Supporting Information

for

**Sol-Gel Polycondensation of Tetraethyl Orthosilicate (TEOS) in Sugar-Based Porphyrin Organogels: Inorganic Conversion of Sugar-Directed Porphyrinic Fiber Library through Sol-Gel Transcription Processes**

*by*

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Preparation of \( p \)-nitrophenyl-2,3,4,6-tetraacetyl-\( \beta \)-D-galactopyranoside (2a):

\( p \)-Nitrophenyl-\( \beta \)-D-galactopyranoside (3.0 g, 10 mmol) was dissolved in acetic acid anhydrous (15 mL) and pyridine (15 mL) mixed solvent and stirred for 5 hours at an ice bath temperature. After checking the disappearance of a TLC (silica gel, methanol:chloroform = 1:20 (v/v)) spot of the starting material, cold water was added into the reaction solution. The stirring of the mixture for an hour gave the white precipitate. The white precipitate filtered out was washed with water and dried in vacuo to give \( p \)-nitrophenyl-2,3,4,6-tetraacetyl-\( \beta \)-D-galactopyranoside (4.7 g, 10 mmol, 99%).

M.p. 136.2~136.5 °C; \( [\alpha]^25_D = -12.0 \) (c = 1.3 in CHCl\(_3\)); \( ^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 2.03 \) (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.21 (s, 3 H; Ac), 4.12-4.24 (m, 3 H; H\(_5\), H\(_6\), H\(_6\)' ), 5.14 (dd, \( J_{2,4} = 3.5 \) Hz, \( J_{3,4} = 10 \) Hz, 1 H; H\(_3\) ), 5.17 (d, \( J = 8.0 \) Hz, 1 H; H\(_1\) ), 5.48 (d, \( J = 3.5 \) Hz, 1 H; H\(_4\) ), 5.53 (dd, \( J_{1,2} = 8.0 \) Hz, \( J_{2,3} = 10 \) Hz, 1 H; H\(_2\) ), 7.08 (d, \( J = 8.9 \) Hz, 2 H; Ar-H), 8.22 (d, \( J = 8.9 \) Hz, 2 H; Ar-H); \( ^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta \# 20.571 \) (CH\(_3\) ), 20.649 (CH\(_3\) ), 20.685 (CH\(_3\) ), 20.714 (CH\(_3\) ), 61.342 (CH\(_2\) ), 66.662 (CH), 68.268 (CH), 70.579 (CH), 71.475 (CH), 98.624 (CH), 116.583 (CH), 125.818 (CH), 143.248 (Cq),
161.199 (Cq), 169.277 (CH), 170.062 (CH), 170.124 (CH), 170.310 (CH); ATR-IR: ν 1740, 1517, 1346, 1221, 1045 cm⁻¹; MALDI-TOF MS (matrix: dithranol): calcd m/z for [M + Na]⁺: 492.11; found 493.17; EA: calcd for C₂₀H₂₃NO₁₂: C 51.13, H 4.94, N 2.98; found C 51.09, H 4.96, N 2.98. 2b, 2c, 2d and 2e were synthesized by the same procedure as that of 2a. We thus recorded only their analytical data.

**p-Nitrophenyl-2,3,4,6-tetraacetyl-α-D-galactopyranoside** (2b):

*p-Nitrophenyl-α-D-galactopyranoside* (3.0 g, 10 mmol) furnished 2b (4.7 g, 10 mmol, 99%).

M.p. 126.3~126.5 ℃; [α]D²³ = + 184.0 (c = 1.3 in CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 1.94 (s, 3 H; Ac), 2.05 (s, 3 H; Ac), 2.09 (s, 3 H; Ac), 2.19 (s, 3 H; Ac), 4.05-4.27 (m, 3 H; H₅, H₆, H₆'), 5.32 (dd, J₁₂ = 3.5 Hz, J₂₃ = 11 Hz, 1 H; H₂), 5.53 (d, J = 3.5 Hz, 1 H; H₄), 5.57 (dd, J₃₄ = 3.5 Hz, J₂₃ = 11 Hz, 1 H; H₃), 5.89 (d, J = 3.5 Hz, 1 H; H₁), 7.18 (d, J = 8.8 Hz, 2 H; Ar-H), 8.23 (d, J = 8.8 Hz, 2 H; Ar-H); ¹³C NMR (150 MHz, CDCl₃): δ = 20.572 (CH₃), 20.665 (CH₃), 20.718 (CH₃), 61.318 (CH₂), 67.190 (CH), 67.403 (CH), 67.542 (CH), 67.835 (CH), 94.761 (CH), 116.582 (CH), 125.859 (CH), 143.105 (Cq), 160.872 (Cq), 170.016 (CH₃), 170.211 (CH₃), 170.355 (CH₃); ATR-IR: ν? 1748, 1515, 1346, 1220, 1043 cm⁻¹; MALDI-TOF MS (matrix: dithranol): calcd m/z for [M + Na]⁺: 492.11; found 492.89; EA: calcd for C₂₀H₂₃NO₁₂: C 51.13, H 4.94, N 2.98; found C 51.05, H 4.95, N 2.97.
\textbf{\textit{p}}-\textit{Nitrophenyl-2,3,4,6-tetraacetyl-\textit{\textbeta}}-\textit{D-glucopyranoside} (2c):

\textit{p}-\textit{Nitrophenyl-\textbeta}-\textit{D-gulucopyranoside} (3.0 g, 10 mmol) furnished 2c (4.6 g, 9.7 mmol, 97%).

