

Self-Assembly of Dendron Rodcoil Molecules into Nanoribbons

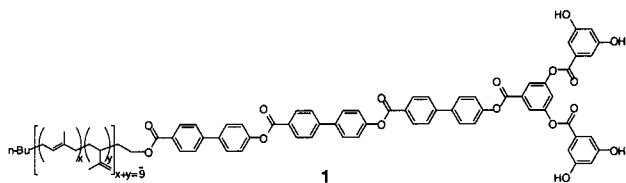
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One of the expectations in science is the discovery of materials with surprising properties or functionality based on designed molecules that self-order or fold. The focus on self-assembly throughout the 90s has generated very useful knowledge toward this expectation and many prospects are on the horizon.^{1–6} Learning how to control the dimensionality and shape of self-assembled structures through molecular design remains a challenge.

We report here on the self-assembly of molecules **1** which we refer to as dendron rodcoils (DRC) because of their blocked covalent architecture consisting of coil-like, rodlike, and dendritic segments. These molecules are synthesized in 15 steps with an



overall yield of 40% (see Supporting Information). Extremely dilute solutions (as low as 0.2 wt %) of **1** in various organic solvents undergo spontaneous gelation, producing birefringent soft solids with a blue-violet hue. Formation of a birefringent gel strongly suggests self-assembling behavior of molecules **1** in organic solvents.

The bulky geometry of the dendron relative to the rod could frustrate the formation of two-dimensional assemblies. Nonetheless, the identical aromatic rod-dendron segments of molecules **1** should be strongly driven to aggregate in one dimension through noncovalent interactions. These could involve hydrogen bonding among hydroxyl groups in the periphery of the dendron as well as aromatic π – π stacking of biphenyl units. We used transmission electron microscopy (TEM) to study self-assembly of molecules **1** in organic solvents. Figure 1 shows a micrograph obtained from a 0.004 wt % solution of the DRC in dichloromethane cast onto a TEM grid. The unstained sample clearly shows one-dimensional objects with a strikingly uniform width of 10 nm. Most of the strands shown in Figure 1 have lengths on the order of micrometers. We also observed isolated strands as long as 10

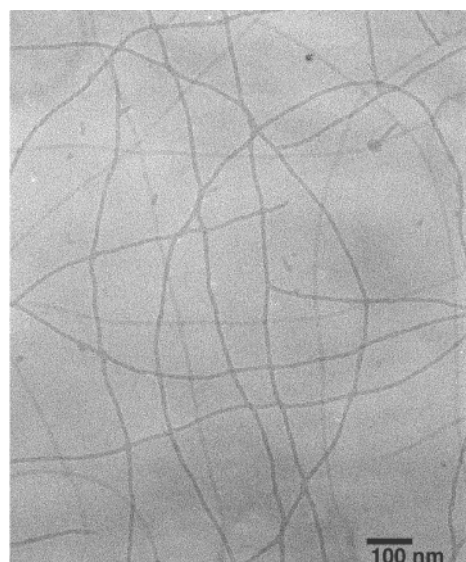


Figure 1. Bright-field TEM micrograph of unstained DRC nanoribbons formed in dichloromethane.

μm , and thus their aspect ratio can be as high as 1000. The fully extended length of an average-size DRC molecule is ~ 6.5 nm, and thus the 10 nm width is consistent with a bimolecular packing of DRC molecules. A head-to-head packing of molecules could generate the narrow structures observed by TEM. Examination of the one-dimensional structures by atomic force microscopy (AFM) reveals their uniform thickness of 2 nm, clearly indicating a ribbonlike shape (see Supporting Information). Therefore, the self-assembly of DRC molecules results in the formation of nanoribbons 10×2 nm and several μm long, which we conclude lie flat on the carbon substrates used for imaging. Small-angle X-ray scattering (SAXS) experiments on the gels did not reveal peaks even when a synchrotron source was used, suggesting that the gels contain one-dimensional structures that are not highly aggregated and therefore lack the necessary structural coherence to generate X-ray diffraction.

We synthesized a series of molecules analogous to **1** to probe the role played by hydrogen bonding in self-assembly. In addition to **1**, three other structures were synthesized that differed only in the number of hydroxyl groups present in the dendron segment. Molecules **2** do not contain hydroxyls at all, whereas **3** and **4** contain two and six hydroxyl groups, respectively (Table 1). Molecules **2** form isotropic solutions when dissolved in organic solvents, and gelation was never observed in this system (see Supporting Information). When only two hydroxyl groups are present (material **3**), gelation is still not observed when molecules are dissolved at elevated temperature. Once these solutions are cooled to room-temperature precipitation occurs. Therefore, the presence of at least four hydroxyl groups per molecule is necessary for solvent gelation by the network of self-assembled nanoribbons. As expected, the same gelation behavior described for **1** was observed for molecules **4** which contain six hydroxyl groups in their dendron. A second series of molecules (**5**–**7**) was synthesized in order to probe the role of aromatic interactions in self-assembly. In this series all of the molecules have identical dendron segments with four hydroxyl groups and therefore retain the same capacity to form hydrogen bonds. However, the molecules differ in the number of biphenyl ester units forming their rod segment. Interestingly, results from these studies indicate that aromatic interactions play an important synergistic role together with hydrogen bonds in triggering self-assembly. As shown in Table 1, molecules **5** (with one biphenyl-ester unit) do not gel organic

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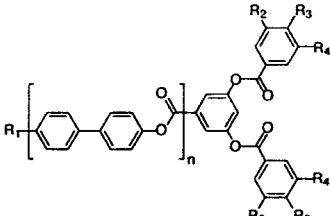
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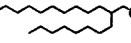
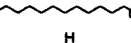
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Table 1. Structure and Behavior in Dichloromethane of DRC Analogs and Model Compounds


molecules	R ₁	n	R ₂	R ₃	R ₄	behavior in CH ₂ Cl ₂
2	PI9-(CH ₂) ₂ -OCO	3	H	H	H	solution
3	PI9-(CH ₂) ₂ -OCO	3	H	H	OH	insoluble material
4	PI9-(CH ₂) ₂ -OCO	3	OH	OH	OH	gel
5	PI9-(CH ₂) ₂ -OCO	1	OH	H	OH	solution
6	PI9-(CH ₂) ₂ -OCO	2	OH	H	OH	weak gel
7	PI9-(CH ₂) ₂ -OCO	4	OH	H	OH	gel
8	PB9-(CH ₂) ₂ -OCO	3	OH	H	OH	gel
9	PS9-PI9-(CH ₂) ₂ -OCO	3	OH	H	OH	solution
10	PS9-PB9-(CH ₂) ₂ -OCO	3	OH	H	OH	solution
11		3	OH	H	OH	gel
12		3	OH	H	OH	insoluble material
13	H	3	OH	H	OH	insoluble material
14	H	1	OH	H	OH	solution

solvents or produce the characteristic blue-violet hue. In contrast, the addition of a second biphenyl-ester unit in molecules **6** results in the formation of a gel but one that is mechanically weak relative to that formed by **1**. Self-assembly is enhanced in molecules **7** containing 4 biphenyl ester units (in comparison with DRC **1**), as indicated by the fact that gelation is now observed in a larger variety of solvents. For example, birefringent gels are obtained when molecules **7** are dissolved in the monomeric polar solvents methyl methacrylate and butyl methacrylate at 1 wt %, whereas molecules **1** only form clear solutions in these same solvents at this concentration.

