Electronic Supplementary Information for

Use of solvent to regulate the degree of polymerisation in weakly associated supramolecular oligomers

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I. Materials and Methods

All chemicals were purchased from Sigma-Aldrich, and used as received unless indicated otherwise. All reactions were carried out under an atmosphere of anhydrous nitrogen. THF was dried using a VAC solvent purifier and triethylamine was dried over calcium hydride and distilled under nitrogen immediately prior to use. Analytical thin-layer chromatography (TLC) was performed using aluminium sheets precoated with silica gel 60F (Merck 5554), which were inspected by UV-light (254 nm) prior to development with I₂ vapor. Column chromatography was performed using silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points (m.p.) were determined with a Büchi melting point apparatus and are uncorrected. 1D and 2D NMR spectra were recorded on a Bruker AVANCE III 400 MHz Spectrometer or a 600MHz Varian DirectDrive, where ¹H NMR was recorded at 400 MHz (or 600 MHz) at 298 K, and ¹³C NMR was recorded at 100 MHz at 298 K. The NMR samples were dissolved in deuterated solvents purchased from Cambridge Isotope Labs or SigmaAldrich and TMS or the residual solvent were used as internal standard. IR spectra were recorded on a Walters Ultima Magnetic Sector mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia, USA.

AFM imaging was performed at room temperature in the tapping mode on a PicoScanTM AFM (molecular imaging) scanner with maximum scan size of $6 \times 6 \mu m$. All images were acquired using a 225-µm silicon single-crystal cantilever (BudgetSensors) with a typical tip radius of 10 nm and resonance frequency of 190 kHz.

X-Ray data were collected using a graphite monochromator with MoK α radiation ($\lambda = 0.71075$ Å). Data were collected on either a Rigaku SCX-Mini diffractometer with a Mercury 2 CCD at 153 K or on a Rigaku AFC-12 with a Saturn 724+ CCD at 100 K. The data were collected at these reduced temperatures using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in the following sections for each sample. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.^{S1} The structures were solved by direct methods using SIR97^{S2} and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-97.^{S3} Structure analysis was aided by use of the programs PLATON98^{S4} and WinGX.^{S5} The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times$ Ueq of the attached atom $(1.5 \times$ Ueq for methyl hydrogen atoms). The function, $\Sigma_w(|F_0|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_0))^2 + (a \times$ P)² + (b × P)] where a and b were constants suggested during refinement and P = $(|F_0|^2 + 2|F_c|^2)/3$. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.^{S6} Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).^{S7} All figures were generated using SHELXTL/PC.^{S8} Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

II. Experimental Procedures

Compound 1 was prepared according to the reported procedure.^{S9}

Ethane-1,2-diyl bis(3,5-dinitrobenzoate) (2): 1,2-Ethanediol (0.408 g, 6.73 mmol) and 3,5dinitrobenzoyl chloride (3.180 g, 13.8 mmol)) were dissolved in anhydrous THF and degassed with N₂ for 15 min before triethylamine (4 equiv.) was added slowly. The reaction mixture was heated under reflux overnight before being cooled to room temperature. The yellow suspension was concentrated *in vacuo* providing a beige solid, which was dissolved in CH₂Cl₂ (300 mL) and washed with H₂O (2 × 200 mL), before being dried (MgSO₄). The solution was evaporated onto Celite® and purified by column chromatography (300 mL SiO₂, 5 cm Ø, eluent CH₂Cl₂). The colourless band ($R_f = 0.3$) was collected and concentrated to give ethane-1,2-diyl bis(3,5-dinitrobenzoate) (2) as a white powder (2.91 g, 98%): m.p. 172.5–172.8 °C; ¹H NMR (600 MHz, CDCl₃, 298 K, TMS): $\delta = 4.87$ (s, 4H), 9,17 (d, J = 2.2 Hz, 4H), 9.26 (t, J = 2.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): $\delta = 64.1$, 122.8, 129.6, 133.1, 148.8, 162.4; HRMS (CI): m/z: calcd for C₁₆H₁₀N₄O₁₂⁺ 450.0290; found 450.0291 (M⁺); IR (KBr) ν/cm^{-1} = 3100 (m), 2883 (w), 1735 (s), 1630 (m), 1597 (w), 1546 (s), 1462 (m), 1347 (s), 1270 (s), 1162 (s), 1078 (m), 1044 (w), 923 (m), 854 (w), 774 (w), 722 (s); elemental analysis calcd (%) for C₁₆H₁₀N₄O₁₂: C 42.68, H 2.24, N 12.44; found: C 42.50, H 2.24, N 12.20.