M.p. 99.3~99.5 °C; [\alpha]_{D}^{23} = + 236.0 (c = 1.3 in CHCl\textsubscript{3}); \textit{\textit{\textit{\textit{\text{}}}}H NMR (600 MHz, CDCl\textsubscript{3}) \delta = 2.04 (s, 3 H; Ac), 2.05 (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.08 (s, 3 H; Ac), 4.02-4.28 (m, 3 H; H\textsubscript{5}, H\textsubscript{6}, H\textsubscript{6}'), 5.08 (dd, \textit{J}_{1, 2} = 3.4 Hz, \textit{J}_{2, 3} = 10 Hz, 1 H; H\textsubscript{5}), 5.17 (t, \textit{J} = 10 Hz, 1 H; H\textsubscript{4}), 5.69 (t, \textit{J} = 10 Hz, 1 H; H\textsubscript{5}), 5.85 (d, \textit{J} = 3.4 Hz, 1 H; H\textsubscript{1}), 7.21 (d, \textit{J} = 8.9 Hz, 2 H; Ar-H), 8.23 (d, \textit{J} = 8.9 Hz, 2 H; Ar-H); \textit{\textit{\textit{\text{}}}}C NMR (150 MHz, CDCl\textsubscript{3}) \delta = 20.561 (CH\textsubscript{3}), 20.599 (CH\textsubscript{3}), 20.638 (CH\textsubscript{3}), 20.677 (CH\textsubscript{3}), 61.372 (CH\textsubscript{2}), 67.989 (CH), 68.690 (CH), 69.664 (CH), 70.114 (CH), 94.166 (CH), 116.527 (CH), 125.893 (CH), 143.204 (Cq), 160.600 (Cq), 169.473 (C=O), 170.090 (C=O), 170.397 (C=O); ATR-IR: \nu \approx 1734, 1519, 1353, 1221, 1033 cm\textsuperscript{-1}; MALDI-TOF MS (matrix: dithranol): calcd \textit{m/z} for [M + Na]\textsuperscript{+}: 492.11; found 492.98; EA: calcd for C\textsubscript{20}H\textsubscript{23}NO\textsubscript{12}: C 51.13, H 4.94, N 2.98; found C 51.07, H 4.96, N 2.98.

\textbf{\textit{p}}-\textit{Nitrophenyl-2,3,4,6-tetraacetyl-\textit{\textalpha}}-\textit{D-mannopyranoside} (2d):

\textit{p}-\textit{Nitrophenyl-\textalpha}-\textit{D-mannopyranoside} (3.0 g, 10 mmol) furnished 2d (4.7 g, 10 mmol, 99%).

M.p. 145.1~145.2 °C; [\alpha]_{D}^{23} = + 112.0 (c = 1.3 in CHCl\textsubscript{3}); \textit{\textit{\textit{\text{}}}}H NMR (600 MHz, CDCl\textsubscript{3}) \delta = 2.03 (s, 3 H; Ac), 2.05 (s, 3 H; Ac), 2.06 (s, 3 H; Ac), 2.22 (s, 3 H; Ac), 4.00-4.29 (m, 3 H; H\textsubscript{5}, H\textsubscript{6}, H\textsubscript{6}'), 5.39 (t, 10 Hz, 1 H; H\textsubscript{5}), 5.46-5.47 (m, 1 H; H\textsubscript{4}), 5.54 (dd, \textit{J}_{2, 3} = 3.5 Hz,
$J_{3,4} = 10 \text{ Hz, 1 H; } H_3)$, 5.62-5.63 (m, 1 H; $H_3$), 7.21 (d, $J = 8.9$ Hz, 2H; Ar-H), 8.23 (d, $J = 8.9$ Hz, 2H; Ar-H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta = 20.665$ (CH$_3$), 20.685 (CH$_3$), 20.840 (CH$_3$), 61.942 (CH$_2$), 65.582 (CH), 68.508 (CH), 68.942 (CH), 69.827 (CH), 95.695 (CH), 116.467 (CH), 125.867 (CH), 143.172 (Cq), 160.150 (Cq), 169.634 (C=O), 169.944 (C=O), 170.397 (C=O); ATR-IR: $\nu = 1744$, 1520, 1344, 1216, 1026 cm$^{-1}$; MALDI-TOF MS (matrix: dithranol): calcd $m/z$ for [M + Na]$^+$: 492.11; found 492.95; EA: calcd for C$_{20}$H$_{23}$N$_2$O$_{12}$: C 51.13, H 4.94, N 2.98; found C 51.12, H 4.94, N 2.96.