We have also synthesized DRC molecules containing the same rod-dendron part, but different coils. The presence of a diblock coil in molecules **9** and **10** significantly increases their solubility and gelation does not occur. On the other hand, the absence of a coil (compound **13**) resulted in formation of highly insoluble material. Compound **12** containing a fairly short dodecanyl coil was still insoluble, whereas molecule **11** with a larger coil segment (2-octyl-1-dodecanyl) was found to form gels similar to those of DRC **1**. Finally, molecules **15**–**18** (see Supporting Information) containing the same coil and rod as those in DRC **1** but different dendrons (generation 2, 3, 4, and 5) were prepared in order to understand the influence of the dendron's size. These four molecules were soluble in organic solvents, and none of them led to the formation of gels. Thus, at least three biphenyl-ester units in the rod and four hydroxyls in the dendron segment are required to form a robust gel, which is a signature of extensive self-assembly given the large number of molecules in one nanoribbon. Also the dendritic block must be of generation 1, and a coil of length comparable to the rod must be present in the structure (see Supporting Information). On the basis of these findings, and also the disappearance of all aromatic and hydroxyl peaks in the NMR spectra of gels, we conclude that self-assembly involves the aggregation of DRC molecules **1** through hydrogen bonding and aromatic interactions. The oligoisoprene segments, on the other hand, are found by NMR to retain their rotational freedom after gelation (see Supporting Information).

To gain insight into the internal structure of the nanoribbons, we synthesized model compound **14** containing a dendron identical to that present in DRC **1** but covalently attached to only one biphenyl. Figure 2 shows side and top views of the crystal structure of this compound revealing the presence of a ribbonlike structure composed of tetrameric cycles (upper and middle right). The tetramers are formed by hydrogen bonds among dendritic

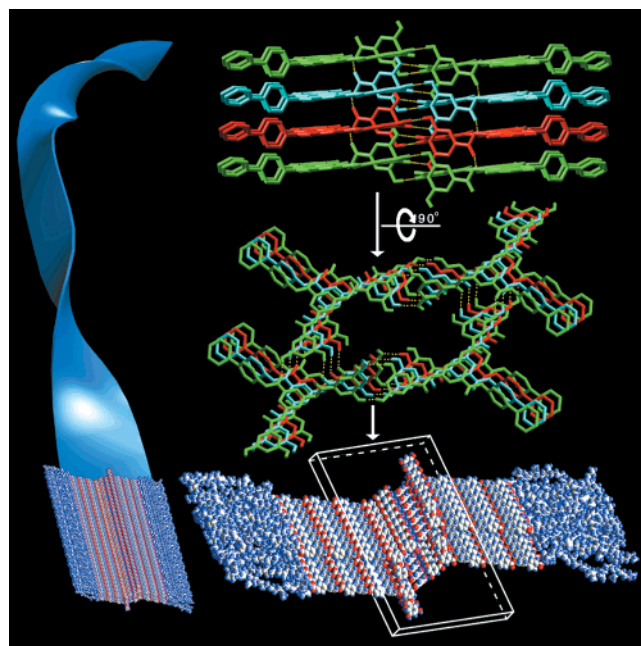


Figure 2. Side view of the ribbonlike structure taken directly from the crystal structure of **14** shows color-coded hydrogen-bonded tetramers (upper right) stacked on top of each other along the [100] direction of the crystal (top view is shown in the middle right). Schematic (left and bottom right) representation of the proposed structure for a DRC nanoribbon.

segments and are stacked on top of each other along the *a* axis of the crystal. The crystal structure reveals eight hydrogen bonds that stitch the tetramers along the axis of the ribbon. Two OH- -OH and two OH- -O=C hydrogen bonds form the cyclic tetramer, whereas four OH- -OH and four OH- -O=C hydrogen bonds connect adjacent tetramers along the ribbon axis (hydrogen bonds are shown in yellow). The biphenyl units are stacked 4.93 Å apart, a distance that should allow for π - π stacking interactions among them. The thickness of the tetrameric cycles from the crystal structure is about 2 nm, which is in excellent agreement with the thickness of the DRC nanoribbons, as determined by AFM. Twisting of the nanoribbons into helical structures has also been observed by TEM (see Supporting Information). Thus, on the basis of these data as well as the crystal structure of the model compound **14**, we envision the structure of the ribbons as depicted in Figure 2 (bottom right, and left).

We have demonstrated that dendron rodcoil molecules **1** self-assemble via hydrogen bonding and π - π stacking interactions into well-defined nanoribbons with uniform width and thickness (10 × 2 nm) and lengths that can be 1000 times greater. These structures can build networks that cause solvents to gel at self-assembler contents as low as 0.2 wt %. The type of self-assembly described here offers a synthetic route to well-defined one-dimensional organic nanostructures.

