Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Synthesis, characterization, and self-assembled nanofibers of carbohydrate-functionalized mono- and di(2,2':6',2''-terpyridinyl)arenes

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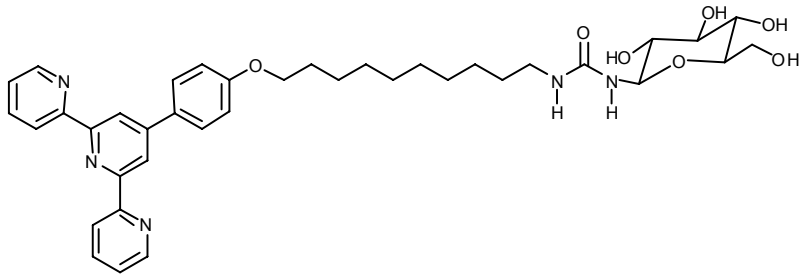
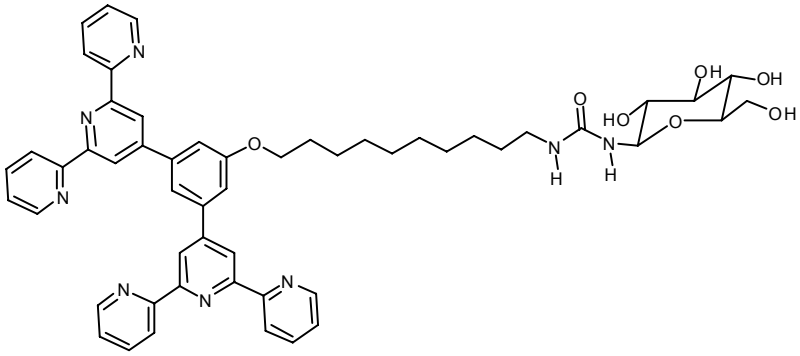
Experimental Section

General Procedures. Chemicals were commercially purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al_2O_3 (IB-F) or SiO_2 (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al_2O_3, Brockman Activity I (60-325 mesh) or SiO_2 (60-200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Mercury 300 or Varian NMRS 500 spectrometer using $CDCl_3$, except where noted. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap Mass Spectrometer (ESI-MS) or a Bruker Reflex III MALDI time-of-flight (TOF) mass spectrometer (Billerica, MA). TEM images were obtained on a JEOL JEM-1230 transmission electron microscope with an accelerating voltage of 120 KV.

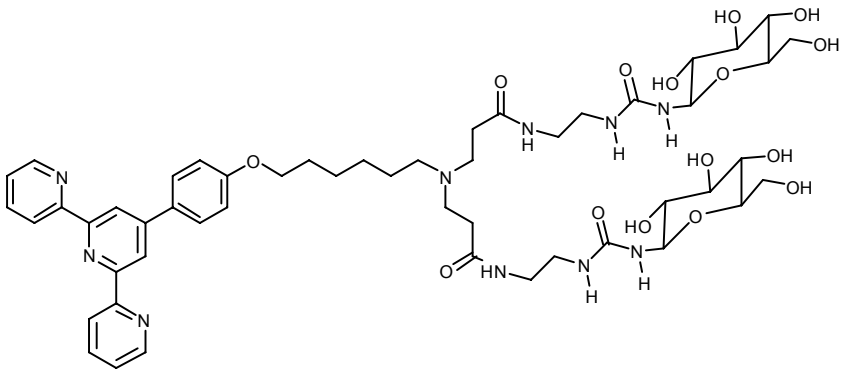


***O*-{10-[*N*'-(β-D-glucopyranosyl)ureido]decyl}-4-(4'-terpyridinyl)phenol (11).** To a stirred solution of *O*-{10-[*N*'-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)ureido] decyl-4-(4'-terpyridinyl)phenol (**10** in manuscript) (100 mg, 100 μmol) in MeOH (20 mL), Et_3N (1 mL) was added. After stirring at 35 ºC for 24 h, the solvent and the excess Et_3N were removed in vacuo to give a residue that was recrystallized from MeOH/H_2O (1:1) to afford **11**, as a white solid: 67 mg, 83%; m.p. 153-155 ºC; ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 8.76 (2H, d, J = 4.5 Hz, Py$H^{6,6''}$), 8.71-8.62 (4H, m, Py$H^{3',5'}$ and Py$H^{3,3''}$), 8.03 (2H, m, Py$H^{4,4''}$), 7.87 (2H, d, J = 8.4 Hz, Ar$H^{3,5}$), 7.52 (2H, m, Py$H^{5,5''}$), 7.11 (2H, d, J = 8.4 Hz, Ar$H^{2,6}$), 6.33 (1H, d, J = 9.3 Hz, CON*H*), 5.95 (1H, t, J = 5.4 Hz, CH_2NHCO),