Fig. S1 1 H NMR spectrum (600 MHz, 298 K, CDCl₃) of **2**.



Fig. S2 ¹³C NMR spectrum (100 MHz, 298 K, CDCl₃) of **2**.



Fig. S3 Chemical ionisation mass spectrum of 2.

Propane-1,3-diyl bis(3,5-dinitrobenzoate) (3): 1,3-Propanediol (0.499 g, 6.56 mmol) and 3,5dinitrobenzoyl chloride (3.182 g, 13.8 mmol) were dissolved in anhydrous THF and degassed with N₂ for 15 min before triethylamine (4 equiv.) was added slowly. The reaction mixture was heated under reflux overnight before being cooled to room temperature. The yellow suspension was concentrated *in vacuo* to give beige solid, which was dissolved in CH₂Cl₂ (200 mL) and washed with H₂O (2 × 200 mL), before being dried (MgSO₄). The solution was evaporated onto Celite® and purified by column chromatography (300 mL SiO₂, 5 cm Ø, eluent CH₂Cl₂). The colourless band ($R_f = 0.3$) was collected and concentrated to give propane-1,3-diyl bis(3,5-dinitrobenzoate) (**3**) as a white powder (2.68 g, 88%): m.p. 181.2–181.4 °C; ¹H NMR (600 MHz, CDCl₃, 298 K, TMS): $\delta = 2.42$ (quintet, J = 6.3 Hz, 2H), 4.66 (t, J = 6.3 Hz, 4H), 9.16 (d, J = 2.2 Hz, 4H), 9.25 (t, J = 2.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): $\delta = 28.0$, 63.2, 122.7, 129.4, 133.5, 148.8, 162.5; HRMS (ESI): m/z: calcd for C₁₇H₁₂N₄O₁₂Na⁺ 487.0344; found 487.0351 [M + Na]⁺; elemental analysis calcd (%) for C₁₇H₁₂N₄O₁₂: C 43.98, H 2.61, N 12.07; found: C 43.73, H 2.61, N 11.85.



Fig. S4 1 H NMR spectrum (600 MHz, 298 K, CDCl₃) of **3**.





Butane-1,4-diyl bis(3,5-dinitrobenzoate) (4): Butane-1,4-diol (0.500 g, 5.55 mmol) and 3,5dinitrobenzoyl chloride (2.814 g, 12.2 mmol) were dissolved in anhydrous THF and degassed with N₂ for 15 min before triethylamine (4 equiv.) was added slowly. The reaction mixture was heated under reflux overnight, before being cooled to room temperature. The yellow suspension was concentrated *in vacuo* affording a beige solid, which was dissolved in CH₂Cl₂ (200 mL) and washed with H₂O (2 × 150 mL), before being dried (MgSO₄). The solution was evaporated onto Celite® and purified by column chromatography (200 mL SiO₂, 4 cm Ø, eluent CH₂Cl₂). The colorless band ($R_f = 0.3$) was collected and concentrated to give butane-1,4-diyl bis(3,5-dinitrobenzoate) (4) as a white powder (2.35 g, 89%): m.p. 192.2–192.5 °C; ¹H NMR (600 MHz, CDCl₃, 298 K, TMS): $\delta = 1.97-2.13$ (m, 4H), 4.44–4.68 (m, 4H), 9.17 (d, J = 2.1 Hz, 4H), 9.24 (t, J = 2.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): $\delta = 162.6$, 148.9, 133.9, 129.6, 122.7, 66.3, 25.4; HRMS (ESI): *m/z*: calcd for C₁₈H₁₄N₄O₁₂Na⁺ 501.0500; found 501.0505 [M + Na]⁺; elemental analysis calcd (%) for C₁₈H₁₄N₄O₁₂: C 45.20, H 2.95, N 11.71; found: C 44.64, H 2.95, N 11.22.