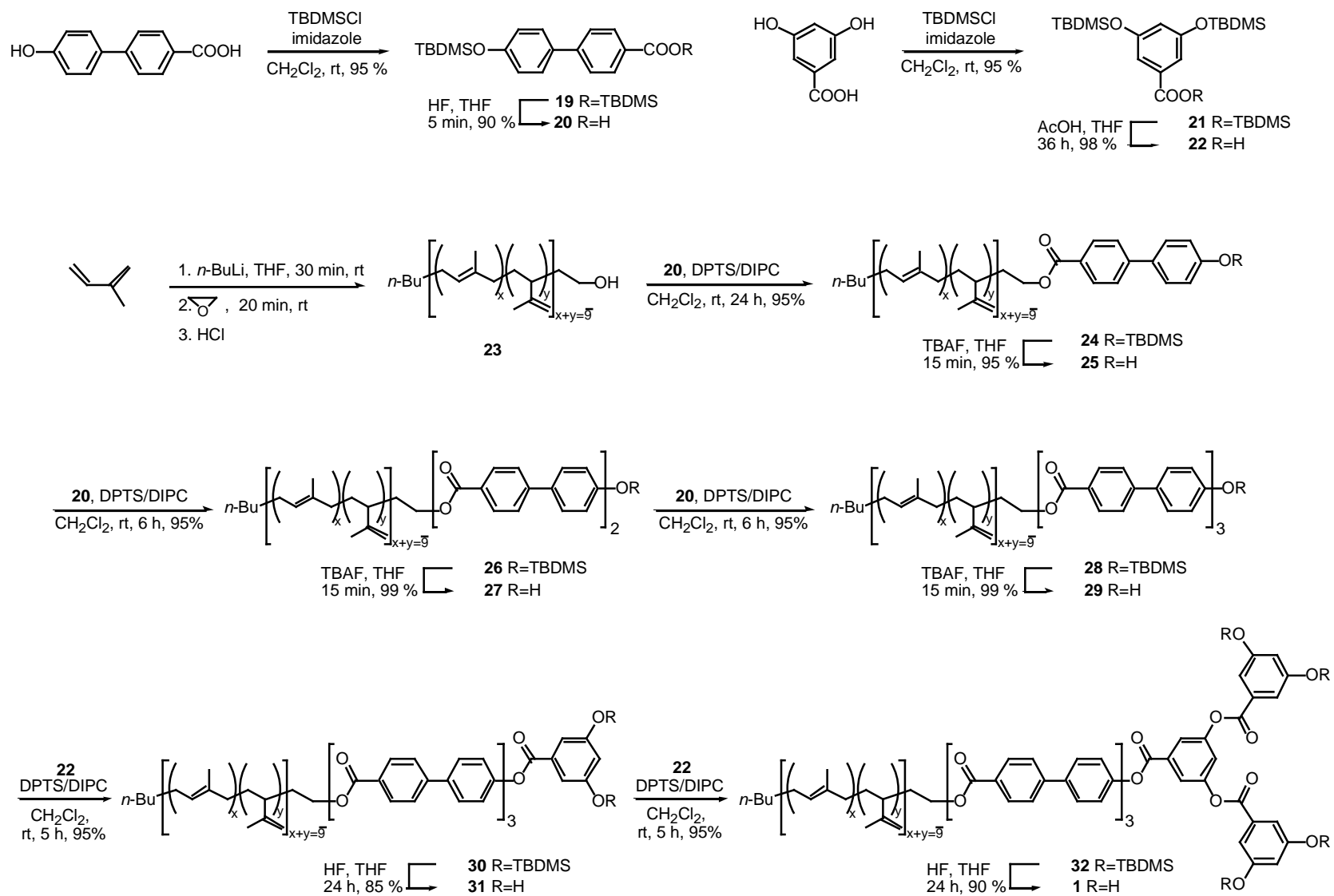
Acknowledgment. This work was supported by the U.S. Army Research Office, the National Science Foundation, and the Department of Energy. E.D.S. thanks NSERC of Canada for a graduate scholarship.

Supporting Information Available: Synthesis of **1**, AFM image and height profiles of ribbons, NMR of DRC gel and solution, TEM of twisted nanoribbons (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

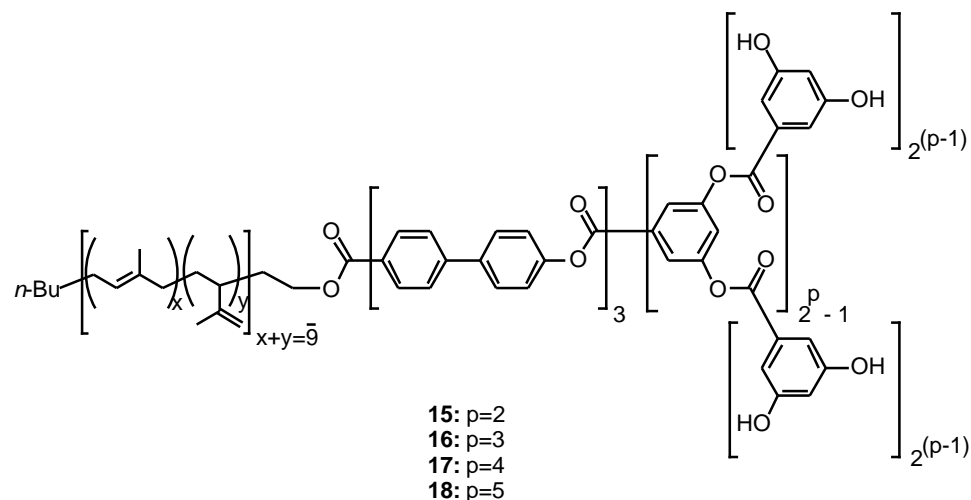
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(7) Crystal data for compound **14**: C₃₃H₂₂O₁₀, *M* = 578.51, triclinic, *P*1̄, *a* = 4.9341 (5) Å, *b* = 19.219 (2) Å, *c* = 33.022 (3) Å, α = 85.805 (2)°, β = 88.850 (2)°, γ = 88.669 (2)°, *V* = 3121.6 (6) Å³, *Z* = 4.

Scheme 1



Synthesis of DRC molecules **1**.



Structure of DRC molecules containing dendritic blocks of different generation (**15:** G_2 ; **16:** G_3 ; **17:** G_4 ; **18:** G_5).

Experimental Section

General. Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and benzene were redistilled from Na^+ /benzophenone ketyl and 4-(N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared as described elsewhere. Isoprene was redistilled under nitrogen atmosphere and dried over calcium hydride before use. The ^1H NMR and spectra were recorded on solution in $\text{THF-}d_8$ on a Varian Unity 500 (500 MHz) or Varian Unity 400 (400 MHz) spectrometers. ^{13}C NMR spectra were recorded at 125 MHz on a Varian Unity 500 spectrometer using $\text{THF-}d_8$ as the solvent and the solvent carbon signal as internal standard. The following abbreviations are used: Ar' refers to aromatic rings derived from biphenyl fragments, Ar'' refers to aromatic rings derived from 3,5-dihydroxybenzoic acid. High resolution field desorption mass spectra were collected on a Micromass 70-VSE spectrometer operating at 8 KV

acceleration voltage and 4 KV extraction plate voltage. Matrix assisted laser desorption ionization (MALDI) mass spectra were obtained on a VG TofSpec spectrometer using dithranol silver trifluoroacetate as a matrix. Synthesis and characterization of molecules **2-18** will be reported elsewhere.