4.93 (1H, d, J = 4.5 Hz, O*H*), 4.86-4.82 (2H, m, O*H*), 4.57 (1H, t, J = 9.1 Hz, GluH^1), 4.44 (1H, t, J = 5.7 Hz, CH_2OH), 4.03 (2H, br, OCH_2), 3.64-3.59 (1H, m, GluH^6), 3.44-3.40 (1H, m, GluH^6), 3.20-3.13 (1H, m, Glu*H*), 3.06-2.86 (5H, m, CH_2NH and Glu*H*), 1.73 (2H, br, CH_2) and 1.50-1.15 (14H, br, CH_2); ^{13}C NMR [75 MHz, $(CD_3)_2SO$]: δ 159.9, 157.2, 155.6, 155.1, 149.4, 149.0, 137.5, 129.4, 128.2, 124.5, 120.9, 117.3, 115.3, 81.2, 77.9, 77.7, 73.0, 70.1, 67.7, 61.0, 39.2, 30.0, 29.1, 28.9, 26.5 and 25.6; ESI-MS (m/z) 686.3 $[M+H]^+$ (Calcd. m/z = 686.4) 708.3 $[M+Na]^+$ (Calcd. m/z = 708.4). *Anal*. Calcd. for $C_{38}H_{47}N_5O_7$: C, 66.55; H, 6.91; N, 10.21. Found: C, 65.82; H, 6.98; N, 10.01.

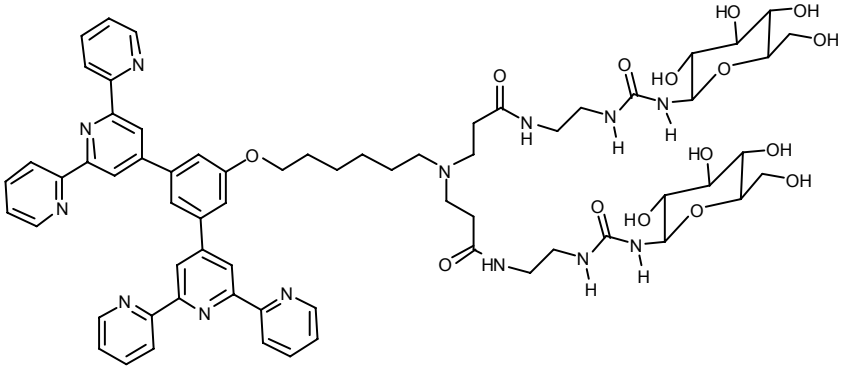


***O*-{10-[*N*'-(β-D-glucopyranosyl)ureido]decyl}-3,5-di(4'-terpyridinyl)phenol (13)** was prepared according to the procedure for **11**. A mixture of *O*-{10-[*N*'-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)ureido]decyl}-3,5-di(4'-terpyridin yl)phenol (**12** in manuscript) (70 mg, 60 μmol) and Et_3N (1 mL) in MeOH (20 mL) gave **13** (50 mg, 85%), which was recrystallized from MeOH. m.p. 153-155 ºC; ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 8.76 (4H, d, J = 4.6 Hz, Py$H^{6,6''}$), 8.72 (4H, s, Py$H^{3',5'}$), 8.65 (4H, d, J = 7.9 Hz, Py$H^{3,3''}$), 8.02 (4H, t, J = 7.6 Hz, Py$H^{4,4''}$), 7.8 (1H, s, ArH^4), 7.52 (4H, m, Py$H^{5,5''}$), 7.46 (2H, s, Ar$H^{2,6}$), 6.36 (1H, d, J = 9.1 Hz, CON*H*), 5.95 (1H, t, J = 5.3 Hz, CH_2NHCO), 4.97 (1H, d, J = 4.5 Hz, O*H*), 4.90-4.86 (2H, m, O*H*), 4.56 (1H, t, J = 9.1 Hz, GluH^1), 4.48 (1H, t, J = 5.7 Hz, CH_2OH), 4.15 (2H, br, OCH_2), 3.63-3.58 (1H, m, GluH^6), 3.44-3.40 (1H, m, GluH^6), 3.19-3.12 (1H, m, Glu*H*), 3.08-2.85 (5H, m, CH_2NH and Glu*H*), 1.76 (2H, br, CH_2) and 1.50-1.15 (14H, br, CH_2); ^{13}C NMR [75 MHz, $(CD_3)_2SO$]: δ 160.0, 157.1, 155.5, 154.9, 149.3, 148.9, 140.0, 137.3, 124.5, 120.9, 118.2, 117.4, 113.7, 81.2, 77.9, 77.7, 73.0, 70.1, 67.9, 61.0, 39.1, 30.0, 29.1, 29.0, 28.9, 28.8, 26.5 and 25.6; ESI-MS (m/z) 917.6 $[M+H]^+$ (Calcd. m/z = 917.4) 939.6 $[M+Na]^+$ (Calcd. m/z = 939.4).