**$o$-Nitrophenyl-2,3,4,6-tetraacetyl-$\beta$-D-galactopyranoside (2e):**

$o$-Nitrophenyl-$\beta$-D-galactopyranoside (1.5 g, 5.0 mmol) furnished 2e (2.4 g, 5.0 mmol, 99%). M.p. 162.2~162.3 °C; $[\alpha]_{D}^{24} = +84.0$ ($c = 1.3$ in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$); $\delta = 2.02$ (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.14 (s, 3 H; Ac), 2.19 (s, 3 H; Ac), 4.06-4.28 (m, 3 H; H$_5$, H$_6$, H$_6'$), 5.07 (d, $J_{1,2} = 8.0$ Hz, 1 H; H$_1$), 5.11 (dd, $J_{2,3} = 10$ Hz, $J_{3,4} = 3.2$ Hz, 1 H; H$_3$), 5.47 (d, $J = 2.9$ Hz, 1 H; H$_4$), 5.56 (dd, $J_{1,2} = 8.1$ Hz, $J_{2,3} = 10$ Hz, 1 H; H$_3$), 7.21 (t, $J = 7.8$ Hz, 1 H; Ar-H), 7.36 (d, $J = 8.5$ Hz, 1 H; Ar-H), 7.53 (t, $J = 7.8$ Hz, 1 H; Ar-H), 7.79 (d, $J = 8.2$ Hz, 1 H; Ar-H); $^{13}$C NMR (150 MHz, CDCl$_3$); $\delta = 20.589$ (CH$_3$), 20.668 (CH$_3$), 61.334 (CH$_3$), 66.718 (CH), 67.853 (CH), 70.579 (CH), 71.407 (CH), 100.770 (CH), 119.780 (CH), 123.783 (CH), 125.146 (CH), 133.661 (CH), 169.944 (C=O), 170.397 (C=O), 170.634 (C=O), 170.944 (C=O).
141.525 (Cq), 149.316 (Cq), 169.413 (C=O), 170.147 (C=O), 170.193 (C=O), 170.310 (C=O); ATR-IR: ν = 1744, 1533, 1369, 1217, 1068 cm\(^{-1}\); MALDI-TOF MS (matrix: dithranol): calcd \(m/z\) for [M + Na]\(^+\): 492.11; found 492.82; EA: calcd for C\(_{20}\)H\(_{23}\)NO\(_{12}\); C 51.13, H 4.94, N 2.98; found C 51.14, H 4.91, N 2.96.

**p-Aminophenyl-2,3,4,6-tetraacetyl-β-D-galactopyranoside** (3a):

\(p\)-Nitrophenyl-2,3,4,6-tetraacetyl-β-D-galactopyranoside (2a) (3.3 g, 7.0 mmol) was dissolved in dried ethyl acetate (30 mL) under nitrogen. Pd/C (80 mg) was added into the solution and the atmosphere was displaced by hydrogen. After the solution was stirred for four hours at room temperature, the disappearance of a TLC (silica gel, methanol:chloroform = 1:7 (v/v)) spot for the starting material and the generation of the amino compound (detected by ninhydrine indication reagent) were checked. The solution was filtered and the filtrate was concentrated under reduced pressure to give \(p\)-aminophenyl-2,3,4,6-tetraacetyl-β-D-galactopyranoside (3a) (2.3 g, 5.3 mmol, 74%).

M.p. 53.2~53.4 °C; [\(\alpha\)]\(^{24}\) = + 12.0 (c = 1.3 in CHCl\(_3\)); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 2.01\) (s, 3 H; Ac), 2.05 (s, 3 H; Ac), 2.09 (s, 3 H; Ac), 2.18 (s, 3 H; Ac), 3.54 (brs, 2 H; NH), 3.98-4.25 (m, 3 H; H\(_5\), H\(_6\), H\(_6^\prime\)), 4.87 (d, \(J = 8.1\) Hz, 1 H; H\(_1\)), 5.08 (dd, \(J_{2,3} = 10\) Hz, \(J_{3,4} = 3.1\) Hz, 1 H; H\(_3\)), 5.30-5.31 (m, 1 H; H\(_4\)), 5.43-5.46 (m, 1 H; H\(_2\)), 6.60 (d, \(J = 8.9\) Hz, 2H; Ar-H), 6.84 (d, \(J = 8.9\) Hz, 2 H; Ar-H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 20.571\)
(CH₃), 20.649 (CH₃), 20.685 (CH₃), 20.714 (CH₃), 61.342 (CH₂), 66.662 (CH), 68.268 (CH), 70.579 (CH), 71.475 (CH), 98.624 (CH), 116.583 (CH), 125.818 (CH), 143.248 (Cq), 161.199 (Cq), 169.277 (C=O), 170.062 (C=O), 170.124 (C=O), 170.310 (C=O); ATR-IR: ν = 3455, 3373, 1740, 1509, 1210, 1040 cm⁻¹; MALDI-TOF MS (matrix: dithranol): calcd m/z for [M + Na]⁺: 462.14; found 462.86; EA: calcd for C₂₀H₂₅NO₁₂?0.70 CH₃OH: C 53.83, H 6.07, N 3.03; found C 53.52, H 5.76, N 2.94. The same procedure was applied for the preparation of 3b, 3c, 3d, and 3e. We thus recorded only their analytical data.

