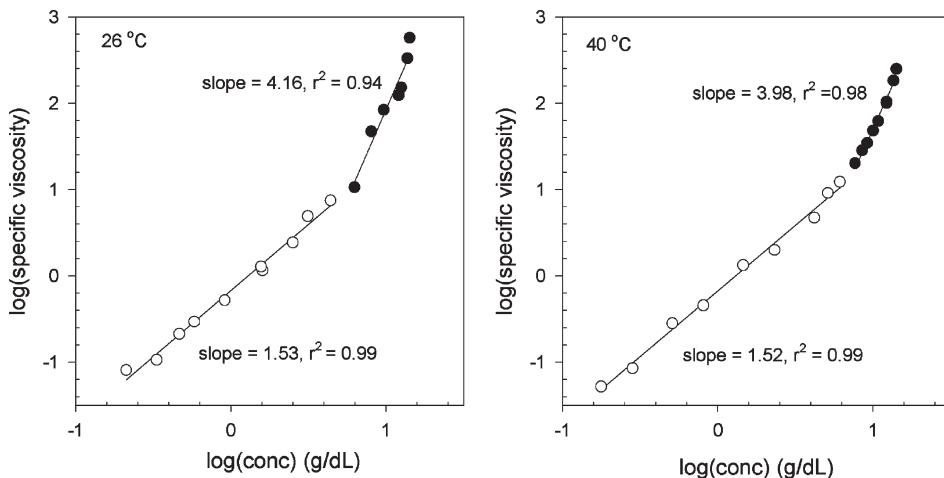


Figure 3. Double–logarithmic plots of specific viscosity vs concentration of supramolecular dendronized polymer **6** ($n = 3$) in CHCl_3 solutions at (left) 26 °C and (right) 40 °C.

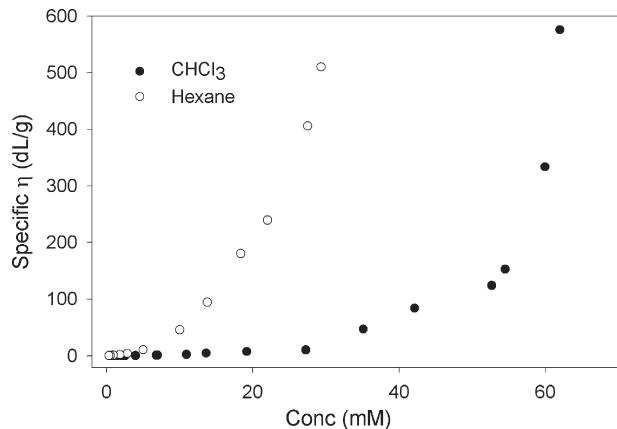


Figure 4. Specific viscosity of supramolecular dendronized polymer **6** ($n = 3$) in CHCl_3 (●) and hexane (○) at 26 °C.

a peak with an R_h of 20 nm was found, which corresponded to a polymer chain consisted of 10–15 monomer units based on the molecular dimension of the rigid backbone (see Supporting Information for details). However, at a sample concentration of 10 mg/mL, an additional aggregation peak at 200 nm began to emerge. Because of this aggregation effect, we were unable to extract the actual MW value of the individual supramolecular polymer chain **6** at higher concentrations by DLS.

5. Viscosity Properties of Supramolecular G3 Dendronized Polymer **6.** The solution viscosity of the G3 supramolecular dendronized polymer **6** was measured at 26 and 40 °C in CHCl_3 in a concentration range of 1–60 mM. It was found that the specific viscosity (η_{sp}) increased nonlinearly with concentration. The corresponding double–logarithmic plots of η_{sp} against concentration showed a change of slope at 26 mM (6 g/dL) (Figure 3). Below this concentration the slope of the line was around 1.5, while above this the slope became 4.0–4.2. For covalent, noninteracting polymer chains, the theoretical slope is 1.0. Hence, a slope of 1.5 at the diluted concentration range suggested that the polymeric species were interacting even in diluted solutions and the degree of polymerization (DP) increased gradually. At the higher concentration range, the relatively high slope of 4.0 indicated that very strong concentration dependent association of individual monomer units, which was a characteristic feature of supramolecular polymers. These values are also