***O*-{6-[*N*,*N*-Di(2-(2-(*N*'-(β-D-glucopyranosyl)ureido)ethyl)carbamoylethyl)amino**

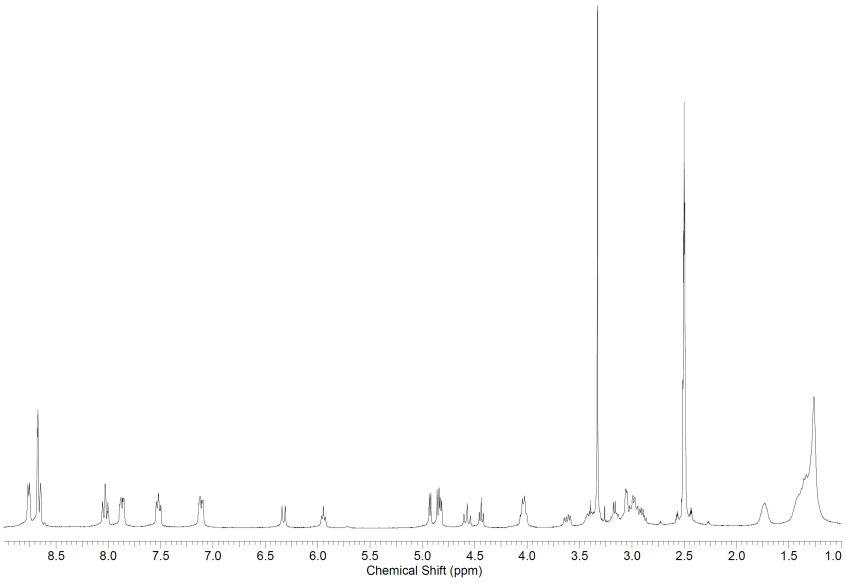
]hexyl}-4-(4'-terpyridinyl)phenol (19) was prepared according to the procedure for **11**. To a solution of *O*-{6-[*N,N*-Di(2-(2-(*N*'-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) ureido)ethyl)carbamoylethyl)amino]hexyl}-4-(4'-terpyridinyl)phenol (**18** in manuscript) (150 mg, 100 μmol) in MeOH (20 mL), Et_3N (1 mL) was added to give **19** as a white solid (100 mg, 88%), which was recrystallized from cold MeOH: m.p. 140-142 ºC; ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 8.77 (2H, d, *J* = 4.9 Hz, Py*H*$^{6,6"}$), 8.69 (2H, s, Py*H*$^{3',5'}$), 8.66 (2H, d, *J* = 8.2 Hz, Py*H*$^{3,3"}$), 8.03 (2H, t, *J* = 8.2 Hz, Py*H*$^{4,4"}$), 7.94 (2H, br, CON*H*), 7.89 (2H, d, *J* = 6.3 Hz, Ar*H*^{3,5}), 7.53 (2H, t, *J* = 6.0 Hz, Py*H*$^{5,5"}$), 7.14 (2H, d, *J* = 6.4 Hz, Ar*H*^{2,6}), 6.51 (2H, d, *J* = 9.2 Hz, CON*H*-Glu), 6.04 (2H, br, CH_2NHCO), 4.91 (2H, d, *J* = 4.6 Hz, O*H*), 4.84-4.81 (4H, m, O*H*), 4.58 (2H, t, *J* = 8.9 Hz, Glu*H*^{1}), 4.44 (2H, t, *J* = 5.7 Hz, CH_2OH), 4.06 (2H, t, *J* = 5.4 Hz, OCH_2), 3.64-3.61 (2H, m, Glu*H*^{6}), 3.44-3.39 (2H, m, Glu*H*^{6}), 3.20-3.15 (2H, m, Glu*H*^{3}), 3.07 (12H, br, $NHCH_2CH_2NH$, Glu*H*^{4} and Glu*H*^{5}), 2.96-2.92 (2H, m, Glu*H*^{2}), 2.64 (4H, t, *J* = 7.1 Hz, $N(CH_2)_2$), 2.38 (2H, t, *J* = 6.7 Hz, CH_2N), 2.20 (4H, t, *J* = 7.1 Hz, CH_2CO), 1.78-1.73 (2H, m, OCH_2CH_2), 1.48-1.39 (4H, m, CH_2) and 1.35-1.29 (2H, m, CH_2); ^{13}C NMR [125 MHz, $(CD_3)_2SO$]: δ 171.6, 159.9, 157.2, 155.6, 155.1, 149.3, 149.0, 137.4, 129.3, 128.1, 124.4, 120.9, 117.2, 115.2, 81.2, 77.9, 77.6, 72.9, 70.0, 67.6, 61.0, 52.7, 49.4, 38.9, 33.2, 28.7, 26.7, 26.5 and 25.5; MALDI-TOF (m/z) 1063.5 $[M+H]^+$ (Calcd. m/z = 1063.5) 1085.5 $[M+Na]^+$ (Calcd. m/z = 1085.5) 1101.4 $[M+K]^+$ (Calcd. m/z = 1101.4). *Anal*. Calcd. for $C_{51}H_{70}N_{10}O_{15}$: C, 57.62; H, 6.64; N, 13.17. Found: C, 57.36; H, 6.82; N, 13.02.