Fig. S7 ¹H NMR spectrum (600 MHz, 298 K, CDCl₃) of 4.





Fig. S9 Electrospray ionisation mass spectrum of 4.



Fig. S10 Concentration dependent ¹H NMR spectra of **1** in trichloromethane solution at room temperature. Note that no evidence for the self-aggregation of **1** could be seen.

III. Solution State Analyses

1. UV-Vis-NIR spectroscopic analyses



Fig. S11 UV-Vis-NIR spectra recorded upon dilution of equal amount of **1** and **2-4** in chloroform solution (left) and corresponding binding isotherm analyses (right).^{S10}



Fig. S12 Variable temperature absorption spectroscopy experiments of 1 (0.20 mM) and 2 (0.20 mM) carried out in DCE. a) Temperature-dependent degree of aggregation, α_{agg} , calculated from the absorption at 450 nm and the corresponding isodesmic fit. b) Number-averaged degree of polymerization, DP_N , as a function of temperature and the expected continuation of the data. c) Elongation equilibrium, K_e , as a function of temperature and the expected continuation of the data. d) Van't Hoff plot.



Fig. S13 Variable temperature absorption spectroscopy experiment of 1 (0.05 mM) and 2 (0.05 mM) carried out in MCH. a) Temperature-dependent degree of aggregation, α_{agg} , calculated from the absorption at 450 nm and the corresponding isodesmic fit. b) Number-averaged degree of polymerization, DP_N , as a function of temperature and the expected continuation of the data. c) Elongation equilibrium, K_e , as a function of temperature and the expected continuation of the data. d) Van't Hoff plot.

2. NMR spectroscopic analyses - DOSY experiments



Fig. S14 Full view of the ¹H 2D DOSY NMR Spectra of a) $(1 \cdot 2)_n$, b) $(1 \cdot 3)_n$ and c) $(1 \cdot 4)_n$ recorded at 14 mM ([1] = [2] = [3] = [4] = 7 mM) solution in CDCl₃ (top) and the corresponding crystal structures (bottom).

IV. Solid State Analyses

1. Atomic Force Microscopy (AFM)



Fig. S15 AFM images of equal amounts of 1 and 4. 10μ L of 1 and 4 in dichloromethane (50 μ M) was drop-cast onto freshly cleaved highly oriented pyrolytic graphite (HOPG) and allowed to slowly evaporate at 278 K.

2. X-ray Single Crystallographic Analyses



Fig. S16 View of $(1 \cdot 2)_n$. Displacement ellipsoids are scaled to the 50% probability level. The complex repeats along the b-axis, with molecules related by x, 1+y, z.

| Empirical formula | $C_{85.50}H_{95.50}Cl_{4.50}N_8O_{12}S_{24}$ | |
|---------------------------------|--|------------------------------|
| Formula weight | 2356.16 | |
| Temperature | 153(2) K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions: | a = 21.397(6) Å | $\alpha = 78.315(7)^{\circ}$ |
| | b = 22.344(6) Å | $\beta = 84.749(6)^{\circ}$ |
| | c = 22.907(6) Å | $\gamma = 79.607(6)^{\circ}$ |
| Volume | $10532(5) \text{ Å}^3$ | |
| Ζ | 4 | |
| Density (calculated) | 1.486 Mg/m^3 | |
| Absorption coefficient | 0.661 mm ⁻¹ | |
| F(000) | 4884 | |
| Crystal size | $0.25\times0.06\times0.04~\text{mm}^3$ | |
| Theta range for data collection | 1.89 to 25.00° | |
| Index ranges | -25<=h<=25, -26<=k<=26, -27<=l<=27 | |
| Reflections collected | 92564 | |

| Independent reflections | 36998 [R(int) = 0.2260] |
|---|---|
| Completeness to theta = 25.00° | 99.8% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 1.00 and 0.821 |
| Refinement method | Full-matrix-block least-squares on F ² |
| Data / restraints / parameters | 36998 / 1612 / 2440 |
| Goodness-of-fit on F ² | 1.164 |
| Final R indices [I>2sigma(I)] | R1 = 0.1478, wR2 = 0.2394 |
| R indices (all data) | R1 = 0.3141, $wR2 = 0.3375$ |
| Largest diff. peak and hole | $1.105 \text{ and } -1.648 \text{ e.}\text{Å}^{-3}$ |
| CCDC number | 988770 |

Table S1 Crystal data and refinement parameters of $(1 \cdot 2)_n$.