General procedure for esterification reaction. The acid (1.2 eq), pherol or hydroxyl-terminated oligoisoprene (1 eq), DPTS (1.6 eq), and CH_2Cl_2 were combined in a flask with stirring bar under nitrogen atmosphere. 1,3-Diisopropyl carbodiimide (DIPC) (1.6 eq) was added after 10 minutes and the reaction was allowed to stir for several hours. Urea impurities were then removed by precipitating the concentrated reaction mixture into methanol (3 times). The precipitate was dissolved in CH_2Cl_2 and the crude product was purified by flash chromatography as outlined in the following text.

General procedure for the deprotection reaction using tetrabutyl ammonium fluoride (TBAF). The TBDMS-protected phenol (1 eq) was dissolved in THF and cooled to $-78\text{ }^\circ\text{C}$. TBAF (1.0 M solution in THF, 1.2 eq) was added via syringe and the reaction was stirred for 15 minutes at $-78\text{ }^\circ\text{C}$. The reaction was quenched with acetic acid. The reaction was diluted with CH_2Cl_2 and washed with H_2O . The organic layer was collected, dried, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography as outlined in the following text.

General procedure for the deprotection reaction using hydrofluoric acid. The TBDMS-protected product (1 eq) was dissolved in THF in a plastic vessel. Hydrofluoric acid (49 % aq. solution) was added via syringe (20 eq) and the reaction mixture was allowed to stir for 24 hours. The reaction was diluted by CH_2Cl_2 and quenched by saturated solution of sodium bicarbonate. The resultant mixture was washed several times with water and the crude product was purified by flash chromatography as outlined in the following text.

Compound 19. A dry flask was charged with 4'-hydroxy-4-biphenylcarboxylic acid (1 eq), imidazole (2.2 eq), and CH₂Cl₂. After stirring for 10 min., *tert*-butyldimethylsilylchloride (2.2 eq) was added. The solution was stirred for 1 hour at room temperature, then diluted with CH₂Cl₂ and washed several times with water. The organic layers were dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. The product was purified by flash chromatography eluting with CH₂Cl₂ to give **19** as a colorless liquid. Yield: 88 %. ¹H NMR (500 MHz, THF-*d*₈) 0.26 (br s, 12H, OSi(CH₃)₂C(CH₃)₃), 1.04 (br s, 18H, OSi(CH₃)₂C(CH₃)₃), 6.96 (d, 2H, *J* = 8.5 Hz, Ar'*H*), 7.60 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.69 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 8.16 (d, 2H, *J* = 8.4 Hz, Ar'*H*); FD-MS *m/z* 442 (M⁺); (Found: C, 67.72; H, 8.71; Si, 12.35. Calc. for C₂₅H₃₈O₃Si₂: C, 67.87; H, 8.60; Si, 12.67 %).

Compound 20. Compound **19** (1 eq.) was placed into a plastic vessel and dissolved in THF. Hydrofluoric acid (5 eq.) was added via syringe and the reaction mixture was stirred for 5 minutes. The reaction was then diluted by CH₂Cl₂ and quenched by saturated solution of sodium bicarbonate. The resultant mixture was washed several times with water and the resultant product was recrystallized from hexane/CH₂Cl₂ (7:3 vol.) to give **20** as white crystals. Yield: 90 %. ¹H NMR (500 MHz, THF-*d*₈) 0.24 (s, 6H, OSi(CH₃)₂C(CH₃)₃), 1.02 (s, 9H, OSi(CH₃)₂C(CH₃)₃), 6.94 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.58 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.66 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 8.06 (d, 2H, *J* = 8.4 Hz, Ar'*H*); FD-MS *m/z* 328 (M⁺); (Found: C, 70.12; H, 7.55; Si, 8.39. Calc. for C₁₉H₂₄O₃Si: C, 69.51; H, 7.32; Si, 8.54 %).

Compound 21. 3,5-dihydroxybenzoic acid (1 eq) and imidazole (3.8 eq) were dissolved in CH₂Cl₂. *tert*-Butyldimethylsilyl chloride (3.5 eq) was added and the solution stirred overnight. The resulting mixture was diluted with CH₂Cl₂, washed with water and dried over MgSO₄. The solvent was removed by rotary evaporation and the product was purified by flash chromatography (CH₂Cl₂) to give **21** as a colorless liquid. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.23 (s, 12H, OSi(CH₃)₂C(CH₃)₃), 0.47 (s, 6H,

COOSi(CH₃)₂C(CH₃)₃), 1.01 (br s, 27H, Si(CH₃)₂C(CH₃)₃), 6.60 (t, 1H, $J = 2.2$ Hz, Ar''H), 7.22 (d, 2H, $J = 2.4$ Hz, Ar''H); ¹³C NMR (125 MHz, THF-*d*₈) -4.31, 0.17, 18.98, 19.19, 26.17, 115.65, 117.31, 133.97, 157.96, 167.40; FD-MS m/z 496 (M⁺); (Found: C, 60.63; H, 9.74; Si, 16.69. Calc. for C₂₅H₄₈O₄Si₃: C, 60.48; H, 9.68; Si, 16.94 %).

Compound 22. Compound **21** was dissolved in THF/H₂O/AcOH mixture (50:10:40 vol.) and stirred for 24 h. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography eluting with CH₂Cl₂ gradually increasing to 10 % THF/CH₂Cl₂ to give **22** as white needle-like crystals. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.22 (s, 12H, MH₃, THF-*d*₈) -4.29, 18.88, 26.10, 115.47, 117.09, 133.80, 157.41, 167.21; FD-MS m/z 382 (M⁺); (Found: C, 59.73; H, 8.99; Si, 14.61. Calc. for C₁₉H₃₄O₄Si₂: C, 59.69; H, 8.90; Si, 14.65 %).

Molecules 23. 100 mL of benzene and 100 mL of THF were placed in a flask, *n*-BuLi (1 eq) was added followed by the addition of isoprene (9 eq). The reaction was stirred for 30 min, then quenched by ethylene oxide gas for 15 minutes followed by addition of 10 mL of HCl/THF (1:2). The solvent was removed by rotatory evaporation. The crude material was purified by flash chromatography eluting with 40% CH₂Cl₂/hexane gradually increasing to CH₂Cl₂ to give **23** as a colorless liquid. Yield: 70 %. ¹H NMR (500 MHz, THF-*d*₈) 0.5-2.8 (br m, 70H aliphatic), 3.61 (br m, 2H, CH₂OH), 4.5-5.2 (br m, 14H vinyl); FD-MS m/z 730, 663, 596, 797, 864; (Found: C, 85.57; H, 12.42. Calc. for C₅₁H₈₆O₂: C, 83.83; H, 11.78 %).