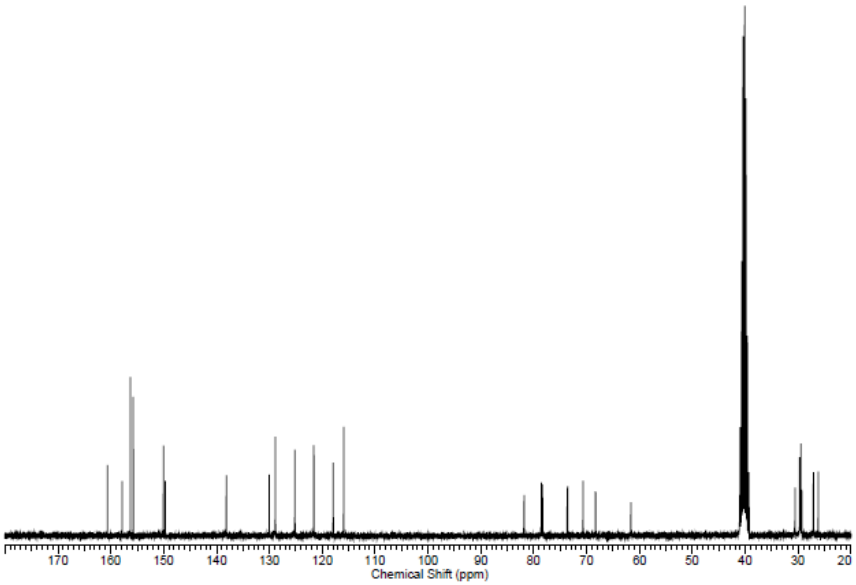


***O*-{6-[*N,N*-Di(2-(2-(*N*'-(β-D-glucopyranosyl)ureido)ethyl)carbamoylethyl)amino]hexyl}-3,5-di(4'-terpyridinyl)phenol (21)** was prepared according to the procedure for **11**. To a solution of **20** (75 mg, 50 μmol) in MeOH (20 mL), Et_3N (1 mL) was added to give **21** as a white solid (50 mg, 84 %), which was recrystallized from MeOH: m.p. 166-169 ºC; ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 8.77 (4H, d, *J* = 4.2 Hz, Py*H*$^{6,6"}$), 8.73 (4H, s, Py*H*$^{3',5'}$), 8.66 (4H, d, *J* = 8.0 Hz, Py*H*$^{3,3"}$), 8.03 (4H, t, *J* = 7.6 Hz, Py*H*$^{4,4"}$), 7.94 (2H, br, CON*H*), 7.80 (1H, s, Ar*H*^{4}), 7.52 (4H, t, *J* = 4.8 Hz, Py*H*$^{5,5"}$), 7.48 (2H, s, Ar*H*^{2,6}), 6.51 (2H, d, *J* = 9.0 Hz, CON*H*-Glu), 6.04 (2H, br, CH_2NHCO), 4.91 (2H, d, *J* = 4.5 Hz, O*H*), 4.84-4.81 (4H, m, O*H*), 4.58 (2H, t, *J* = 9.0 Hz, Glu*H*^{1}), 4.44 (2H, t, *J* = 5.2 Hz, CH_2OH), 4.18 (2H, t, *J* = 5.6 Hz, OCH_2), 3.64-3.61 (2H, m, Glu*H*^{6}), 3.43-3.39 (2H, m, Glu*H*^{6}), 3.20-3.15 (2H, m, Glu*H*^{3}), 3.07 (12H, br, $NHCH_2CH_2NH$, Glu*H*^{4} and Glu*H*^{5}), 2.96-2.92 (2H, m, Glu*H*^{2}), 2.64 (4H, t, *J* = 6.9 Hz, $N(CH_2)_2$), 2.39 (2H, t, *J* = 6.9 Hz, CH_2N), 2.20 (4H, t, *J* = 7.3 Hz, CH_2CO), 1.79 (2H, b, OCH_2CH_2), 1.49 (2H, b, CH_2), 1.43 (2H, br, CH_2) and 1.35 (2H, br, CH_2); ^{13}C NMR [125 MHz, $(CD_3)_2SO$]: δ 171.5, 160.1, 157.2, 155.6, 154.9, 159.3, 149.1, 140.2, 137.4, 124.5, 120.9, 118.4, 117.6, 113.8, 81.2, 77.9, 77.6, 72.9, 70.0, 68.0, 60.9, 52.7, 49.4, 39.1, 38.9, 33.2, 28.9, 26.8, 26.5 and