*p*-Aminophenyl-2,3,4,6-tetraacetyl-α-D-galactopyranoside (3b): Hydrogenation of 2b (3.3 g, 7.0 mmol) furnished 3b (2.5 g, 5.8 mmol, 80%). M.p. 47.9~48.3 °C; [α]D = +164.0 (c = 1.3 in CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 1.98 (s, 3 H; Ac), 2.02 (s, 3 H; Ac), 2.08 (s, 3 H; Ac), 2.16 (s, 3 H; Ac), 3.58 (brs, 2 H; NH), 4.06-4.42 (m, 3 H; H₅, H₆, H₆'), 5.25 (dd, J₁,₂ = 3.5 Hz, J₂,₃ = 11 Hz, 1 H; H₂), 5.52-5.53 (m, 1 H; H₄), 5.54 (dd, J₃,₄ = 3.1 Hz, J₂,₃ = 11 Hz, 1 H; H₃), 5.60 (d, J = 3.5 Hz, 1 H; H₅), 6.61 (d, J = 8.8 Hz, 2 H; Ar-H), 6.85 (d, J = 8.8 Hz, 2 H; Ar-H); ¹³C NMR (150 MHz, CDCl₃): δ = 20.630 (CH₃), 20.645 (CH₃), 20.687 (CH₃), 20.771 (CH₃), 61.635 (CH₂), 66.930 (CH), 67.614 (CH), 67.979 (CH), 68.054 (CH), 96.039 (CH), 116.015 (CH), 118.401 (CH), 142.237 (Cq), 149.236 (Cq), 170.050 (C=O), 170.240 (C=O), 170.373 (C=O), 170.417 (C=O);
ATR-IR: $\nu = 3452, 3372, 1738, 1509, 1208, 1042$ cm$^{-1}$; MALDI-TOF MS (matrix: dithranol): calcd m/z for [M + Na]$^+$: 462.14; found 462.93; EA: calcd for C$_{20}$H$_{25}$NO$_{12}$?0.25 CH$_3$OH: C 54.36, H 5.86, N 3.03; found C 54.20, H 5.72, N 3.11.

$p$-Aminophenyl-2,3,4,6-tetraacetyl-β-D-glucopyranoside (3c): Hydrogenation of 2c (3.3 g, 7.5 mmol) furnished 3c (2.8 g, 6.5 mmol, 90%). M.p. 44.8~45.0 °C; [$\alpha$]$^2_{D}$ = +184.0 (c = 1.3 in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$): δ = 2.04 (s, 3 H; Ac), 2.05 (s, 3 H; Ac), 2.06 (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 3.82 (brs, 2 H; NH), 4.06-4.27 (m, 3 H; H$_5$, H$_6$, H$_6'$), 5.00 (dd, $J_1, 2 = 3.4$ Hz, $J_2, 3 = 10$ Hz, 1 H; H$_2$), 5.14 (t, $J = 10$ Hz, 1 H; H$_4$), 5.58 (d, $J = 3.4$ Hz, 1 H; H$_1$), 5.68 (t, $J = 10$ Hz, 1 H; H$_3$), 6.65 (d, $J = 8.9$ Hz, 2 H; Ar-H), 6.89 (d, $J = 8.9$ Hz, 2 H; Ar-H); $^{13}$C NMR (150 MHz, CDCl$_3$); δ = 20.625 (CH$_3$), 20.668 (CH$_3$), 20.693 (CH$_3$), 20.730 (CH$_3$), 61.710 (CH$_2$), 67.769 (CH), 68.424 (CH), 70.115 (CH), 70.568 (CH), 95.185 (CH), 116.375 (CH), 118.046 (CH), 141.459 (Cq), 149.337 (Cq), 169.653 (C=O), 170.183 (C=O), 170.610 (C=O); ATR-IR: $\nu = 3453, 3377, 1742, 1509, 1207, 1032.52$ cm$^{-1}$; MALDI-TOF MS (matrix: dithranol): calcd m/z for [M + Na]$^+$: 462.14; found 462.49; EA: calcd for C$_{20}$H$_{25}$NO$_{12}$?0.30 CH$_3$OH: C 54.30, H 5.88, N 3.12; found C 54.16, H 5.71, N 3.03.

$p$-Aminophenyl-2,3,4,6-tetraacetyl-α-D-mannopyranoside (3d): Hydrogenation of 2d (3.3 g, 7.5 mmol) furnished 3d (2.2 g, 5.1 mmol, 71%). M.p. 33.2~33.5 °C; [$\alpha$]$^2_{D}$ = +
112.0 (c = 1.3 in CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 2.02 (s, 3 H; Ac), 2.06 (s x 2, 6 H; Ac x 2), 2.21 (s, 3 H; Ac), 2.69 (brs, 2 H; NH), 4.08-4.30 (m, 3 H; H₅, H₆, H₆'), 5.35 (t, J = 10 Hz, 1 H; H₄), 5.36-5.37 (m, 1 H; H₁), 5.41-5.42 (m, 1 H; H₂), 5.54 (dd, J₂,₃ = 3.2 Hz, J₃,₄ = 10 Hz, 1 H; H₃), 6.63 (d, J = 8.9 Hz, 2 H; Ar-H), 6.90 (d, J = 8.9 Hz, 2 H; Ar-H); ¹³C NMR (150 MHz, CDCl₃): δ = 20.718 (CH₃), 20.906 (CH₃), 62.281 (CH₂), 66.130 (CH), 68.949 (CH), 68.981 (CH), 69.568 (CH), 96.805 (CH), 116.196 (CH), 118.016 (CH), 141.804 (Cq), 148.775 (Cq), 169.791 (C=O), 169.952 (C=O), 170.030 (C=O), 170.605; ATR-IR: ν = 3456, 3373, 1738, 1509, 1368, 1206, 1033 cm⁻¹; FAB MS (HR): calcd m/z for C₂₀H₂₅NO₁₀: 439.1478; found 439.1484.