Molecules 24. This was prepared from **23** and compound **20** and was purified by flash chromatography eluting with hexane/CH₂Cl₂ (1:1 vol.) to give **24** as a colorless liquid. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.23 (s, 6H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 80H aliphatic), 4.29 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.95 (d, 2H, $J = 8.6$ Hz,

Ar'*H*), 7.55 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 7.67 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 8.04 (d, 2H, *J* = 8.5 Hz, Ar'*H*); GPC (254 nm, THF) PDI=1.09, M_n =1520.

Molecules 25. This was prepared from **24** and was purified by flash chromatography eluting with 5% THF/CH₂Cl₂ to give **25** as a colorless liquid. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.5-2.8 (br m, 70H aliphatic), 4.26 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.83 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 7.52 (d, 2H, *J* = 8.3 Hz, Ar'*H*), 7.65 (d, 2H, *J* = 8.2 Hz, Ar'*H*), 8.02 (d, 2H, *J* = 8.5 Hz, Ar'*H*), 8.45 (s, 1H, Ar'*OH*); GPC (254 nm, THF) PDI=1.07, M_n =1380.

Molecules 26. This was prepared from **25** and compound **20** and was purified by flash chromatography eluting with CH₂Cl₂ to give **26** as a colorless liquid. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.25 (s, 6H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 80H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.97 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.40 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 7.62 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.80 (m, 6H, Ar'*H*), 8.11 (d, 2H, *J* = 8.5 Hz, Ar'*H*), 8.22 (d, 2H, *J* = 8.4 Hz, Ar'*H*); GPC (254 nm, THF) PDI=1.07, M_n =1760.

Molecules 27. This was prepared from **26** and was purified by flash chromatography eluting with 5% THF/CH₂Cl₂ to give **27** as a tacky solid. Yield: 87 %. ¹H NMR (500 MHz, THF-*d*₈) 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.87 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.38 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 7.59 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.77 (m, 6H, Ar'*H*), 8.09 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 8.21 (d, 2H, *J* = 8.4 Hz, Ar'*H*), 8.51 (s, 1H, Ar'*OH*); GPC (254 nm, THF) PDI=1.08, M_n =1610.

Molecules 28. This was prepared from **27** and compound **20** and was purified by flash chromatography eluting with 5% THF/CH₂Cl₂ to give **28** as a white solid. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.26 (s, 6H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 80H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.98 (d, 2H, *J* = 8.6 Hz, Ar'*H*), 7.41 (m, 4H, Ar'*H*), 7.66 (d,

2H, $J = 8.6$ Hz, Ar' H), 7.80 (m, 6H, Ar' H), 7.85 (d, 2H, $J = 8.7$ Hz, Ar' H), 7.89 (d, 2H, $J = 8.6$ Hz, Ar' H), 8.11 (d, 2H, $J = 8.5$ Hz, Ar' H), 8.24 (d, 2H, $J = 8.6$ Hz, Ar' H), 8.29 (d, 2H, $J = 8.4$ Hz, Ar' H); GPC (254 nm, THF) PDI=1.07, M_n =1970.

Molecules 29. This was prepared from **28** and was purified by flash chromatography eluting with 40% THF/CH₂Cl₂ to give **29** as a white solid. Yield: 99 %. ¹H NMR (500 MHz, THF- d_8) 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.87 (d, 2H, $J = 8.6$ Hz, Ar' H), 7.40 (m, 4H, Ar' H), 7.59 (d, 2H, $J = 8.6$ Hz, Ar' H), 7.77 (m, 6H, Ar' H), 7.82 (d, 2H, $J = 8.6$ Hz, Ar' H), 7.87 (d, 2H, $J = 8.4$ Hz, Ar' H), 8.10 (d, 2H, $J = 8.5$ Hz, Ar' H), 8.22 (d, 2H, $J = 8.4$ Hz, Ar' H), 8.29 (d, 2H, $J = 8.3$ Hz, Ar' H), 8.53 (s, 2H, Ar'OH); GPC (254 nm, THF) PDI=1.07, M_n =1820.

Molecules 30. This was prepared from **29** and compound **22** and was purified by flash chromatography eluting with 5% THF/CH₂Cl₂ to give **30** as a white solid. Yield: 89 %. ¹H NMR (500 MHz, THF- d_8) 0.27 (s, 12H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 88H aliphatic), 4.31 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.70 (t, 1H, $J = 2.2$ Hz, Ar'' H), 7.32 (d, 2H, $J = 2.0$ Hz, Ar'' H), 7.40 (m, 6H, Ar' H), 7.78 (m, 4H, Ar' H), 7.84 (d, 4H, $J = 8.4$ Hz, Ar' H), 7.88 (d, 4H, $J = 8.2$ Hz, Ar' H), 8.10 (d, 2H, $J = 8.5$ Hz, Ar' H), 8.29 (d, 4H, $J = 8.1$ Hz, Ar' H); GPC (254 nm, THF) PDI=1.08, M_n =2190.

Molecules 31. This was prepared from **30** and was purified by flash chromatography eluting with 15% THF/CH₂Cl₂ to give **31** as a white solid. Yield: 85 %. ¹H NMR (500 MHz, THF- d_8) 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.49 (t, 1H, $J = 2.2$ Hz, Ar'' H), 7.08 (d, 2H, $J = 2.4$ Hz, Ar'' H), 7.40 (m, 6H, Ar' H), 7.78 (m, 4H, Ar' H), 7.82 (d, 4H, $J = 8.6$ Hz, Ar' H), 7.86 (d, 4H, $J = 8.6$ Hz, Ar' H), 8.09 (d, 2H, $J = 8.5$ Hz, Ar' H), 8.29 (d, 4H, $J = 8.3$ Hz, Ar' H), 8.52 (s, 2H, Ar''OH); GPC (254 nm, THF) PDI=1.08, M_n =2050.

Molecules 32. This was prepared from **31** and compound **22** and was purified by flash chromatography eluting with CH₂Cl₂ to give **32** as a white solid. Yield: 95 %. ¹H NMR (500 MHz, THF-*d*₈) 0.26 (s, 24H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 106H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.68 (t, 2H, *J* = 2.3 Hz, Ar''*H*), 7.33 (d, 4H, *J* = 2.3 Hz, Ar''*H*), 7.42 (m, 6H, Ar'*H*), 7.60 (t, 1H, *J* = 2.2 Hz, Ar''*H*), 7.79 (m, 4H, Ar'*H*), 7.85 (d, 4H, *J* = 8.6 Hz, Ar'*H*), 7.90 (d, 4H, *J* = 8.4 Hz, Ar'*H*), 8.04 (d, 2H, *J* = 2.2 Hz, Ar''*H*), 8.10 (d, 2H, *J* = 8.5 Hz, Ar'*H*), 8.29 (d, 4H, *J* = 8.0 Hz, Ar'*H*); GPC (254 nm, THF) PDI=1.08, M_n=3060.

