

## Supporting Information

### **Solvatochromism of dye-labeled dendronized polymers of generation numbers 1-4: Comparison to dendrimers**

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## 1. Materials and methods:

Compounds **1a** (3,5-bis(3-(tert-butoxycarbonylamino)propoxy) benzoic acid methyl ester) and **1d** (3,5-bis[3-(tert-butoxycarbonylamino)propoxy]benzoic acid N-hydroxysuccinimide ester) were purchased from Synwit Technology, China. Compounds **1b** and **1c** were prepared according to literature procedures.<sup>[1]</sup> Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol. Methacryloyl chloride (MAC) was obtained from Acros and freshly distilled before use. The dendronization procedure followed a literature protocol.<sup>[2]</sup> Other reagents and solvents were purchased at reagent grade from Sigma-Aldrich, Fluka or Acros and used without further purification. Silica gel 60Å (230-400 mesh) from Fluka was used for column chromatography. Thin-layer chromatography was carried out with pre-coated aluminium plates (silica gel 60 F254, Merck).

<sup>1</sup>H-NMR (300MHz) and <sup>13</sup>C-NMR (75.5 MHz) spectra were recorded on a Bruker NMR spectrometer (AV 300). NMR spectra at elevated temperatures were recorded on a Bruker NMR spectrometer (AV 500; <sup>1</sup>H-NMR (500MHz) and <sup>13</sup>C-NMR (125 MHz)). CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as solvents. The solvent signal was used as an internal standard (<sup>1</sup>H: δ=7.26 ppm, <sup>13</sup>C: δ=77.16 ppm for CHCl<sub>3</sub>; <sup>1</sup>H: δ=2.50 ppm, <sup>13</sup>C: δ=39.52 for DMSO).

Mass spectrometry was performed by the MS-Service of the “Laboratorium für Organische Chemie, ETH Zürich” on a Bruker solariX (FT/ICR) ESI ETD Maldi Instrument.

Analytical gel permeation chromatography (GPC) was done on a Malvern VISCOTEK GPCmax+TDA equipped with refractive index (RI), viscosity and light scattering (RALS, LALS) detectors, and LiBr (1 g/L) in DMF as eluent at 45° C. Universal calibration was performed with poly(methyl methacrylate) standards in the range of M<sub>p</sub>=2 680-3 900 000 Da (Polymer Laboratories Ltd, UK). TGA analysis was performed under N<sub>2</sub> with a Q500 thermogravimetric analyzer, TA Instruments (heating rate: 10 °C/min).

UV-Vis spectroscopy measurements were carried out on a UV-Vis-NIR spectrophotometer V-670, Jasco Inc. equipped with a Peltier temperature control (EC-717) using semi-Micro Cells 110-QS, V=1.4 mL, l=1 cm (Hellma). Measurements were performed at 25 °C if not directly stated otherwise. Solvents were used as received. Diluted solutions were prepared to match the absorbance range of 0.1–1 (at λ<sub>max</sub>). Solutions were left to equilibrate for 1 h before measurement.

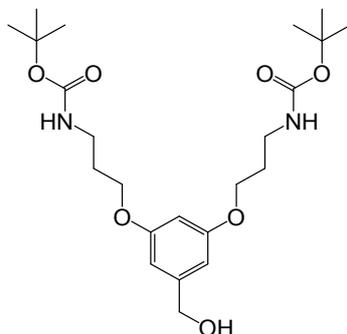
Fluorescence spectra were recorded on a Spex Fluorolog 2 Series spectrofluorometer, Spex Industries Inc. using a Fluorescence Macro Cell 101-QS, V=3.5 mL, l=1 cm. Spectra were recorded in emission mode with an excitation wavelength of 350 nm.

AFM measurements were carried out on a Nanoscope IIIa Multi Mode Scanning probe microscope (Digital Instruments) operated in the tapping mode with an “E” scanner at room temperature in air. Olympus silicon OMCL-AC160TS-R3 cantilevers (from Atomic Force F&E GmbH) were used, typical resonance frequency 300 kHz, typical spring constant 26.1 N/m. The samples were prepared by

drop casting the polymer solution (1 mg/L in chloroform) onto freshly cleaved mica (from PLANO W. Plannet GmbH).

## 2. Synthesis and characterization of *hs-PGg* and *ls-PGg*

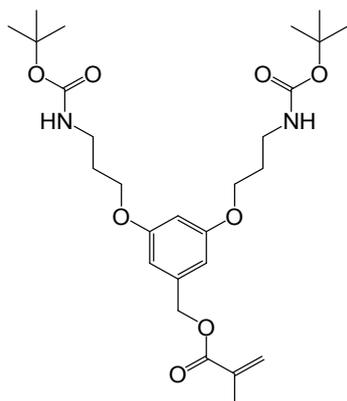
### Dendron **1b**:



Lithium aluminum hydride (LAH) (2.4 M in THF; 34.5 mL, 82.8 mmol) was diluted with THF (50 mL). The solution was cooled to -5 °C. Dendron **1a** (20 g, 41.4 mmol) was dissolved in THF (200 mL) and slowly added to the LAH solution via a dropping funnel. The ice bath was removed and the solution was stirred for 2 h. TLC showed completion of reaction. The solution was cooled again and EA (400 mL) followed by H<sub>2</sub>O (400 mL) was slowly added until no more gas formation was detected. The two phases were separated and the organic phase was washed with H<sub>2</sub>O and brine and dried with MgSO<sub>4</sub>. The solvent was removed. 16.5 g (88% yield) of the product were obtained as a white powder.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 1.44 (s, 18 H, *t*Bu), 1.96 (quint, 4 H, *J* = 6.3 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.30 (t, 4 H, *J* = 6.6 Hz, CH<sub>2</sub>NH), 4.00 (t, 4 H, *J* = 6.0 Hz, OCH<sub>2</sub>), 4.62 (s, 2 H, PhCH<sub>2</sub>OH), 6.36 (s, 1 H, Ph), 6.51 (s, 2 H, Ph)

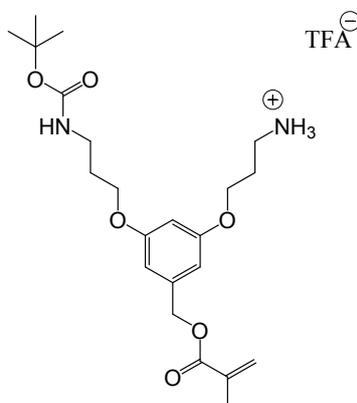
### Macromonomer **1c**:



Dendron **1b** (16.5 g, 36.3 mmol), Et<sub>3</sub>N (15.2 mL, 109 mmol) and 4-dimethylaminopyridine (DMAP) (100 mg, cat.) were dissolved in DCM (300 mL) and cooled to -5 °C. Freshly distilled methacryloyl chloride (5.33 mL, 54.6 mmol) was mixed with DCM (100 mL) and slowly added to the solution containing **1b**. The ice bath was removed and it was stirred for 2 h. TLC showed consumption of SM. The solution was washed with H<sub>2</sub>O and brine and dried with MgSO<sub>4</sub>. The solvent was removed. The product was recrystallized (EA/hexane 1+2) and obtained as a white powder (14.4 g, 76% yield).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 1.44 (s, 18 H, *t*Bu), 1.97 (m, 7 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH, CH<sub>3</sub>), 3.31 (t, 4 H, *J* = 6.4 Hz, CH<sub>2</sub>NH), 3.99 (t, 4 H, *J* = 5.9 Hz, OCH<sub>2</sub>), 4.74 (br, 2H, NH), 5.10 (s, 2 H, PhCH<sub>2</sub>O), 5.59 (s, 1 H, CH<sub>2</sub>), 6.16 (s, 1 H, CH<sub>2</sub>), 6.39 (s, 1 H, Ph), 6.50 (s, 2 H, Ph)