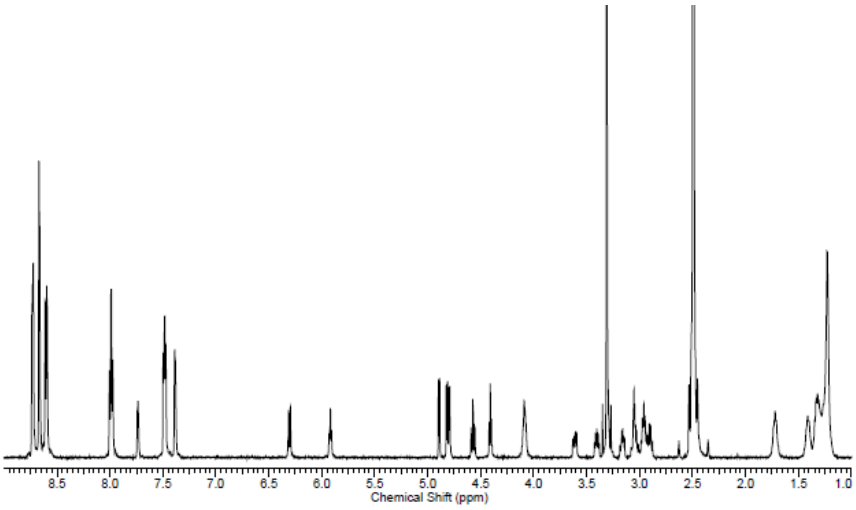
25.5; MALDI-TOF (m/z) 1294.6 $[M+H]^+$ (Calcd. m/z = 1294.6) 1316.7 $[M+Na]^+$ (Calcd. m/z = 1316.6). *Anal*. Calcd. for $C_{66}H_{79}N_{13}O_{15}$: C, 61.24; H, 6.15; N, 14.07. Found: C, 60.15; H, 6.30; N, 14.06.