Molecules 1. This was prepared from **32** and was purified by flash chromatography eluting with CH₂Cl₂ gradually increasing to 10 % THF/CH₂Cl₂ to give **1** as a white solid. Yield: 90 %. ¹H NMR (500 MHz, THF-*d*₈) 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.51 (t, 2H, *J* = 2.2 Hz, Ar''*H*), 7.10 (d, 4H, *J* = 2.4 Hz, Ar''*H*), 7.42 (m, 6H, Ar'*H*), 7.58 (t, 1H, *J* = 2.2 Hz, Ar''*H*), 7.79 (m, 4H, Ar'*H*), 7.85 (d, 4H, *J* = 8.6 Hz, Ar'*H*), 7.89 (d, 4H, *J* = 8.4 Hz, Ar'*H*), 8.01 (d, 2H, *J* = 2.2 Hz, Ar''*H*), 8.10 (d, 2H, *J* = 8.5 Hz, Ar'*H*), 8.29 (d, 4H, *J* = 8.1 Hz, Ar'*H*), 8.59 (s, 4H, Ar''OH); ¹³C NMR (125 MHz, THF-*d*₈) 14.45, 19.23, 23.54, 24.98, 28.08, 30.00, 32.77, 40.24, 43.03, 45.82, 63.43, 65.22, 67.91, 108.91, 108.97, 109.01, 112.3, 121.57, 123.18, 123.25, 127.67, 127.90, 128.98, 129.09, 129.14, 129.42, 130.82, 131.47, 131.59, 132.03, 138.07, 146.06, 152.52, 152.61, 152.93, 160.06, 164.03, 164.97, 166.21; GPC (254 nm, THF) PDI=1.08, M_n=2340.

General procedure for the preparation of the DRC gels. Solid material **1** and dichloromethane (CH₂Cl₂) were placed into a capped vessel and heated to 70-80 °C. Complete dissolution of **1** resulted in formation of a viscous solution with a blue-violet hue which turned into a gel within several minutes at 70 °C. The vessel was cooled to room temperature, and the gels obtained were optically transparent and exhibited a blue-violet color. Neither phase separation nor precipitation were observed in these systems and

the gels remained stable for unlimited periods of time. Temperature induced melting of the gels was never observed even when the sealed vessel was heated to 100 °C (61 °C above the boiling point of CH₂Cl₂), at which point the vapor pressure destroys the container. Thus, the gel structure is thermally irreversible unlike most if not all organogels. The gels formed could only be disassembled by polar solvents such as tetrahydrofuran which can effectively compete for hydrogen bonding with hydroxyl groups of the DRC **1** as determined by FTIR experiments. The critical gelation point in CH₂Cl₂ was found to be 0.2 wt % (i.e. the lowest concentration at which the gel can sustain its own weight upon the inversion of the container).

Dynamic light scattering experiments were performed on dilute solutions of DRC in dichloromethane. The results indicate the growth of rod-like structures in solution. The radius of gyration (RG) of these structures was found to be dependant on concentration, aging time and the temperature. The initial average value of RG for the freshly prepared dilute solutions in dichloromethane (0.01 wt. %) was 250 nm. These data will be published in detail elsewhere.

Gelation behavior of some analogous molecules. DRC molecules **2** form clear non-viscous solutions in all the organic solvents tested (dichloromethane, chloroform, benzene, toluene, styrene, dibromomethane, bromoform, iodoform, chlorobenzene, dichlorobenzene, methyl methacrylate, butyl methacrylate, THF, DMF, DMSO and so on). NMR experiments of solutions of **2** in various solvents indicate the absence of any appreciable aggregation at least within the concentration range from 0.5 to 5 wt %. All the signals were highly resolved and their width and position were found to be independent of concentration.

DRC molecules **6** formed gels at much higher concentration relative to that of DRC **1**. The critical gelation concentration for **6** was five times higher (close to 1 wt %). At this particular concentration the gels formed by **6** can be easily fractured by the slightest shaking or tapping and therefore we defined these gels as “mechanically weak” as opposed to robust gels of **1** which do not fracture at this concentration.