### Macromonomer **2a**:

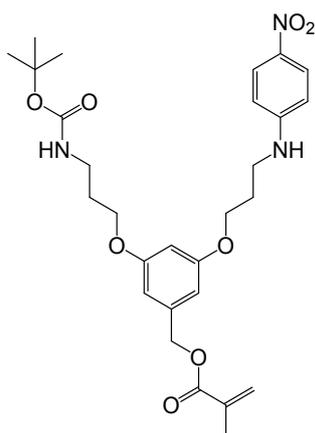


Macromonomer **1c** (20 g, 38.3 mmol) was dissolved in DCM (80 mL) and the solution was cooled to -5 °C. Trifluoroacetic acid (TFA) (10 ml, 131 mmol) was mixed with DCM (120 mL) and slowly added to the solution of **1c**. The ice bath was removed and the reaction mixture was stirred for 24 h. TLC was used to monitor reaction progress. TFA (5 mL, 19.2 mol) in DCM (15 mL) was added to the reaction solution at -5 °C. After 48 h, TFA (5 mL, 19.2 mol) in DCM (15 mL) was again added to the cooled reaction solution. After in total four days the reaction was finished. MeOH was added to quench the reaction. Addition and removal of MeOH was repeated three times. A column was made (eluent: CHCl<sub>3</sub>/MeOH (10+2) + 1% Et<sub>3</sub>N). The product was acidified and obtained as a pale oil (12 g, 59% yield).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 1.41 (s, 9 H, *t*Bu), 1.94 (m, 5 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH, CH<sub>3</sub>), 2.15 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.17 (br, 2 H, CH<sub>2</sub>NH), 3.27 (br, 2 H, CH<sub>2</sub>NH), 3.96 (t, 2 H, *J* = 5.9 Hz, OCH<sub>2</sub>), 4.02 (m, 2 H, OCH<sub>2</sub>), 4.86 (br, 1 H, NH), 5.06 (s, 2 H, PhCH<sub>2</sub>O), 5.58 (s, 1 H, CH<sub>2</sub>), 6.14 (s, 1 H, CH<sub>2</sub>), 6.38 (s, 1 H, Ph), 6.45 (s, 1 H, Ph), 6.49 (s, 1 H, Ph), 8.14 (br, 3 H, NH<sub>3</sub>)

MALDI-MS: m/z: 423.25 [M]<sup>+</sup>

### Macromonomer **2b**:



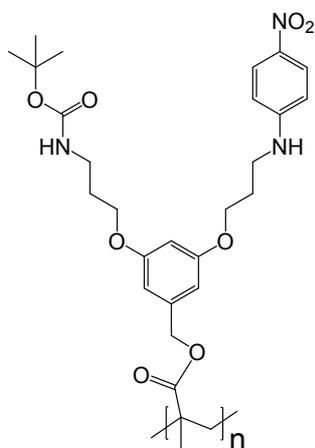
Macromonomer **2a** (1.3 g, 2.42 mmol) was dissolved in DMF (35 mL). Et<sub>3</sub>N (2 mL, 14.3 mol) and *p*-fluoronitrobenzene (0.771 mL, 7.27 mmol) were added. The solution was heated to 65 °C and stirred overnight. The product was purified by column chromatography (eluent: hexane/ethyl acetate (10+1) gradient towards pure ethyl acetate). The product (0.93 g, 70% yield) was obtained as a yellow powder.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 1.44 (s, 9 H, *t*Bu), 1.97 (m, 5 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH, CH<sub>3</sub>), 2.13 (quint, 2 H, *J* = 6.3 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.32 (dt, 2 H, *J* = 6.4 Hz, CH<sub>2</sub>NH), 3.45 (t, 2 H, *J* = 6.7 Hz, CH<sub>2</sub>NH), 4.00 (t, 2 H, *J* = 4.0 Hz, CH<sub>2</sub>O), 4.09 (t, 2 H, *J* = 4.1 Hz, CH<sub>2</sub>O), 4.71 (1H, NH), 4.81 (1H, NH), 5.12 (s, 2 H, PhCH<sub>2</sub>O), 5.61 (s, 1 H, CH<sub>2</sub>), 6.17 (s, 1 H, CH<sub>2</sub>), 6.40 (s, 1 H, Ph), 6.53 (m, 4 H, Ph, NO<sub>2</sub>Ph), 8.08 (d, 2 H, NO<sub>2</sub>Ph)

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 18.5, 28.6, 28.7, 29.7, 41.1, 60.5, 66.0, 66.3, 79.5, 101.2, 106.7, 106.8, 111.2, 126.1, 126.6, 136.3, 138.3, 138.8, 153.4, 156.1, 159.6, 160.3, 167.3

MALDI-MS: *m/z*: 566.25 [M+Na]<sup>+</sup>

### Polymer *hs*-**PG1**:



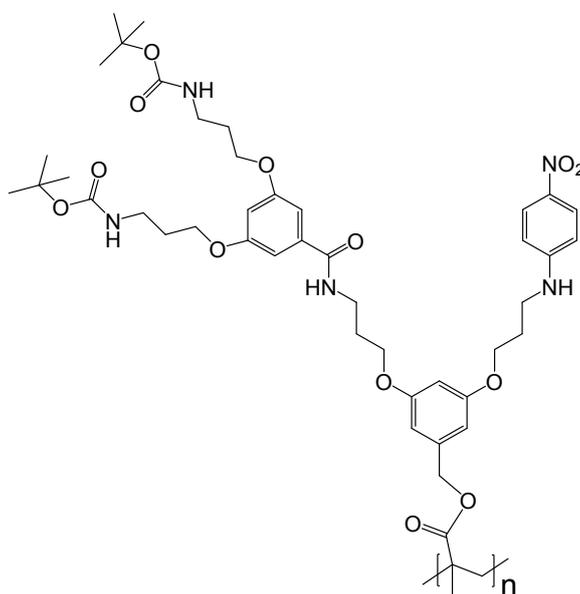
Macromonomer **2b** (0.387 g, 0.712 mmol) was placed in a Schlenk tube and dissolved in dry DMF (0.3 mL). AIBN (0.1 M in DMF; 0.237 mL, 0.0237 mmol) was added and the reaction mixture was degassed by several freeze-pump-thaw cycles. The Schlenk tube was placed in a preheated oil bath (65

°C) and slowly stirred for 15 h. The solution became viscous. It was diluted with DCM and precipitated into cold Et<sub>2</sub>O. The precipitate was dissolved in DCM and passed through a short chromatography column (eluent: DCM). The product was freeze dried from dioxane and obtained as a yellow powder (0.26 g, 66% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ= 0.79 (br), 0.97 (br), 1.32 (s, 9 H, *t*Bu), 1.77 (br, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 1.93 (br, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.05 (br, 2 H, CH<sub>2</sub>NH), 3.23 (br, 2 H, CH<sub>2</sub>NH), 3.86 (br, 2 H, OCH<sub>2</sub>), 3.95 (br, 2 H, OCH<sub>2</sub>), 4.79 (br, 2 H, PhCH<sub>2</sub>O), 6.10 (br, 1 H, NH), 6.33 - 6.45 (m, 3 H, Ph), 6.55 (br, 2 H, NO<sub>2</sub>Ph), 6.64 (br, 1 H, NH), 7.89 (br, 2 H, NO<sub>2</sub>Ph).

GPC: M<sub>n</sub>=86 000 Da, M<sub>w</sub>=143 000 Da, PDI=1.7.