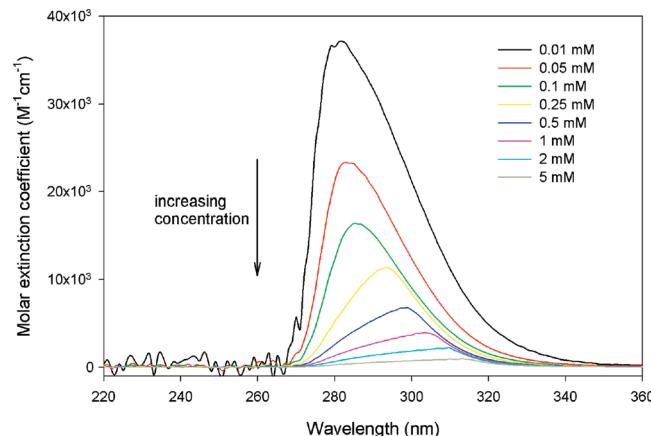


Figure 5. UV absorption spectra of G3 supramolecular dendronized polymer **6** at different concentrations in CHCl_3 at 25 °C.

consistent with other UPy-based supramolecular polymers reported by Meijer.^{15,23a} In addition, the η_{sp} value at 26 °C was twice as high as that at 40 °C of the same concentration. This fact was also reflected by the slightly higher slope (4.16) at 26 °C as compared to that (3.98) at 40 °C, showing the destabilizing entropic effect on monomer association at higher temperature.

Because of the presence of two G3 aliphatic hydrocarbon dendrons, the supramolecular dendronized polymer **6** ($n = 3$) is also soluble in hexane. This unique property enabled us to investigate its viscosity property and the association of the UPy units in hexane. It was found that η_{sp} was about 20–30 times higher in hexane than in CHCl_3 at the same concentration (Figure 4). For example, a solution of the polymer at 27 mM possessed a η_{sp} value of 400 in hexane, but a much smaller value of 15 in CHCl_3 . Unfortunately, the polymer slowly precipitated from hexane once the concentration was above 30 mM. Hence, we were unable to conduct viscosity measurements at higher concentrations to determine the slopes of the double–logarithmic plot of η_{sp} against concentration in hexane. However, based on the much higher viscosity values in hexane, the polymers formed in hexane should have a much higher DP value than that in CHCl_3 . The change of viscosity properties of the G3 polymer **6** with temperature and different solvent systems further demonstrated the dynamic nature of the association process of such supramolecular dendronized polymers.

6. UV–Vis Spectroscopy. In addition to investigating the hydrogen bond mediated one-dimension self-assembly of the UPy units, it is also of interest to understand whether the dimeric UPy rings, belonging to the same or different polymer chains, can interact with each other. Sijbesma and Meijer had demonstrated that dimeric UPys could stack on top of each other to form columnar architecture.^{15c} Hence, concentration dependent UV–vis spectrophotometric studies were also carried out on the G3 dendronized polymer **6**.

UV–vis spectra of the polymer solutions of different concentrations (0.01–5 mM) were recorded in CHCl₃ at 25 °C (Figure 5). A reduction in the molar extinction coefficient along with a significant bathochromic shift of the absorption maximum from 281 to 313 nm were seen with increasing concentration of supramolecular polymer **6**. This observation was consistent with the formation of J-type aggregates