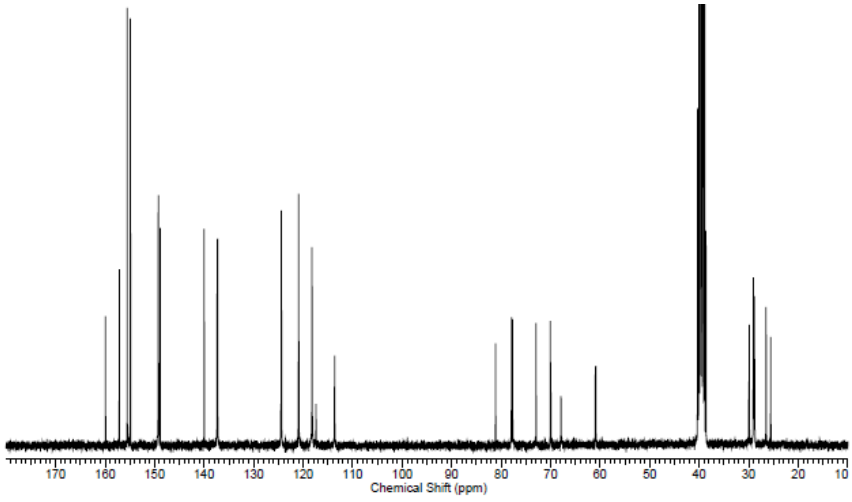
^1H and ^{13}C NMR spectra of **11**



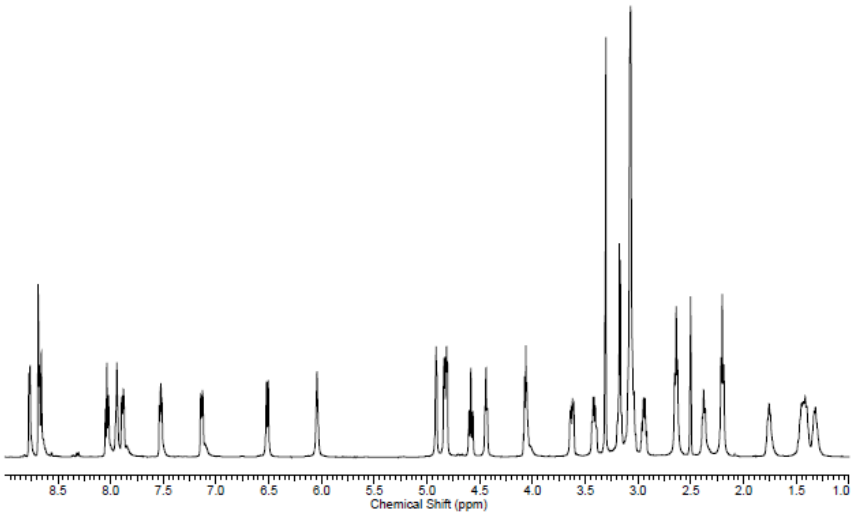


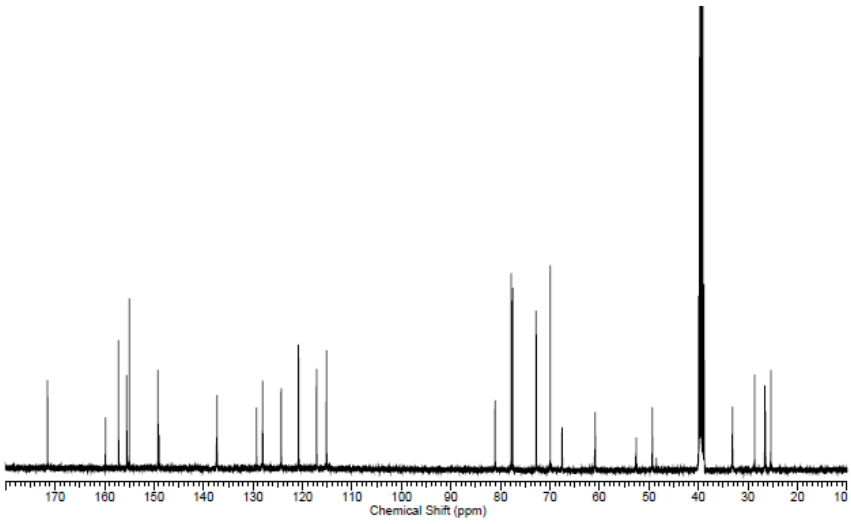
^{1}H and ^{13}C NMR spectra of **13**



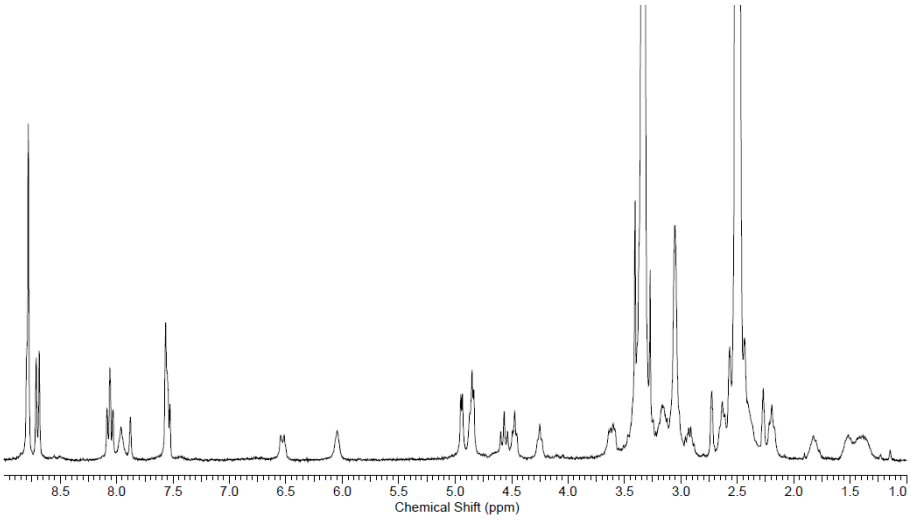


^{1}H and ^{13}C NMR spectra of **19**





^{1}H and ^{13}C NMR spectra of **21**



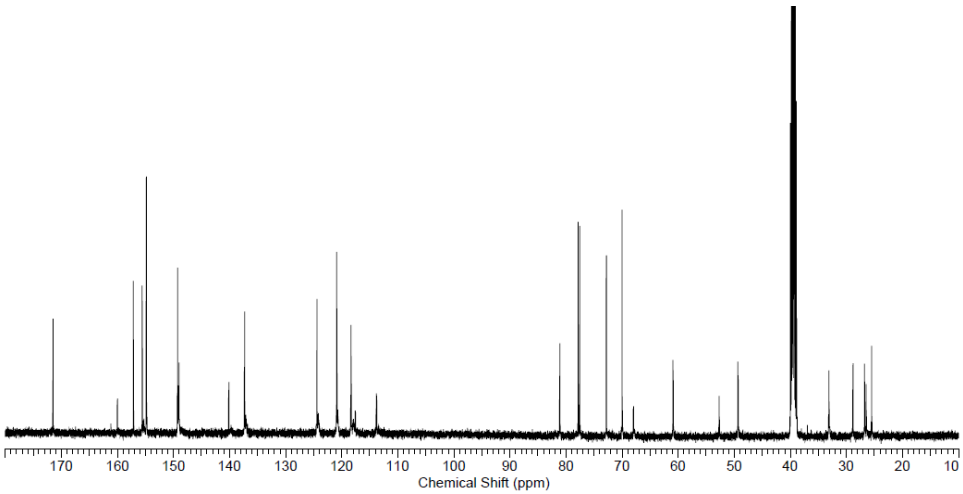


Table S1 Gelation test on the concentration[a]

Concentration (mg/ml)	**11**[b]	**13**[c]	**19**[d]	**21**[e]
1	P	P	S	P
2	P	PG	S	PG
3	P	G	S	G

[a] Cooling clear solutions with different concentrations from 60 to 20°C; S: solution; P: precipitate; PG: partial gel; G: steady gel. [b] In H_2O/MeOH (1:1). [c] In MeOH. [d] In MeOH or H_2O. [e] In H2O/MeOH (1:2).