### Polymer *hs*-PG2:



TFA (1 mL) was slowly added to *hs*-PG1 (0.175 g, 0.322 mmol) while being kept at -5 °C. After completed addition, the solution was stirred for 15 h at room temperature. Then, the reaction was quenched by addition of MeOH. Addition and removal of MeOH was repeated three times. The product, **3b**, was freeze dried from H<sub>2</sub>O (~100% yield). Polymer **3b** (0.179 g, 0.321 mol) was dissolved in DMF (3 mL). Et<sub>3</sub>N (0.175 mL, 1.25 mmol) and DMAP (0.02 g, cat.) were added. The solution was cooled to -10 °C and **1d** (1.07 g, 1.89 mmol) was slowly added. Then, the ice bath was removed and the reaction solution was stirred for two days. Then again **1d** (0.36 g, 0.636 mmol) was added at -10 °C. After one more day, **1d** (0.36 g, 0.636 mmol) was added at -10 °C. After three further days the reaction was finished. The solvent was removed and the product was precipitated into cold Et<sub>2</sub>O. For further purification column chromatography was done (eluent: DCM). The product was freeze dried from dioxane and obtained as a yellow powder (0.201 g, 70% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ= 0.82 (br), 0.98 (br), 1.33 (s, 18 H, *t*Bu), 2.00–1.70 (m, 8 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.07, 3.20, 3.35 (3x br, 8 H, CH<sub>2</sub>NH), 3.94 (br, 8 H, OCH<sub>2</sub>), 4.80 (br, 2 H, PhCH<sub>2</sub>O), 6.1-6.6 (m, 9 H, Ph, NO<sub>2</sub>Ph, NH), 6.93 (br, 2 H, Ph), 7.83 (br, 2 H, NO<sub>2</sub>Ph), 7.98 (br, 1 H, NH).

GPC: M<sub>n</sub>=151 000 Da, M<sub>w</sub>=348 000 Da, PDI=2.3.

TGA: 23% (22% theor.)

Fluorescence Quantification: 99.98%

#### Polymer *hs-PG3*:

TFA (1 ml) was added to a cooled flask containing *hs-PG2* (0.120 g, 0.134 mmol). After addition the ice bath was removed and the solution was left to stir for 15 h. Then, the reaction was quenched by addition of MeOH. Addition and removal of MeOH was repeated three times. The product was freeze dried from H<sub>2</sub>O (~100% yield). Then, it was dissolved in DMF (2 mL). Et<sub>3</sub>N (0.073 mL, 0.523 mmol) and DMAP (0.02 g, cat.) were added. The solution was cooled to -5 °C and **1d** (0.442 g, 0.781 mmol) was added in several portions. The cooling was removed and the solution was stirred for three days. Again **1d** (0.147 g, 0.260 mmol) was slowly added to the cooled reaction solution. After five more days **1d** (0.147 g, 0.260 mmol) was slowly added. After seven more days the solvent was evaporated and the mixture was precipitated into cold Et<sub>2</sub>O. The precipitate was dissolved in DCM and column chromatography was done (eluent: DCM). The product was freeze dried from dioxane and obtained as a yellow powder (0.18 g, 85% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ= 1.33 (s, 36 H, *t*Bu), 2.02–1.70 (m, 16 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.08, 3.19, 3.36 (3 x br, 16 H, CH<sub>2</sub>NH), 3.96 (br, 16 H, OCH<sub>2</sub>), 4.81 (br, 2 H, PhCH<sub>2</sub>O), 6.6–6.1 (m, 13 H, Ph, NO<sub>2</sub>Ph, NH), 6.94 (br, 5 H, Ph), 7.80 (br, 2 H, NO<sub>2</sub>Ph), 8.02 (br, 4 H, NH).

GPC: M<sub>n</sub>=241 000 Da, M<sub>w</sub>=419 000 Da, PDI=1.7.

TGA: 25% (25% theor.)

Fluorescence Quantification: 99.98%

#### Polymer *hs-PG4*:

TFA (1 mL) was added to a cooled flask containing *hs-PG3* (0.108 g, 0.0677 mmol). The ice bath was removed and the solution was stirred for 15 h. Then, the reaction was quenched by MeOH addition. Addition and removal of MeOH was repeated three times. The product was freeze dried from H<sub>2</sub>O (~100% yield). Then, it was dissolved in DMF (2 mL). Et<sub>3</sub>N (0.074 mL, 0.531 mmol) and DMAP (0.02 g, cat.) were added and the solution was cooled to -5 °C. Slowly **1d** (0.452 g, 0.799 mmol) was added. After the addition the solution was warmed to room temperature and stirred for five days. Then again **1d** (0.151 g, 0.267 mmol) was added at -5 °C. After seven more days **1d** (0.151 g, 0.267 mmol) was added. The solvent was removed after eight additional days of stirring. The reaction mixture was precipitated into cold Et<sub>2</sub>O. A column chromatography was applied (eluent: DCM). The product was freeze dried from dioxane and obtained as a yellow powder (0.135 g, 65% yield).

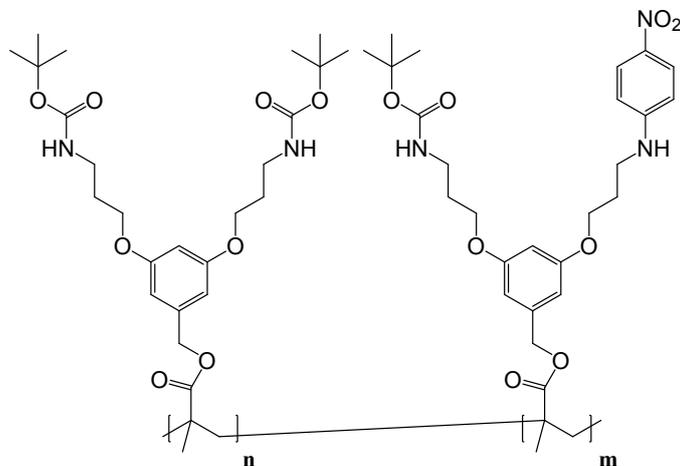
<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ= 1.33 (s, 72 H, *t*Bu), 2.02–1.73 (m, 32 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.07, 3.38 (2 x br, 32 H, CH<sub>2</sub>NH), 3.96 (br, 32 H, OCH<sub>2</sub>), 6.6–6.1 (m, 16 H, Ph, NO<sub>2</sub>Ph, NH), 6.94 (br, 12 H, Ph), 8.04 (br, 4 H, NO<sub>2</sub>Ph, NH).

GPC: M<sub>n</sub>=274 000 Da, M<sub>w</sub>=630 000 Da, PDI=2.3.

TGA: 25% (26% theor.)

Fluorescence Quantification: 99.99%

### Polymer *ls*-PG1:



Macromonomers **1c** (1 g, 1.91 mmol) and **2b** (0.022 g, 0.0405 mmol) were dissolved in dry DMF (1.4 mL). AIBN (0.1M in DMF; 0.191 mL, 0.0191 mmol) was added. The solution was degassed by several freeze-pump-thaw cycles. The flask was put into an oil bath (65 °C) and slowly stirred for 15 h. The solution became viscous. The heating was stopped and DCM was added. The product was passed through a short chromatography column (eluent: DCM). The solvent was removed and the product freeze dried from dioxane. A slightly yellow powder was obtained (0.94 g, 92% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ = 0.78 (br), 0.97 (br), 1.36 (s, 18 H, *t*Bu), 1.81 (br, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.09 (br, 4 H, CH<sub>2</sub>NH), 3.90 (br, 4 H, OCH<sub>2</sub>), 4.80 (br, 2 H, PhCH<sub>2</sub>O), 6.13 (br, 2 H, NH), 6.36 (br, 1 H, Ph), 6.41 (br, 2 H, Ph).

GPC: M<sub>n</sub>=281 000 Da, M<sub>w</sub>=1 090 000 Da, PDI=3.9.