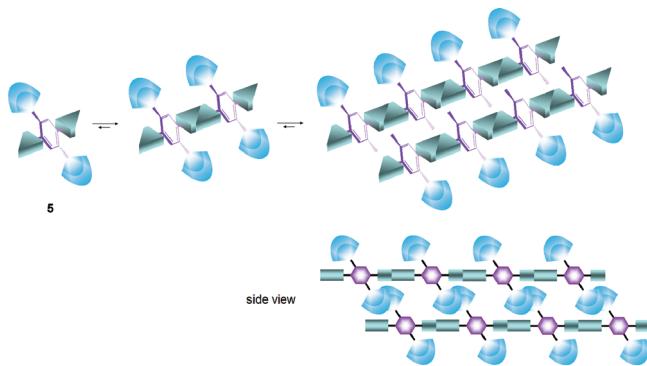


Figure 6. Schematic representation of self-assembly of macromonomer **5** via hydrogen bonding and formation of slipped J-type aggregates. The aromatic cores, UPy units and the dendrons are in purple, dark green, and blue, respectively. For clarity, the dendrons are removed in some of the structures.

with increasing concentration of UPy units.²⁵ Hence, it appeared that the dimeric UPy units aligned themselves in a stair-case fashion with a small slippage angle (Figure 6). This stacking arrangement could also avoid interchain dendron repulsion. Furthermore, it should be noted that the plane of the dimeric UPy rings might not align in a coplanar manner to the central aromatic cores. As a result, the two large dendrons are tilted away from the plane of the UPy rings so as to avoid steric blocking of the UPy units from dimerization. This proposed self-assembly structure is in many ways reminiscent to that proposed by Würthner on hydrogen bond-mediated main chain supramolecular polymers based on a perylene bisimide skeleton.²⁶

7. Scanning Electron Microscopy. As the two UPy units are aligned in an angle of 180° on a rigid aromatic spacer, the resulting supramolecular polymer should possess a linear structure. Hence, scanning electron microscopy (SEM) was used to study the morphology of the polymer in the solid state. Samples of the G3 supramolecular polymer **6** were prepared from THF solutions containing different substrate concentrations (0.1, 0.5, and 1.0 mg/mL) and then spin-coated on a silicon wafer either at low (300 rpm) or high (1500 rpm) angular speed. After that, the samples were coated with gold particles before examinations (Figure 7).

It was found that fibrous structures with high aspect ratio were predominantly found in the samples irrespective of spinning rate and sample concentration. Linear arrangement of the two UPy units as well as the large G3 hydrocarbon dendrons forced the supramolecular polymer backbone to become extended such that interdendron repulsion could be minimized. Bent strings were also found but they appeared to arise from interchain winding or overlaying of two separate fibers (Figure 7b). The polymer fibers were of different lengths but most of them were between 10–100 μm. Assuming each dendronized monomer was fully stretched, the head