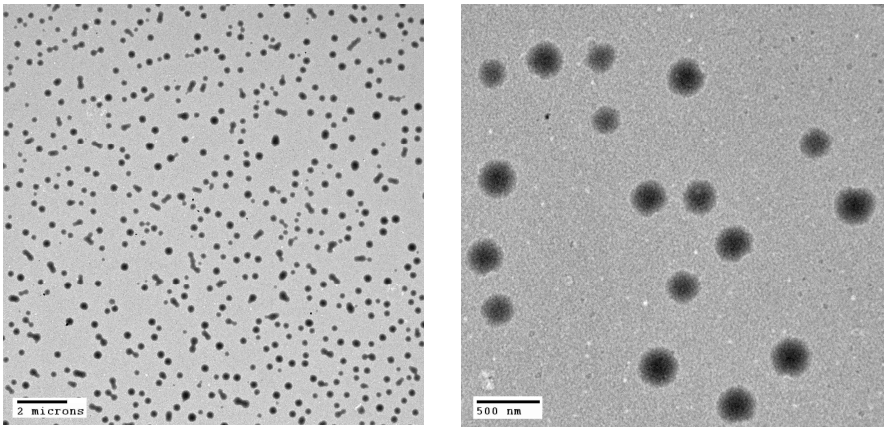


Fig. S1 TEM images of self-assembled **19**.

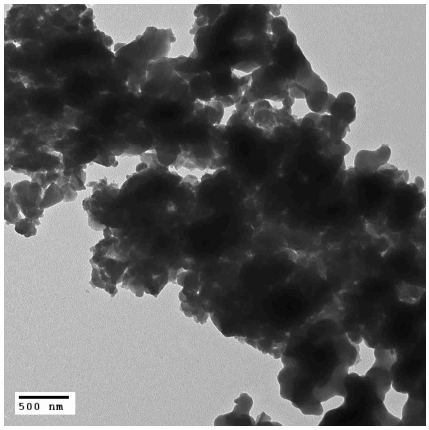


Fig. S2 A TEM image of self-assembled **13** after the addition of $FeCl_2$.

Molecular modeling of the stacked aggregate was accomplished using the Forcite module in the Materials Studio program v4.2.0.0 available from Accelrys Software, Inc. The electrostatic potential surface was generated by using the Jaguar module from Schrödinger, Inc.

Aggregate construction pictured in Figure 3B started with energy determination and minimization of two stacked *bis*(terpyridine) monocarbohydrates (i.e. **13**). Notably, the electrostatic term suggested further geometry optimization.