### Polymer *ls*-PG2:

TFA (5 mL) was slowly added to *ls*-PG1 (0.665 g, 1.27 mmol) at -10 °C. The solution was left to stir for eight hours. The reaction was quenched with MeOH. The solvent was added and removed three times. It was freeze dried from H<sub>2</sub>O. The obtained powder was dissolved in DMF (15 mL). Et<sub>3</sub>N (0.71 mL, 5.09 mmol) and DMAP (0.08 g, cat.) were added and it was cooled to -10 °C. Dendron active ester **1d** (7.2 g, 12.7 mmol) was added in several portions. It was stirred at room temperature for two days. Again **1d** (1.4 g, 2.48 mmol) was added. After one more day **1d** (1.4 g, 2.48 mmol) was added. After three additional days the solvent was evaporated and the product was precipitated into cold Et<sub>2</sub>O. This was followed by column chromatography (eluent: DCM). The product was freeze dried from dioxane and obtained as a pale-yellow, fluffy powder (1.1 g, 71% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ = 1.32 (s, 36 H, *t*Bu), 1.78, 1.89 (2 x br, 12 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.06, 3.34 (2 x br, 12 H, CH<sub>2</sub>NH), 3.91 (br, 12 H, OCH<sub>2</sub>), 6.6–6.1 (m, 10 H, Ph, NH), 6.91 (br, 5 H, Ph), 7.96 (br, 4 H, NH).

GPC: M<sub>n</sub>=926 000 Da, M<sub>w</sub>=2 420 000 Da, PDI=2.6.

TGA: 31% (32% theor.)

Fluorescence Quantification: 99.99%

#### Polymer *ls*-PG3:

A flask containing *ls*-PG2 (0.75 g, 0.613 mmol) was cooled to -10 °C and slowly TFA (8.5 mL) was added. The cooling was removed and it was stirred for eight hours. The reaction was quenched with MeOH, followed by three times removal and addition of MeOH. The product was freeze dried from H<sub>2</sub>O. The deprotected product, Et<sub>3</sub>N (0.65 mL, 4.66 mmol) and DMAP (0.06 g, cat.) were dissolved in DMF (17 mL) and the solution was cooled to -10 °C. Slowly **1d** (4 g, 7.07 mmol) was added. The solution was stirred at room temperature for three days, after which again **1d** was added (1.33 g, 2.35 mmol). After five more days **1d** was again added (1.33 g, 2.35 mmol). After seven additional days the solvent was removed and the product was precipitated into cold Et<sub>2</sub>O followed by a short DCM column. The product was freeze dried from dioxane and obtained as a pale-yellow powder (1.12 g, 70% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ= 1.29 (s, 72 H, *t*Bu), 1.76, 1.86 (2 x br, 28 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.04, 3.31 (br, 28 H, CH<sub>2</sub>NH), 3.89 (br, 28 H, OCH<sub>2</sub>), 6.11 (br, 8 H, NH), 6.47 (br, 9 H, Ph), 6.89 (br, 12 H, Ph), 7.95 (br, 6 H, NH).

GPC: M<sub>n</sub>=2 350 000 Da, M<sub>w</sub>=5 970 000 Da, PDI=2.5.

TGA: 29% (30% theor.)

#### Polymer *ls*-PG4:

TFA was added to a flask containing *ls*-PG3 (0.75 g, 0.286 mmol) at -10 °C. The solution was left to stir at room temperature for eight hours. Then the reaction was quenched by repeated addition and removal of MeOH. The product was freeze dried from H<sub>2</sub>O. It was then dissolved in DMF (12 mL). Et<sub>3</sub>N (0.65 mL, 4.66 mmol) and DMAP (0.08 g, cat.) were added to the solution, it was cooled to -10 °C and **1d** (3.88 g, 6.86 mmol) was added in small portions. The solution was stirred for five days at room temperature and then **1d** (1.29 g, 2.28 mmol) was added again. After seven more days another portion of **1d** (1.29 g, 2.28 mmol) was added. After eight further days the product was precipitated into Et<sub>2</sub>O. Additionally column chromatography was done (eluent: DCM). The product was freeze dried from dioxane. It was obtained as a pale-yellow powder (1.1 g, 71% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ= 1.27 (s, 144 H, *t*Bu), 2.00–1.61 (m, 60 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.01, 3.31 (2 x br, 60 H, CH<sub>2</sub>NH), 3.86 (br, 60 H, OCH<sub>2</sub>), 6.04 (br, 15 H, NH), 6.44 (br, 15 H, Ph), 6.87 (br, 30 H, Ph), 7.91 (br, 15 H, NH).

GPC: M<sub>n</sub>=2 480 000 Da, M<sub>w</sub>=15 300 000 Da, PDI=6.2.

TGA: 27% (30% theor.)

Fluorescence Quantification: 99.89%

2.1. Table summarizing  $M_n$ ,  $M_w$ ,  $P_n$  and PDI of the DPs studied:

Table S 1: Number and weight average molar mass ( $M_n$  and  $M_w$ ), number average degree of polymerization ( $P_n$ ) and polydispersity index (PDI) of the DPs studied.

	$M_n$ [g/mol]	$M_w$ [g/mol]	$P_n$	PDI
<i>hs-PG1</i>	86 000	143 000	160	1.7
<i>hs-PG2</i>	151 000	348 000	190	2.3
<i>hs-PG3</i>	241 000	419 000	150	1.7
<i>hs-PG4</i>	274 000	630 000	90	2.3
<i>ls-PG1</i>	281 000	1 090 000	540	3.9
<i>ls-PG2</i>	926 000	2 420 000	760	2.6
<i>ls-PG3</i>	2 350 000	5 970 000	900	2.5
<i>ls-PG4</i>	2 480 000	15 300 000	460	6.2

## 2.2. Coverage quantification by fluorescence spectroscopy:

Quantification of each dendronization step was done by reaction of the respective polymer with dansyl chloride and fluorescence spectroscopy of the resultant polymer. The procedure was adapted from the literature.<sup>[3]</sup>

Polymer (20 mg) was dissolved in DCM (1 mL), Et<sub>3</sub>N (10 eq.) was added and it was cooled to -30 °C. A solution of dansyl chloride (0.5 eq per amine) in DCM (1 mL) was added. The solution was stirred at -10 °C for 2 h. MeOH was added and the solvent was removed. The product was precipitated into hexane/ethyl acetate (2+1) and Et<sub>2</sub>O to remove unreacted dansyl chloride. Additionally preparative TLC was done to rid the labelled polymer from impurities. The labelled polymer was dissolved in chloroform and a fluorescence spectrum was recorded (1–2.5 mM).

The polymers showed minor fluorescence already before dansyl labeling. This was considered negligible since the signal had very small influence. This additional fluorescence would cause an underestimation of the structural perfection.

### 2.3. MD simulations:

#### Computational methods:

The conformations reported in reference 4 for a PG2, PG3 and PG4 polymer chains with 150 repeat units each one was used as starting point for this study. Simulations were carried out in chloroform and toluene solutions, which were described using explicit solvent molecules. The total number of atoms considering for the simulations in chloroform / toluene were 245512 / 254472, 327357 / 327987 and 415512 / 424527 for PG2, PG3 and PG4, respectively, while the dimensions of the simulation box were  $180 \times 148 \times 248 \text{ \AA}^3$  /  $170 \times 140 \times 230 \text{ \AA}^3$ ,  $203 \times 141 \times 198 \text{ \AA}^3$  /  $175 \times 122 \times 250 \text{ \AA}^3$  and  $334 \times 179 \times 172 \text{ \AA}^3$  /  $300 \times 166 \times 166 \text{ \AA}^3$ , respectively.

The force field parameters of the dendrons were taken from GAFF,<sup>5</sup> as in our previous studies.<sup>4,6</sup> Chloroform molecules were represented by the model of Cieplak *et al.*<sup>7</sup> and Fioroni and Vogt,<sup>8</sup> respectively. Simulations were carried out using the NAMD<sup>9</sup> software and the potential energy function of AMBER.<sup>10</sup> Van der Waals interactions were calculated by applying an atom pair distance cutoff at 10 Å. Electrostatic interactions were extensively computed by means of Ewald summations. The real space term was defined by the van der Waals cutoff, while the reciprocal space was computed by interpolation into an infinite grid of points (particle mesh Ewald) with maximum space grid being 1.2 Å.<sup>11</sup>

Before running the production MD simulations, different consecutive rounds were performed to equilibrate and thermalize the system. First, solvent molecules were thermally relaxed by two consecutive runs, while the polymer chain was kept frozen during 0.5 ns of isothermal and 1.0 ns of isobaric relaxation. Hereafter, all atoms of the system were submitted to 1 ns of heating until the target temperature was reached (298 K), followed by 3 ns of thermal equilibration. Temperature was controlled by the weak coupling method using a time constant for the heat bath coupling of 1 ps. After this, the MD production run of each system at 298 K and 1 atm was 10 ns long. The numerical integration step was set to 2 fs, while the coordinates of the production run were saved every 5000 steps (1000 snapshots for each model).