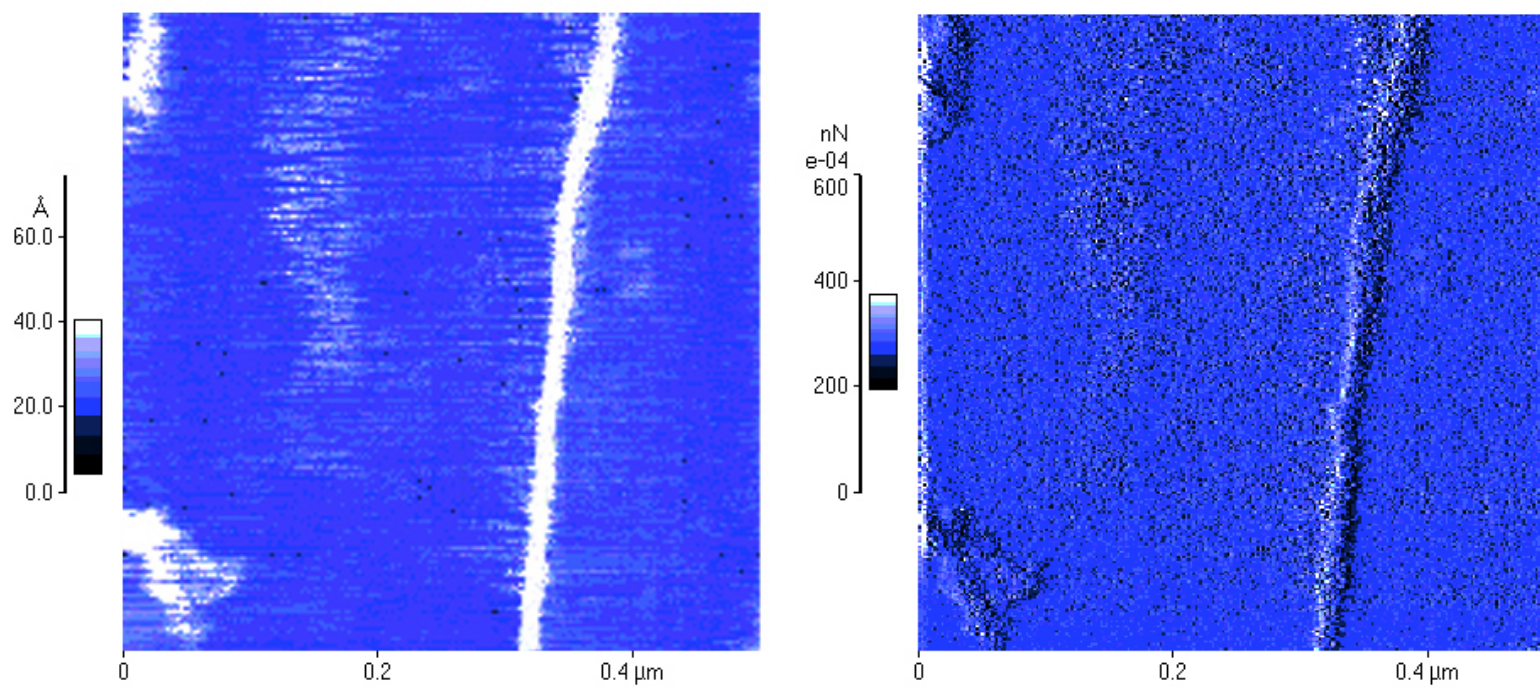


Figure S1. AFM image of a DRC nanoribbon on graphite substrate (0.5 x 0.5 μm). Height contrast image is shown on the left and the phase contrast image of the same area is shown on the right.

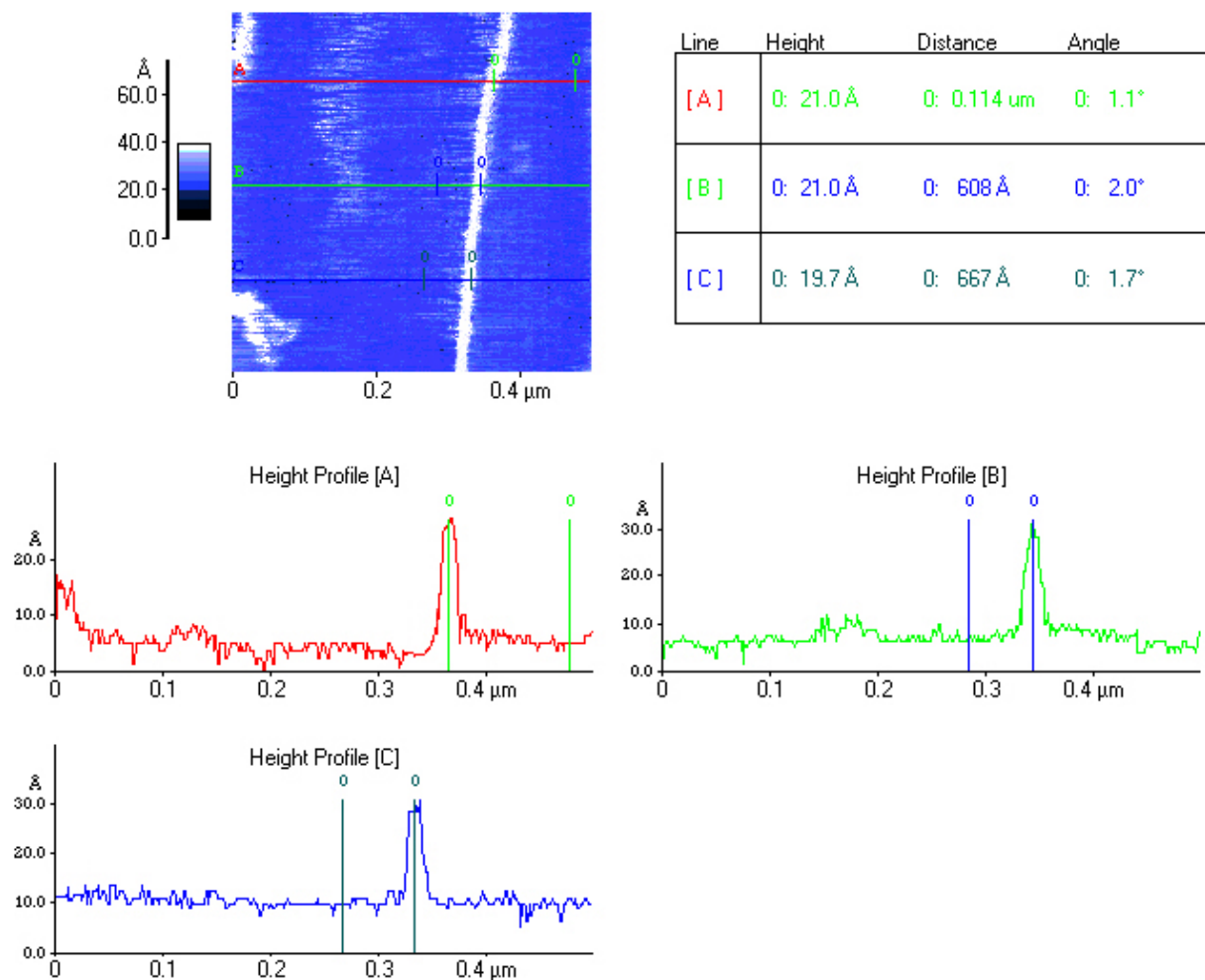


Figure S2. Height profiles of a DRC nanoribbon obtained by AFM. The height (thickness) of the ribbon was measured at 20 different points along the length and was found to be 20 ± 1 Å. Profiles along three arbitrary lines (A,B, and C) are shown and the heights of the ribbon measured from these profiles are indicated in the table. Note that measurements of lateral dimensions by AFM at this scale are not accurate since they are below the lateral limit of resolution imposed by the size of the tip (close to 10 nm). Thus the width of the ribbon appears much larger than it does in TEM.