Fig. S17 View of $(1 \cdot 3)_n$. Displacement ellipsoids are scaled to the 30% probability level.

| Empirical formula | $C_{89}H_{104}Cl_8N_8O_{12}S_{24}$ | |
|---|---|------------------------------|
| Formula weight | 2530.84 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions: | a = 16.645(6) Å | $\alpha = 85.987(2)^{\circ}$ |
| | b = 18.555(7) Å | $\beta = 68.623(2)^{\circ}$ |
| | c = 20.012(6) Å | $\gamma = 81.231(3)^{\circ}$ |
| Volume | 5687(3) Å ³ | |
| Ζ | 2 | |
| Density (calculated) | 1.478 Mg/m ³ | |
| Absorption coefficient | 0.697 mm ⁻¹ | |
| F(000) | 2620 | |
| Crystal size | $0.34\times0.08\times0.04~mm^3$ | |
| Theta range for data collection | 1.38 to 27.50° | |
| Index ranges | -19<=h<=21, -23<=k<=24, 0<=l<=25 | |
| Reflections collected | 26041 | |
| Independent reflections | 26041 [R(int) = 0.0000] | |
| Completeness to theta = 27.50° | 99.7% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00 and 0.725 | |
| Refinement method | Full-matrix-block least-squares on F ² | |
| Data / restraints / parameters | 26041 / 850 / 1229 | |
| Goodness-of-fit on F ² | 1.227 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1385, wR2 = 0.3197 | |
| R indices (all data) | R1 = 0.2256, wR2 = 0.3599 | |
| Largest diff. peak and hole | 1.650 and -0.899 e.Å ⁻³ | |
| CCDC number | 988771 | |

Table S2 Crystal data and refinement parameters of $(1 \cdot 3)_n$.



Fig. S18 View of $(1 \cdot 4)_n$. Displacement ellipsoids are scaled to the 50% probability level.

| Empirical formula | $C_{89}H_{104}Cl_6N_8O_{12}S_{24}$ | |
|------------------------|------------------------------------|-------------------------------|
| Formula weight | 2459.94 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions: | a = 17.3624(12) Å | $\alpha = 103.499(8)^{\circ}$ |
| | b = 17.5374(13) Å | $\beta = 108.269(9)^{\circ}$ |
| | c = 21.322(2) Å | $\gamma = 107.023(8)^{\circ}$ |
| Volume | 5503.9(8) Å ³ | · |
| Ζ | 2 | |
| Density (calculated) | 1.484 Mg/m ³ | |
| Absorption coefficient | 0.671 mm ⁻¹ | |

| F(000) | 2552 |
|---|---|
| Crystal size | $0.30 \times 0.20 \times 0.18 \text{ mm}^3$ |
| Theta range for data collection | 2.97 to 25.00° |
| Index ranges | -20<=h<=19, -20<=k<=20, -23<=l<=25 |
| Reflections collected | 19331 |
| Independent reflections | 19331 [R(int) = 0.0000] |
| Completeness to theta = 25.00° | 99.7% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.714 |
| Refinement method | Full-matrix-block least-squares on F ² |
| Data / restraints / parameters | 19331 / 143 / 1300 |
| Goodness-of-fit on F ² | 1.991 |
| Final R indices [I>2sigma(I)] | R1 = 0.1244, wR2 = 0.3248 |
| R indices (all data) | R1 = 0.1375, wR2 = 0.3295 |
| Largest diff. peak and hole | 1.589 and -1.382 e.Å ⁻³ |
| CCDC number | 988772 |

Table S3. Crystal data and refinement parameters of $(1 \cdot 4)_n$.

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