#### Clarification of how cross-section figures were obtained:

These figures were derived from the last snapshot of the simulation. We cut the simulation boxes in the z-direction considering the length defined by 90 repeat units (all atoms exceeding this threshold were removed). After this, we removed the 90 repeat units of the polymer chain and only the solvent atoms remained in the image.

## 2.4. UV-Vis data:

Graphs presented in the main article (Figure 3a and b) are based on  $\lambda_{\max}$  values comprised in tables S1 and S3. Corresponding UV-Vis spectra from which these values are deduced can be found on the following pages. For the sake of completeness also  $\bar{\nu}_{\max}$  is given in tables S2 and S4. EA: ethyl acetate, 1,2-DCA: 1,2-dichloroethane.

Table S 2:  $\lambda_{\max}$  values (nm) of *hs-PGg* for  $g=0-4$  at 25 °C, \* toluene at 65 °C.

<i>g</i>	Toluene*	Benzene	Dioxane	EA	CHCl <sub>3</sub>	1,2-DCA	Acetone	MeOH	DMF	DMSO
0	361	367	370	372	376	378	383	386	393	399
1	366	374	380	379	385	385	385	388	393	397
2	370	386	385	383	389	386	387	390	393	397
3	389	398	387	387	392	391	389	392	394	397
4	410	398	389	390	394	393	390	394	394	398

Table S 3:  $\bar{\nu}_{\max}$  values (cm<sup>-1</sup>) of *hs-PGg* for  $g=0-4$  at 25 °C, \* toluene at 65 °C.

<i>g</i>	Toluene*	Benzene	Dioxane	EA	CHCl <sub>3</sub>	1,2-DCA	Acetone	MeOH	DMF	DMSO
0	27701	27248	27027	26882	26596	26455	26110	25907	25445	25063
1	27322	26738	26316	26385	25974	25974	25974	25773	25445	25189
2	27027	25907	25974	26110	25707	25907	25840	25641	25445	25189
3	25707	25126	25840	25840	25510	25575	25707	25510	25381	25189
4	24390	25126	25707	25641	25381	25445	25641	25381	25381	25126

Table S 4:  $\lambda_{\max}$  values (nm) of *ls-PGg* for  $g=0-4$  at 25 °C, \* toluene at 65 °C.

<i>g</i>	Toluene*	Benzene	Dioxane	EA	CHCl <sub>3</sub>	1,2-DCA	Acetone	MeOH	DMF	DMSO
0	365	367	370	372	374	373	383	386	393	400
1	380	381	379	379	386	383	386	389	396	400
2	396	397	394	393	399	391	396	399	402	407
3	401	402	398	398	402	397	399	404	403	407
4	405	404	401	402	404	402	404	404	404	407

Table S 5:  $\bar{\nu}_{\max}$  values (cm<sup>-1</sup>) of *ls-PGg* for  $g=0-4$  at 25 °C, \* toluene at 65 °C.

<i>g</i>	Toluene*	Benzene	Dioxane	EA	CHCl <sub>3</sub>	1,2-DCA	Acetone	MeOH	DMF	DMSO
0	27397	27248	27027	26882	26738	26810	26110	25907	25445	25000
1	26316	26247	26385	26385	25907	26110	25907	25707	25253	25000
2	25253	25189	25381	25445	25063	25575	25253	25063	24876	24570
3	24938	24876	25126	25126	24876	25189	25063	24752	24814	24570
4	24691	24752	24938	24876	24752	24876	24752	24752	24752	24570

## 2.5. Degree of swelling $Q_{norm}$ :

The degree of swelling  $Q_{norm}$  was calculated using the following equation

$$Q_{norm} = 1 - \lambda_{norm} = 1 - \frac{\lambda - \lambda_s}{\lambda_{DP} - \lambda_s}$$

where  $\lambda_s$  is the  $\lambda_{max}$  value of  $g=0$  of the given series in the given solvent,  $\lambda_{DP}$  is the  $\lambda_{max}$  value of *hs-PG4* in toluene,  $\lambda$  is the  $\lambda_{max}$  value of the polymer of given  $g$  and solvent, for which  $Q$  is being calculated. A more detailed explanation can be found in the main article.

An example is given for *ls-PG4* in  $CHCl_3$ .  $\lambda_{max}$  of *ls-PG4* in  $CHCl_3$  is 404 nm (see table S3) and corresponds to  $\lambda$  in the equation. For  $\lambda_{DP}$  the  $\lambda_{max}$  value of *hs-PG4* in toluene is applied, which is 410 nm.  $\lambda_s$  equals to  $g=0$  of the *ls-PGg* series in  $CHCl_3$  and is 374 nm. Therefore  $Q_{norm} = 1 - (404 - 374)/(410 - 374) = 0.17$

Note that for calculations on  $Q_{norm}$  a possible gradient of solvent distribution in the DPs was not considered.

Table S 6: Degrees of swelling  $Q_{norm}$  for the *hs-PGg* series.

$g$	Benzene	Dioxane	Toluene	$CHCl_3$	EA	1,2-DCA	Acetone	MeOH
0	1	1	1	1	1	1	1	1
1	0.84	0.75	0.90	0.74	0.82	0.78	0.93	0.92
2	0.59	0.63	0.82	0.62	0.71	0.75	0.85	0.83
3	0.28	0.58	0.43	0.53	0.61	0.59	0.78	0.75
4	0.28	0.53	0	0.47	0.53	0.53	0.74	0.67

Table S 7: Degrees of swelling  $Q_{norm}$  for the *ls-PGg* series.

$g$	Benzene	Dioxane	Toluene	$CHCl_3$	EA	1,2-DCA	Acetone	MeOH
0	1	1	1	1	1	1	1	1
1	0.67	0.78	0.67	0.67	0.82	0.73	0.89	0.88
2	0.3	0.4	0.31	0.31	0.45	0.51	0.52	0.46
3	0.19	0.3	0.2	0.22	0.32	0.35	0.41	0.25
4	0.14	0.23	0.11	0.17	0.21	0.22	0.22	0.25

## 2.6. UV-Vis spectra:

For some spectra scattering subtraction was done. Scattering was subtracted from UV-Vis spectra by nonlinear regression with the equation  $A' = a * \lambda^{-b} + c$ , where  $A'$  is the apparent absorbance caused by scattering,  $a$  and  $b$  are constants and  $c$  is the offset from the baseline. The regression was applied to the wavelength range 530-800 nm. In this range the polymer itself does not absorb, thus absorbance in this range stems solely from scattering. The function was extrapolated to the rest of the spectrum and by subtraction from the measured data, the real absorption spectrum was obtained.<sup>[12]</sup>

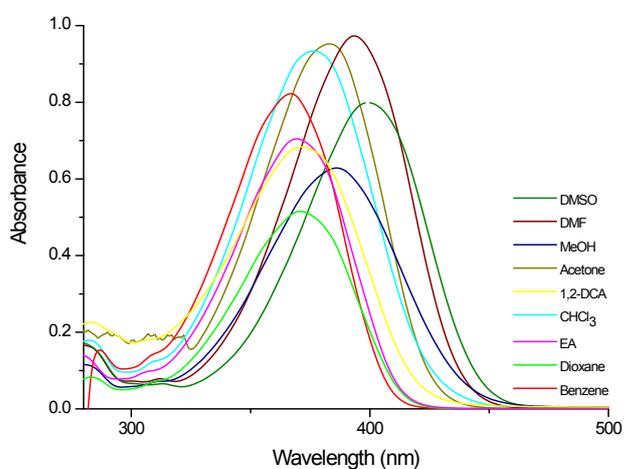


Figure S 1: UV-Vis spectra of **2b** in all solvents except toluene at 25 °C. Results derived from these spectra are signified as  $g=0$  of the *hs-PGg* series in graphs of the main article.