Forcite Energy parameters considered and total energy using a Dreiding forcefield:

```
Data for the dimer of 13.
Total energy                 : 276.58 kcal/mol

Contributions to total energy (kcal/mol):
  Valence energy (diag. terms)  :    90.686
    Bond                       :    32.909
    Angle                      :    31.602
    Torsion                    :    25.618
    Inversion                  :     0.557

    Non-bond energy            :   185.900
    Hydrogen bond              :    -5.312
    van der Waals              :   196.398
    Electrostatic              :    -5.187
```

Following the creation and geometry optimization of larger aggregates, the stacks were arranged to minimize hydrophilic/hydrophobic interactions, solvated and subjected to further geometry minimization. Fig. S3 depicts the result.

Forcite Geometry Optimization parameters considered and total energy using a Conjugate Gradient algorithm and a Dreiding forcefield:

```
Data for the stacked aggregate.
Algorithm                    : Conjugate gradient
Convergence tolerance:
  Energy                     : 0.0001 kcal/mol
  Force                      : 0.005 kcal/mol/A
  Displacement               : 5e-005 A
Maximum number of iterations   : 20000
Motion groups rigid            : NO

---- Energy parameters ----

Forcefield                   : Dreiding
Electrostatic terms:
  Summation method           : Atom based
  Truncation method          : Cubic spline
  Cutoff distance            : 15.5 A
  Spline width               : 1 A
  Buffer width               : 0.5 A

van der Waals terms:
  Summation method           : Atom based
  Truncation method          : Cubic spline
  Cutoff distance            : 15.5 A
  Spline width               : 1 A
```

```
  Buffer width               : 0.5 A

Hydrogen bond terms:
  Summation method            : Atom based
  Truncation method           : Cubic spline
  Cutoff distance             : 4.5 A
  Spline width                : 0.5 A
  Buffer width                : 0.5 A


---- Initial structure ----

Total energy                  : 1629.32 kcal/mol

Contributions to total energy (kcal/mol):
  Valence energy (diag. terms)  :  3693.846
    Bond                      :  1637.354
    Angle                     :  1558.375
    Torsion                   :   488.907
    Inversion                 :     9.211

    Non-bond energy           : -2064.520
    Hydrogen bond             : -2583.714
    van der Waals             :  1749.572
    Electrostatic             : -1230.378

rms force  : 2.882E-001 kcal/mol A
max force  : 6.455E+000 kcal/mol A

---- Final structure ----

Total energy                  : 1481.37 kcal/mol

Contributions to total energy (kcal/mol):
  Valence energy (diag. terms)  :  3678.828
    Bond                      :  1634.877
    Angle                     :  1547.673
    Torsion                   :   488.726
    Inversion                 :     7.553

    Non-bond energy           : -2197.448
    Hydrogen bond             : -2711.902
    van der Waals             :  1736.351
    Electrostatic             : -1221.897

rms force  : 4.610E-003 kcal/mol A
max force  : 2.444E-001 kcal/mol A
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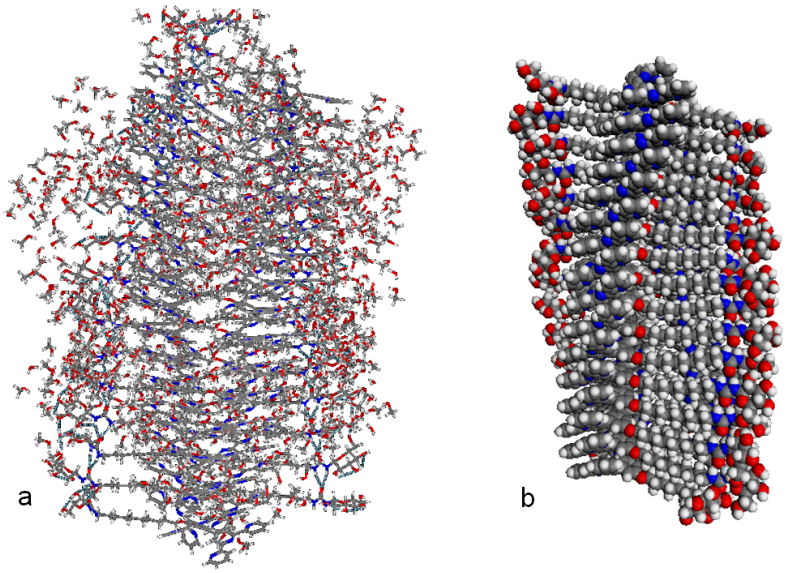

Fig. S3 A solvated (a) and unsolvated (b) geometry optimized, proposed structure for a section of fiber formed from **13**.