**o-Aminophenyl-2,3,4,6-tetraacetyl-β-D-galactopyranoside (3e):** Hydrogenation of 2e (1.7 g, 3.6 mmol) furnished 3e (1.3 g, 3.0 mmol, 85%). M.p. 48.0~48.2 °C; [α]²⁴ D = + 12.0 (c = 1.3 in CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ = 2.02 (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.10 (s, 3 H; Ac), 2.19 (s, 3 H; Ac), 3.81 (brs, 2 H; NH), 4.06-4.25 (m, 3 H; H₅, H₆, H₆'), 4.97 (d, 8.0 Hz, 1 H; H₁), 5.12 (dd, J₂,₃ = 11 Hz, J₃,₄ = 3.3 Hz, 1 H; H₃), 5.47 (d, J = 2.7 Hz, 1 H; H₄), 5.50 (dd, J₁,₂ = 8.1 Hz, J₂,₃ = 10 Hz, 1 H; H₂), 6.67 (t, J = 7.6 Hz, 1 H; Ar-H), 6.71 (d, J = 7.7 Hz, 1 H; Ar-H), 6.88 (t, J = 7.6 Hz, 1 H; Ar-H), 6.93 (d, J = 8.1 Hz, 1 H; Ar-H); ¹³C NMR (150 MHz, CDCl₃): δ = 20.600 (CH₃), 20.666 (CH₃), 20.789 (CH₃), 20.952 (CH₃), 61.335 (CH₂), 66.863 (CH), 68.817 (CH), 70.607 (CH), 71.000
(CH), 100.809 (CH), 115.658 (CH), 115.735 (CH), 118.036 (CH), 124.074 (CH), 137.471 (Cq), 144.482 (Cq), 170.104 (C=O), 170.253 (C=O), 170.385 (C=O), 171.002 (C=O); ATR-IR: \( \nu = 3473, 3377, 1740, 1505, 1367, 1208, 1042 \text{ cm}^{-1} \); MALDI-TOF MS (matrix: dithranol): calcd \( m/z \) for \([M + Na]^+\): 462.14; found 462.44; EA: calcd for \( \text{C}_{20}\text{H}_{25}\text{NO}_{12.025} \cdot 0.25 \text{CH}_3\text{OH}: \) C 54.36, H 5.86, N 3.13; found C 54.26, H 5.77, N 3.15.

**Preparation of 4:** To a dry dichloromethane (40 mL) solution of 5,10,15,20-tetra(4-calboxyphenyl)-21H,23H-porphine (0.79 g, 1.0 mmol) and oxalyl dichloride (4.0 mL, 47 mmol), \( N,N \)-dimethylformamide (0.20 mL, 2.6 mmol) was added and the mixture was stirred for three hours at room temperature under nitrogen. Removal of the solvent under reduced pressure gave 5,10,15,20-tetra(4-calboxyphenyl)-21H,23H-porphine chloride as deep green solid which was donated to the next process without further purification.

**Preparation of 5a:** To a dry tetrahydrofuran (15 mL) solution of 3a (2.3 g, 5.2 mmol), triethylamine (2.0 mL, 15 mmol) was added under nitrogen atmosphere at ice bath temperature. Into the solution, a dry tetrahydrofuran (70 mL) solution of 4 (0.79 g, 1.0 mmol) was added from a dropping funnel over 30 minutes. After checking the disappearance of a TLC (silica gel, methanol:chloroform = 1:20 (v/v)) spot for 3a, the solvents was removed under reduced pressure to give reddish brown solid. Purification was carried out
by column chromatography (silicagel, methanol:chloroform = 1:50 (v/v)) and reprecipitation from chloroform/hexane mixed solvent to give 1d as reddish brown solid in pure form (0.94 g, 0.38 mmol, 38%).  M.p. 158.5-159.8 °C dec.; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = -2.95\) (s, 2 H), 2.04 (s, 3 H; Ac ), 2.07 (s, 3 H; Ac ), 2.13 (s, 3 H; Ac ), 2.20 (s, 3 H; Ac), 4.11-4.27 (m, 3 H; H\(_5\), H\(_6\), H\(_6'\)), 5.08 (d, \(J = 7.9\) Hz, 1 H; H\(_1\)), 5.17 (dd, \(J_{2, 3} = 10\) Hz, \(J_{3, 4} = 2.9\) Hz, 1 H; H\(_3\)), 5.49 (d, \(J = 2.9\) Hz, 1 H; H\(_4\)), 5.53 (t, \(J = 10\) Hz, 1 H, H\(_2\)), 7.08 (d, \(J = 7.9\) Hz, 8 H; Ar-H), 7.67 (d, \(J = 7.9\) Hz, 8 H; Ar-H), 8.11-8.12 (m, 16 H; Ar-H), 8.31 (s, 4H; amide-NH), 8.68 (s, 8 H; \(\beta\)-pyrrole); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 20.628\) (CH\(_3\)), 20.678 (CH\(_3\)), 20.714 (CH\(_3\)), 20.819 (CH\(_3\)), 61.374 (CH\(_2\)), 66.920 (CH), 68.726 (CH), 70.820 (CH), 71.079 (CH), 100.108 (CH), 117.768 (CH), 119.156 (Cq), 122.113 (CH), 125.545 (Cq), 133.441 (Cq), 134.295 (Cq), 134.683 (CH), 145.300 (Cq), 153.959 (Cq), 165.706 (C=O), 169.513 (C=O), 170.147 (C=O), 170.288 (C=O), 170.425 (C=O); ATR-IR: \(\nu = 1747, 1668, 1607, 1509, 1067, 1044\) cm\(^{-1}\); UV/Vis (CHCl\(_3\)): \(\lambda_{\text{max}} (\varepsilon) = 421.0\) (533000), 516.0 (23400), 551.0 (11100), 590.0 (7120), 646.5 (6530 mol\(^{-1}\)dm\(^3\)cm\(^{-1}\)) nm; FAB MS (HR): calcd \(m/z\) for C\(_{128}\)H\(_{123}\)N\(_8\)O\(_{44}\): 2475.7633; found 2475.7632. The same procedure was applied for the preparation of 5b, 5c, 5d, and 5e. We thus recorded only their analytical data.