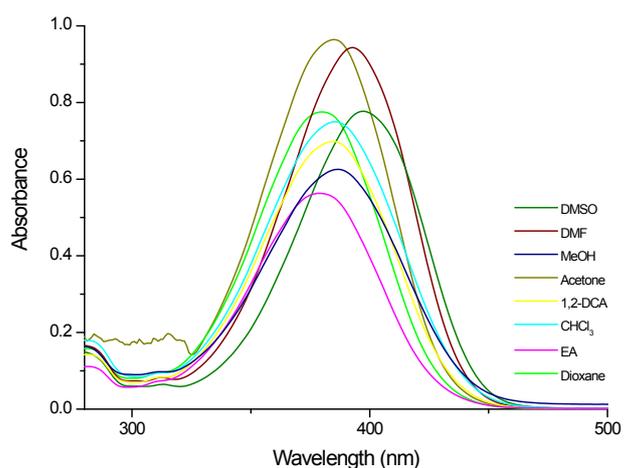


Figure S 2: UV-Vis spectra of *hs-PG1* in all solvents except toluene at 25 °C.

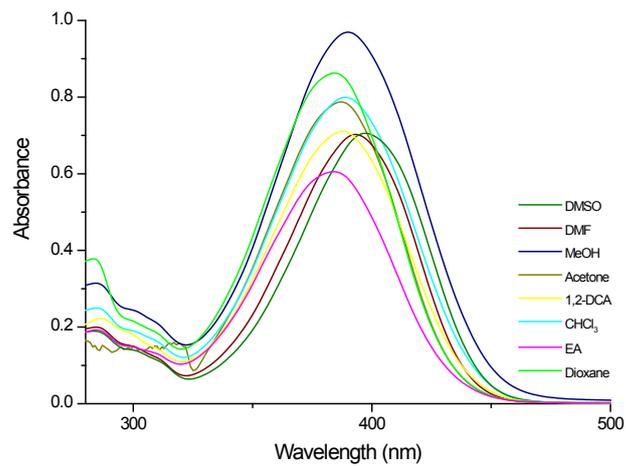


Figure S 3: UV-Vis spectra of *hs-PG2* in all solvents except toluene at 25 °C.

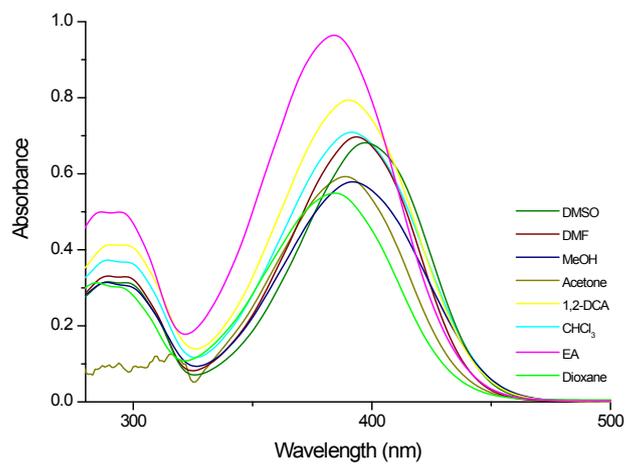


Figure S 4: UV-Vis spectra of *hs-PG3* in all solvents except toluene at 25 °C.

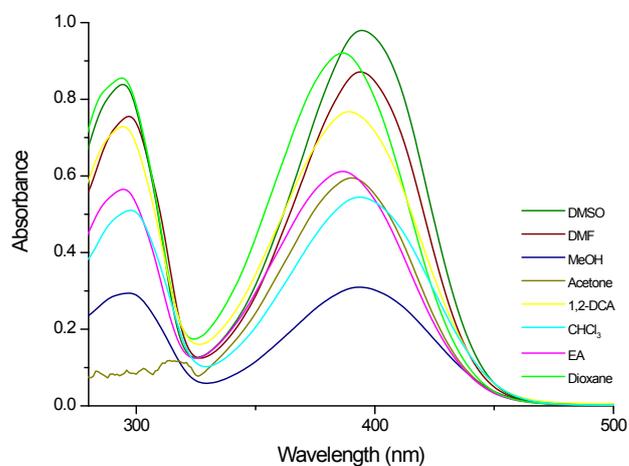


Figure S 5: UV-Vis spectra of *hs-PG4* in all solvents except toluene at 25 °C.

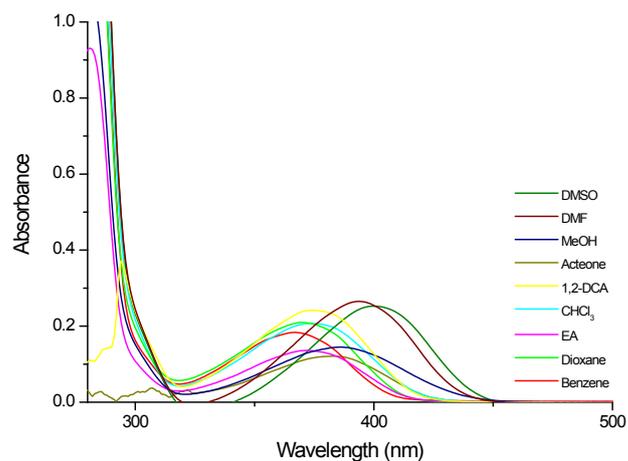


Figure S 6: UV-Vis spectra of **1c:2b** (ratio 98:2) in all solvents except toluene at 25 °C. Results derived from these spectra are signified as  $g=0$  of the *ls-PGg* series in graphs of the main article.

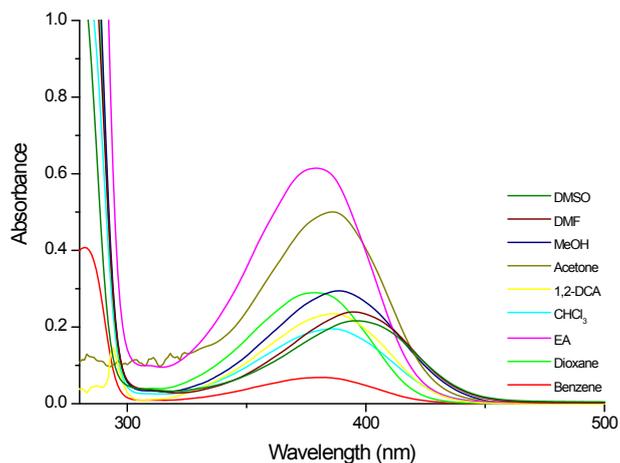


Figure S 7: UV-Vis spectra of *ls-PG1* in all solvents except toluene at 25 °C.

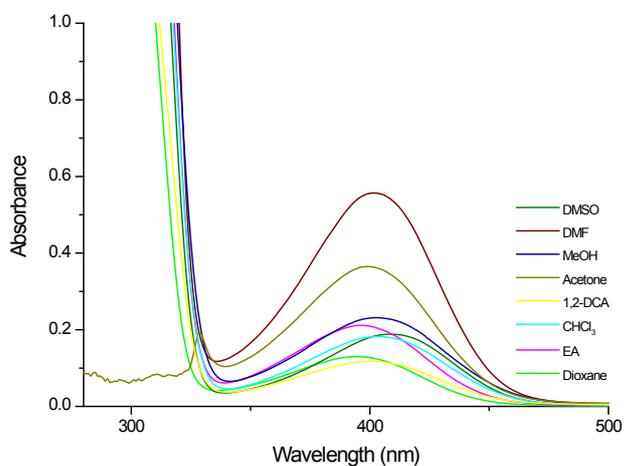


Figure S 8: UV-Vis spectra of *ls-PG2* in all solvents except toluene at 25 °C.