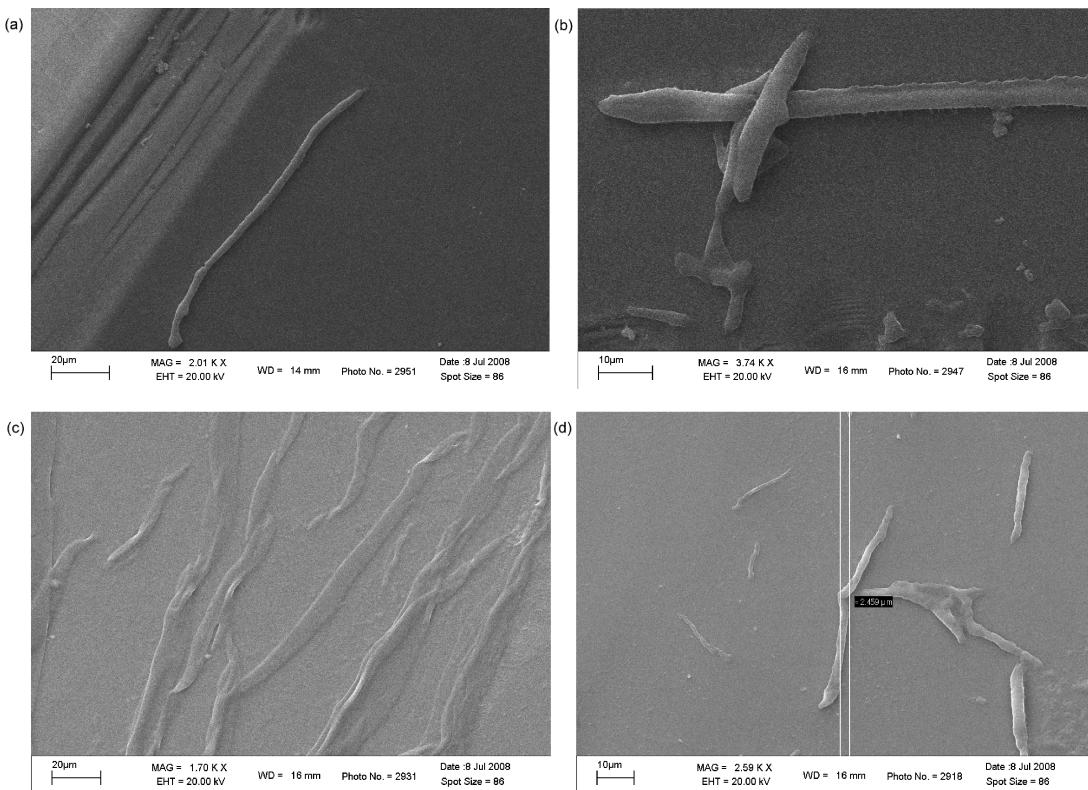


Figure 7. SEM images of G3 supramolecular dendronized polymers **6** prepared under various spin coating conditions on silicon wafers: (a) 0.1 mg/mL at 1500 rpm, (b) 0.5 mg/mL at 300 rpm, (c) 1.0 mg/mL at 300 rpm, and (d) 1.0 mg/mL at 1500 rpm.

to tail distance between the two UPy units is about 2 nm. Hence, a single polymer chain of 10 μm in length will have approximately 5000 monomer units. Moreover, each fiber has a relatively uniform width of 2–3 μm , which indicated that the observed linear structure actually consisted of many polymer chains bundling up together in a manner similar to that reported by Würthner.²⁶ This kind of packing arrangement is facilitated via $\pi-\pi$ stacking interaction between UPy units and hydrophobic interaction between the nonpolar hydrocarbon dendrons.

Conclusion

In this paper, we reported the synthesis and characterization of main chain supramolecular dendronized polymers using a hydrogen bond mediated self-assembly approach. Because of the high crystallinity and poor solubility of such rigid rod polymers, their preparations could not have been accomplished without first securing a clean and high yielding synthetic route to the bifunctional UPy dendritic macromonomers **5**. It was noticed that the nature of the dendrons had a substantial influence on the UPy binding strength, solubility and self-assembly properties. In this study, we found that aliphatic hydrocarbon dendrons were well suited for these purposes. Nonetheless, only the G3 dendrons could confer the resulting supramolecular polymer **6** ($n = 3$) with good solubility to facilitate its characterization and property studies. ^1H NMR and viscosity studies confirmed the reversible, supramolecular nature of the resulting polymer **6**. In particular, viscometry data suggested the associative interaction between the monomers increased nonlinearly with increasing monomer concentration. While the above findings confirmed that the individual UPy units self-assembled to form main chain supramolecular dendronized polymer chains, UV-vis spectroscopic study revealed that individual polymer chains stacked on top of each other via the UPy rings in the form of J-aggregates. SEM morphological study also showed that the resulting polymer had a fibrous structure with a very high aspect ratio. A model was purposed to rationalize how such fibers could be assembled from the dendritic macromonomers. Hence, the self-assembling synthetic approach can offer an alternative route to create dendronized polymers with new and fascinating properties. Having confirmed that the hydrogen bond self-assembled approach could furnish dendronized polymers with high DP values, our next goal is to examine whether rigidification of the dendronized polymer backbone can be realized from using di-UPy dendritic macromonomers having a structural flexible backbone.

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Supporting Information Available: Figures showing ^1H and ^{13}C NMR spectra of all compounds, and DLLS data of G3 supramolecular dendronized polymer **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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