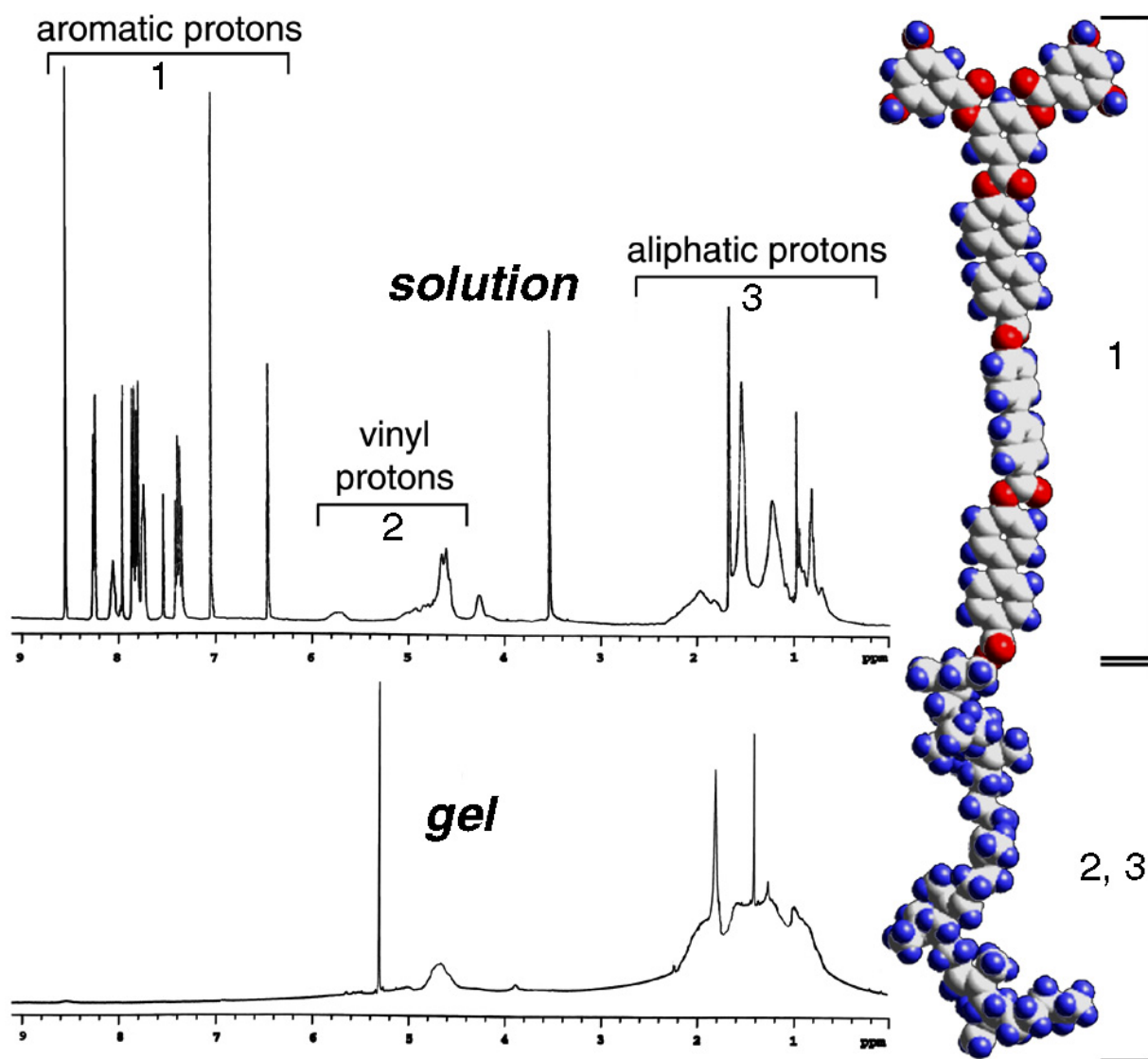


Figure S3. NMR spectra of a solution of dendron rodcoil molecules **1** in THF (top) and 1 wt. % gel in dichloromethane (bottom). A molecular graphic representation of a dendron rodcoil molecule **1** is shown on the right.

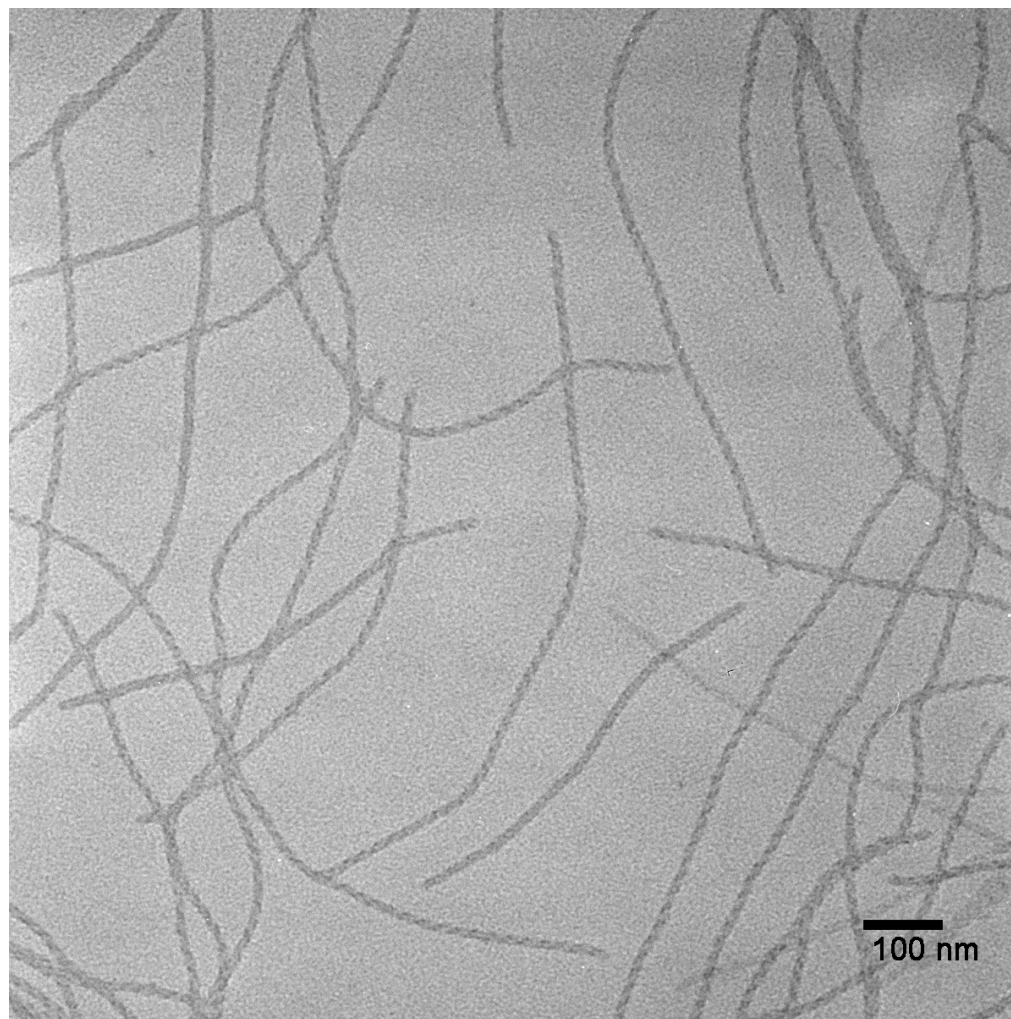


Figure S4. TEM micrograph obtained from a DRC gel in styrene. The structures are helical, as evidenced by the presence of dark lines parallel to each other along the length of the ribbon. These lines represent regions where the ribbon is perpendicular to the substrate.