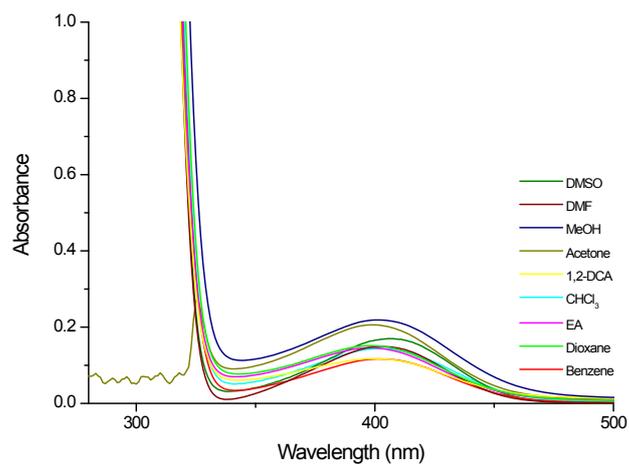


Figure S 9: UV-Vis spectra of *l*-**PG3** in all solvents except toluene at 25 °C. Scattering subtraction was done for *l*-**PG3** in methanol. The derived spectrum, from which also  $\lambda_{\text{max}}$  was extracted, is not shown.

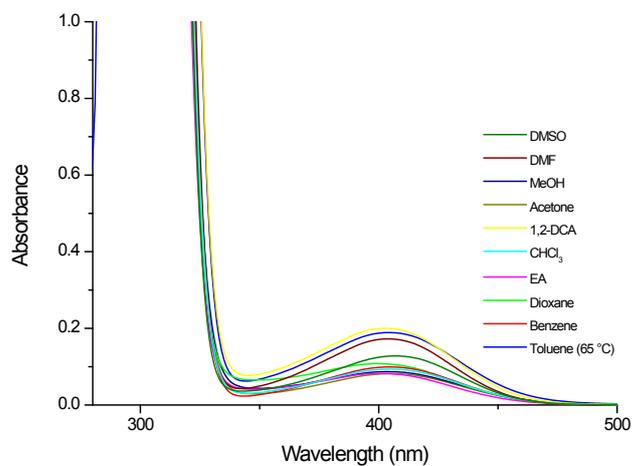
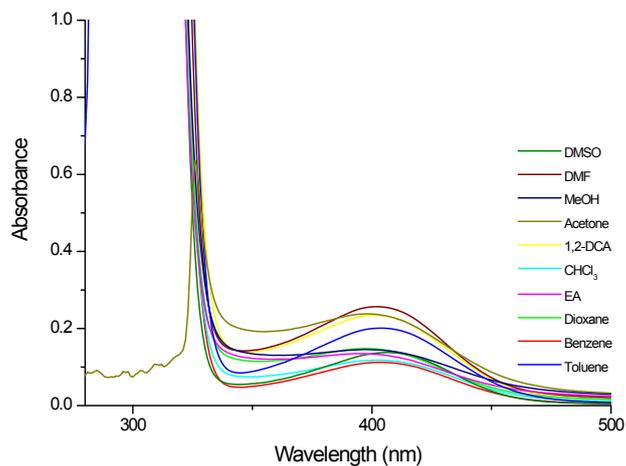


Figure S 10: UV-Vis spectra of *l*-**PG4** in all solvents at 25 °C, except toluene at 65 °C. Spectra as recorded (top) and after scattering subtraction (bottom).

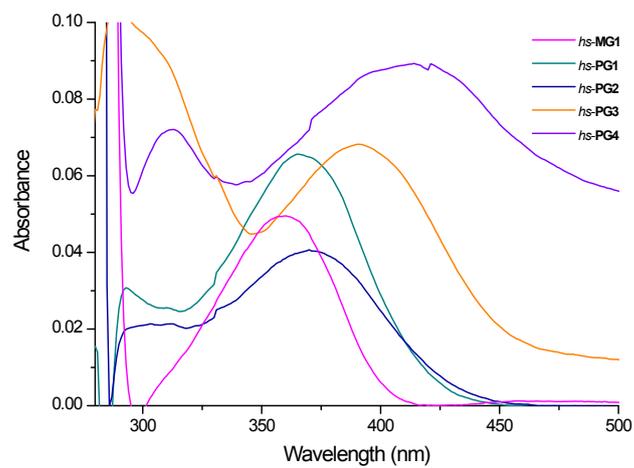


Figure S 11: UV-Vis spectra of the *hs-PGg* series in toluene at 65 °C.

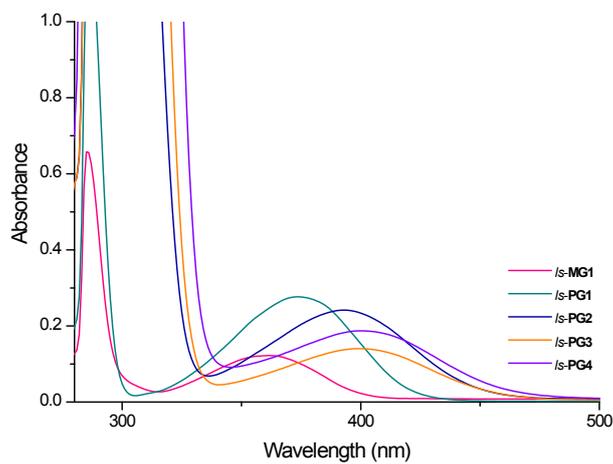


Figure S 12: UV-Vis spectra of the *ls-PGg* series in toluene at 65 °C.

## 2.7. NMR spectra:

Residual solvents are marked with asterisk (\*).

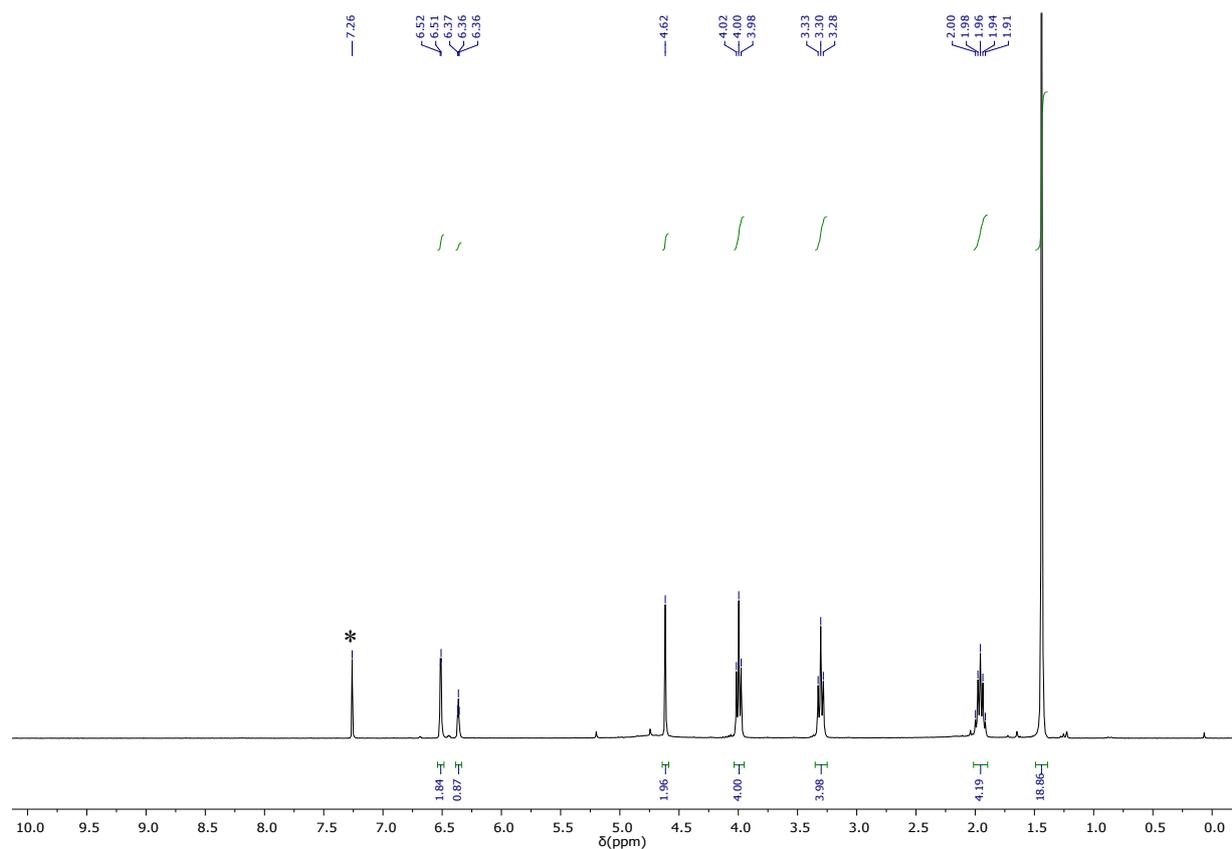


Figure S 13:  $^1\text{H-NMR}$  of **1b** in  $\text{CDCl}_3$  at 298 K.