**Preparation of 5b:** 3b (2.3 g, 5.2 mmol) and 4 (0.79 g, 1.0 mmol) furnished 5b (1.1 g, 0.44
mmol, 44%). M.p. 246.7-247.7 °C dec.; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = -2.78\) (s, 2 H; NH), 2.02 (s, 3 H; Ac), 2.06 (s, 3 H; Ac), 2.13 (s, 3 H; Ac), 2.20 (s, 3 H; Ac), 4.12-4.44 (m, 4 H; H\(_5\), H\(_6\), H\(_6^*\)), 5.33 (dd, \(J_{1, 2} = 3.2\) Hz, \(J_{2, 3} = 11\) Hz, 4 H; H\(_2\)), 5.57 (\(\delta = 3.3\) Hz, 4 H; H\(_3\)), 5.62 (dd, \(J_{2, 3} = 11\) Hz, \(J_{3, 4} = 3.3\) Hz, 4 H; H\(_4\)), 5.82 (dd, \(J = 3.2\) Hz, 4 H; H\(_5\)), 7.17 (d, \(J = 8.7\) Hz, 8 H; Ar-H), 7.71 (d, \(J = 8.7\) Hz, 8 H; Ar-H), 8.10 (s, 4 H; amide-NH), 8.27 (d, \(J = 7.9\) Hz, 8 H; Ar-H), 8.35 (d, \(J = 7.9\) Hz, 8 H; Ar-H), 8.86 (s, 8 H; \(\beta\)-pyrrole); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 20.679\) (CH\(_3\)), 20.805 (CH\(_3\)), 61.507 (CH\(_2\)), 67.217 (CH), 67.527 (CH), 67.836 (CH), 67.874 (CH), 95.359 (CH), 117.525 (CH), 119.283 (Cq), 122.084 (CH), 125.569 (Cq), 125.865 (Cq), 133.118 (Cq), 134.425 (Cq), 134.806 (CH), 145.560 (Cq), 153.370 (Cq), 165.600 (C=O), 170.117 (C=O), 170.223 (C=O), 170.414 (C=O), 170.473 (C=O); ATR-IR: \(\nu = 1747, 1668, 1607, 1509, 1213, 1073, 1044\) cm\(^{-1}\); UV/Vis (CHCl\(_3\)): \(\lambda_{\text{max}}(\epsilon) = 421.5\) (500000), 516.0 (20100), 550.5 (8980), 590.0 (5510), 646.5 (4070 mol\(^{-1}\)dm\(^3\)cm\(^{-1}\)) nm; FAB MS (HR): calcd \(m/z\) for C\(_{128}\)H\(_{123}\)N\(_8\)O\(_{44}\): 2475.7633; found 2475.7605.

**Preparation of 5c:** 3c (2.3 g, 5.2 mmol) and 4 (0.79 g, 1.0 mmol) furnished 5c (1.3 g, 0.44 mmol, 52%). M.p. 172.8-173.6 °C dec.; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = -2.91\) (s, 2H), 2.06 (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.10 (s, 3 H; Ac), 2.11 (s, 3 H; Ac), 3.90-4.37 (m, 12 H; H\(_5\), H\(_6\), H\(_6^*\)), 5.10 (dd, \(J_{1, 2} = 3.3\) Hz, \(J_{2, 3} = 10\) Hz, 4 H; H\(_5\)), 5.20 (t, \(J = 10\) Hz, 8 H;
H₄), 5.29-5.36 (m, 8 H; H₁, H₃), 7.05 (d, J = 7.9 Hz, 8 H; Ar-H), 7.62 (d, J = 7.9 Hz, 8 H; Ar-H), 8.09-8.10 (m, 8 H; Ar-H), 8.22 (s, 4 H; amide-NH), 8.68 (s, 8 H; β-pyrrole); ¹³C NMR (150 MHz, CDCl₃): δ = 20.644 (CH₃), 20.705 (CH₃), 20.758 (CH₃), 61.641 (CH₂), 68.103 (CH), 68.338 (CH), 70.070 (CH), 70.512 (CH), 94.681 (CH), 117.334 (CH), 119.297 (Cq), 122.126 (CH), 125.570 (CH), 133.164 (Cq), 134.420 (Cq), 134.821 (CH), 145.587 (Cq), 153.150 (Cq), 165.592 (C=O), 169.627 (C=O), 170.230 (C=O), 170.630 (C=O); ATR-IR: ν = 1749, 1672, 1608, 1510, 1222, 1042 cm⁻¹; UV/Vis (CHCl₃): λᵥmax (ε) = 421.5 (565000), 516.0 (24800), 550.5 (12200), 590.5 (7840), 647.0 (6410 mol⁻¹dm³cm⁻¹) nm; FAB MS (HR): calcd m/z for C₁₁₂H₁₂₁N₈O₄₄: 2475.7633; found 2475.7639.

Preparation of 5d: 3d (2.2 g, 5.0 mmol) and 4 (0.79 g, 1.0 mmol) furnished 5d (1.0 g, 0.42 mmol, 42%). M.p. 171.4-171.9 °C dec.; ¹H NMR (600 MHz, CDCl₃): δ = -2.78 (s, 2 H), 2.07 (s, 3 H; Ac), 2.09 (s, 3 H; Ac), 2.11 (s, 3 H; Ac), 2.23 (s, 3 H; Ac), 4.13-4.35 (m, 12 H; H₅, H₆, H₆'), 5.41 (t, J = 10 Hz, 4 H; H₄), 5.50 (d, J = 2.9 Hz, 4 H; H₂), 5.56-5.57 (m, 4 H; H₁), 5.60 (dd, J₂,₃ = 3.6 Hz, J₃,₄ = 10 Hz, 4 H; H₃), 7.20 (d, J = 8.9 Hz, 8 H; Ar-H), 7.73 (d, J = 8.9 Hz, 8 H; Ar-H), 8.09 (s, 4 H; amide-NH), 8.28 (d, J = 7.9 Hz, 8 H; Ar-H), 8.36 (d, J = 7.9 Hz, 8 H; Ar-H), 8.86 (s, 8 H; β-pyrrole); ¹³C NMR (150 MHz, CDCl₃): δ = 20.736 (CH₃), 20.779 (CH₃), 20.927 (CH₃), 62.181 (CH₂), 65.975 (CH), 68.903 (CH),
69.246 (CH), 69.429 (CH), 96.185 (CH), 119.289 (Cq), 121.999 (CH), 125.554 (CH), 125.884 (Cq), 133.162 (Cq), 134.445 (Cq), 134.831 (CH), 145.588 (Cq), 152.632 (Cq), 165.580 (C=O), 169.769 (C=O), 170.011 (C=O), 170.059 (C=O), 170.059 (C=O); ATR-IR: $\nu = 1748$, 1672, 1607, 1509, 1214, 1036 cm$^{-1}$; UV/Vis (CHCl$_3$): $\lambda_{\text{max}}$ ($\varepsilon$) = 421.5 (372000), 516.0 (16600), 550.5 (8020), 590.0 (5270), 646.5 (3350 mol$^{-1}$dm$^{-3}$cm$^{-1}$) nm; FAB MS (HR): calcd m/z for C$_{128}$H$_{123}$N$_8$O$_{44}$: 2475.7633; found 2475.7659.

**Preparation of 5e:** 3e (1.2 g, 2.6 mmol) and 4 (0.40 g, 0.50 mmol) furnished 5b (0.58 g, 0.23 mmol, 46%). M.p. 146.1-146.3 °C dec.; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = -2.74 (s, 2H), 1.98 (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.10 (s, 3 H; Ac), 2.11 (s, 3 H; Ac), 4.16-4.30 (m, 12 H; H$_5$, H$_6$, H$_6^\prime$), 5.19 (d, $J$ = 7.5 Hz, 4 H; H$_1$), 5.20 (dd, $J_{2,3} = 9.4$ Hz, $J_{3,4} = 3.4$ Hz, 4 H; H$_3$), 5.50 (d, $J$ = 3.2 Hz, 4 H; H$_4$), 5.67 (dd, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10$ Hz, 4 H; H$_2$), 7.10 (d, $J$ = 8.0 Hz, 4 H; Ar-H), 7.17 (t, $J$ = 7.9 Hz, 4 H; Ar-H), 7.26-7.27 (m, 4 H; amide-NH), 8.39-8.42 (m, 16 H; Ar-H), 8.76 (d, $J$ = 7.9 Hz, 4 H; Ar-H), 8.92-8.94 (m, 12 H; Ar-H, $\beta$-pyrrole); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 20.520 (CH$_3$), 20.617 (CH$_3$), 20.925 (CH$_3$), 61.256 (CH$_2$), 66.715 (CH), 68.710 (CH), 70.402 (CH), 71.367 (CH), 100.451 (CH), 114.558 (CH), 115.659 (CH), 119.411 (CH), 121.107 (CH), 124.188 (CH), 125.931 (CH), 129.224 (Cq), 134.135 (Cq), 134.643 (CH), 145.662 (Cq), 152.632 (Cq), 165.580 (C=O), 169.769 (C=O), 170.011 (C=O), 170.059 (C=O), 170.621 (C=O); ATR-IR: $\nu = 1748$, 1672, 1607, 1509, 1214, 1036 cm$^{-1}$; UV/Vis (CHCl$_3$): $\lambda_{\text{max}}$ ($\varepsilon$) = 421.5 (372000), 516.0 (16600), 550.5 (8020), 590.0 (5270), 646.5 (3350 mol$^{-1}$dm$^{-3}$cm$^{-1}$) nm; FAB MS (HR): calcd m/z for C$_{128}$H$_{123}$N$_8$O$_{44}$: 2475.7633; found 2475.7659.

**Preparation of 5e:** 3e (1.2 g, 2.6 mmol) and 4 (0.40 g, 0.50 mmol) furnished 5b (0.58 g, 0.23 mmol, 46%). M.p. 146.1-146.3 °C dec.; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = -2.74 (s, 2H), 1.98 (s, 3 H; Ac), 2.07 (s, 3 H; Ac), 2.10 (s, 3 H; Ac), 2.11 (s, 3 H; Ac), 4.16-4.30 (m, 12 H; H$_5$, H$_6$, H$_6^\prime$), 5.19 (d, $J$ = 7.5 Hz, 4 H; H$_1$), 5.20 (dd, $J_{2,3} = 9.4$ Hz, $J_{3,4} = 3.4$ Hz, 4 H; H$_3$), 5.50 (d, $J$ = 3.2 Hz, 4 H; H$_4$), 5.67 (dd, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10$ Hz, 4 H; H$_2$), 7.10 (d, $J$ = 8.0 Hz, 4 H; Ar-H), 7.17 (t, $J$ = 7.9 Hz, 4 H; Ar-H), 7.26-7.27 (m, 4 H; amide-NH), 8.39-8.42 (m, 16 H; Ar-H), 8.76 (d, $J$ = 7.9 Hz, 4 H; Ar-H), 8.92-8.94 (m, 12 H; Ar-H, $\beta$-pyrrole); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 20.520 (CH$_3$), 20.617 (CH$_3$), 20.925 (CH$_3$), 61.256 (CH$_2$), 66.715 (CH), 68.710 (CH), 70.402 (CH), 71.367 (CH), 100.451 (CH), 114.558 (CH), 115.659 (CH), 119.411 (CH), 121.107 (CH), 124.188 (CH), 125.931 (CH), 129.224 (Cq), 134.135 (Cq), 134.643 (CH), 145.662 (Cq), 152.632 (Cq), 165.580 (C=O), 169.769 (C=O), 170.011 (C=O), 170.059 (C=O), 170.621 (C=O); ATR-IR: $\nu = 1748$, 1672, 1607, 1509, 1214, 1036 cm$^{-1}$; UV/Vis (CHCl$_3$): $\lambda_{\text{max}}$ ($\varepsilon$) = 421.5 (372000), 516.0 (16600), 550.5 (8020), 590.0 (5270), 646.5 (3350 mol$^{-1}$dm$^{-3}$cm$^{-1}$) nm; FAB MS (HR): calcd m/z for C$_{128}$H$_{123}$N$_8$O$_{44}$: 2475.7633; found 2475.7659.
145.725 (Cq), 165.433 (C=O), 169.929 (C=O), 169.988 (C=O), 170.104 (C=O),
170.269 (C=O); ATR-IR: $\nu$ = 1751, 1679, 1606, 1527, 1218, 1073 cm$^{-1}$; UV/Vis (CHCl$_3$):
$\lambda_{\text{max}}$ [\text{nm}](\varepsilon) = 421.5 (395000), 516.0 (15800), 551.5 (7250), 590.0 (4370), 646.5 (3110
mol$^{-1}$dm$^3$cm$^{-1}$) nm; FAB MS (HR): calcd $m/z$ for $\text{C}_{128}\text{H}_{123}\text{N}_8\text{O}_{44}$: 2475.7633; found
2475.7627.
Figure S1. Plots of the $T_{gel}$s of 1a-c gels against the gelator concentration (DMF:benzyl alcohol = 1:3 (v/v)).
Figure S2. Plots of the $T_{gel}$s of 1a-c gels against the mixing ratio of the solvents (DMF vs. benzyl alcohol).
Figure S3. a) SEM images of the assemblies in the supernatant of 1a gel (DMF:benzyl alcohol = 1:3 (v/v), [1a] = 4.0 g dm$^{-3}$) and b) the enlarged image of a). c) TEM image of the xerogels of 1a gel (DMF:benzyl alcohol = 1:2 (v/v), [1a] = 30 g dm$^{-3}$) stained by phosphotungstic acid.

Table S1. $T_{gel}$ of 1a gel against gelator concentration and solvent ratio.
<table>
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<th>gelator concentration (g dm(^{-3}))</th>
<th>(T_{gel}(^\circ C))</th>
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<tr>
<td>DMF:benzyl alcohol (v/v)</td>
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<td>P</td>
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<td>30</td>
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P: precipitation, S: homogenous solution, and HVS: highly viscous solution.