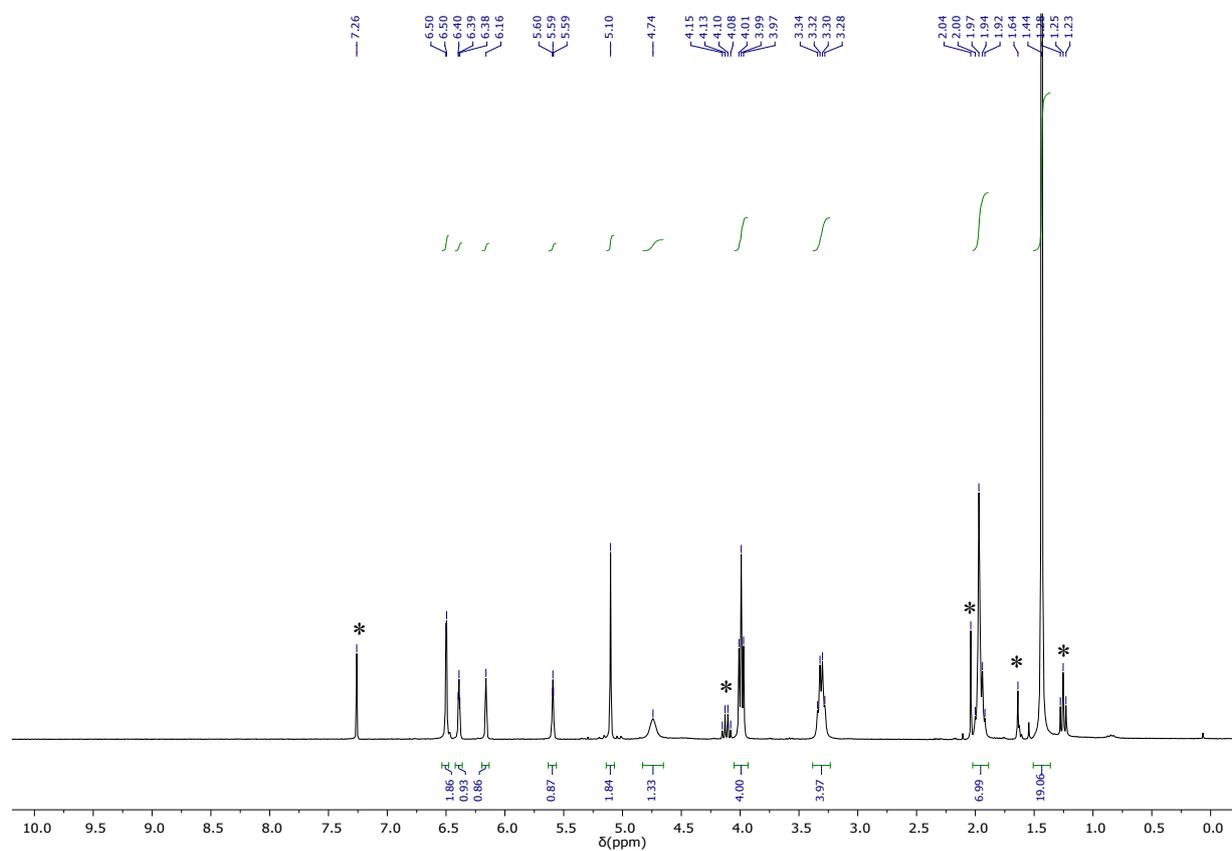


Figure S 14:  $^1\text{H-NMR}$  of **1c** in  $\text{CDCl}_3$  at 298 K.

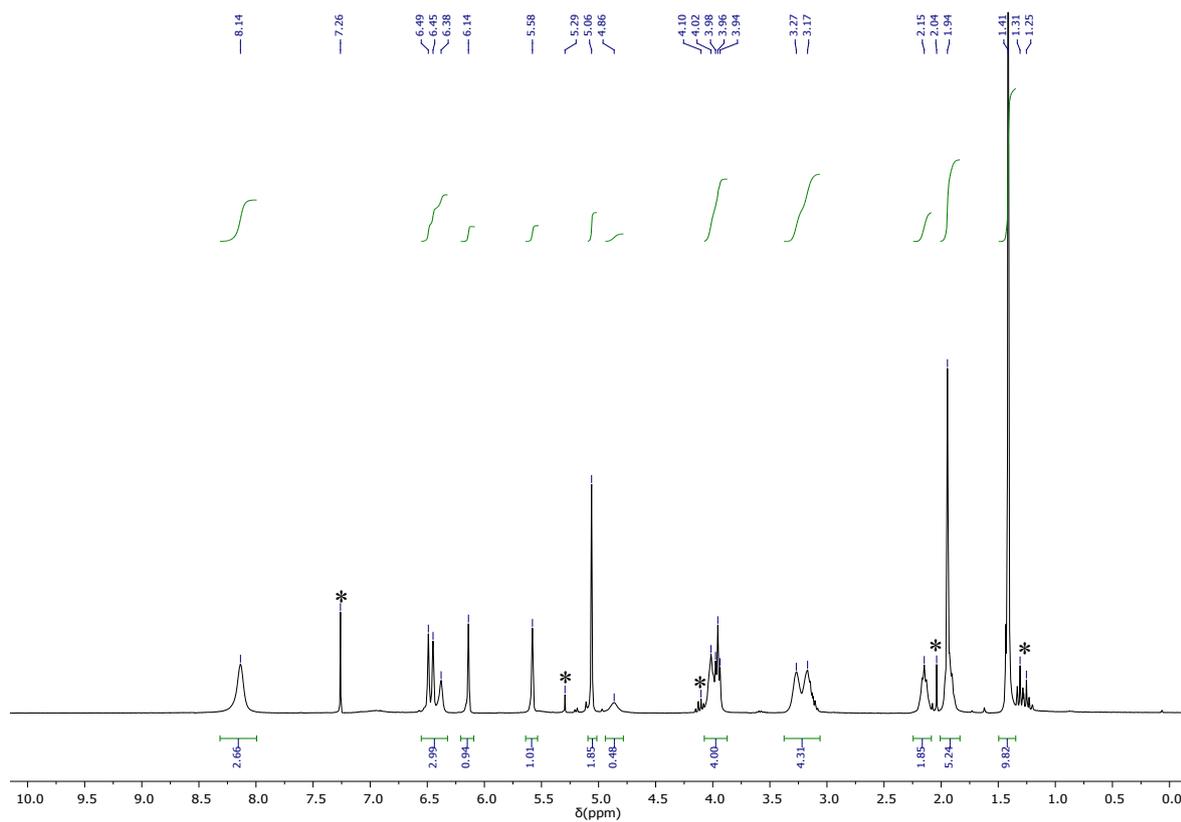


Figure S 15:  $^1\text{H-NMR}$  of **2a** in  $\text{CDCl}_3$  at 298 K.

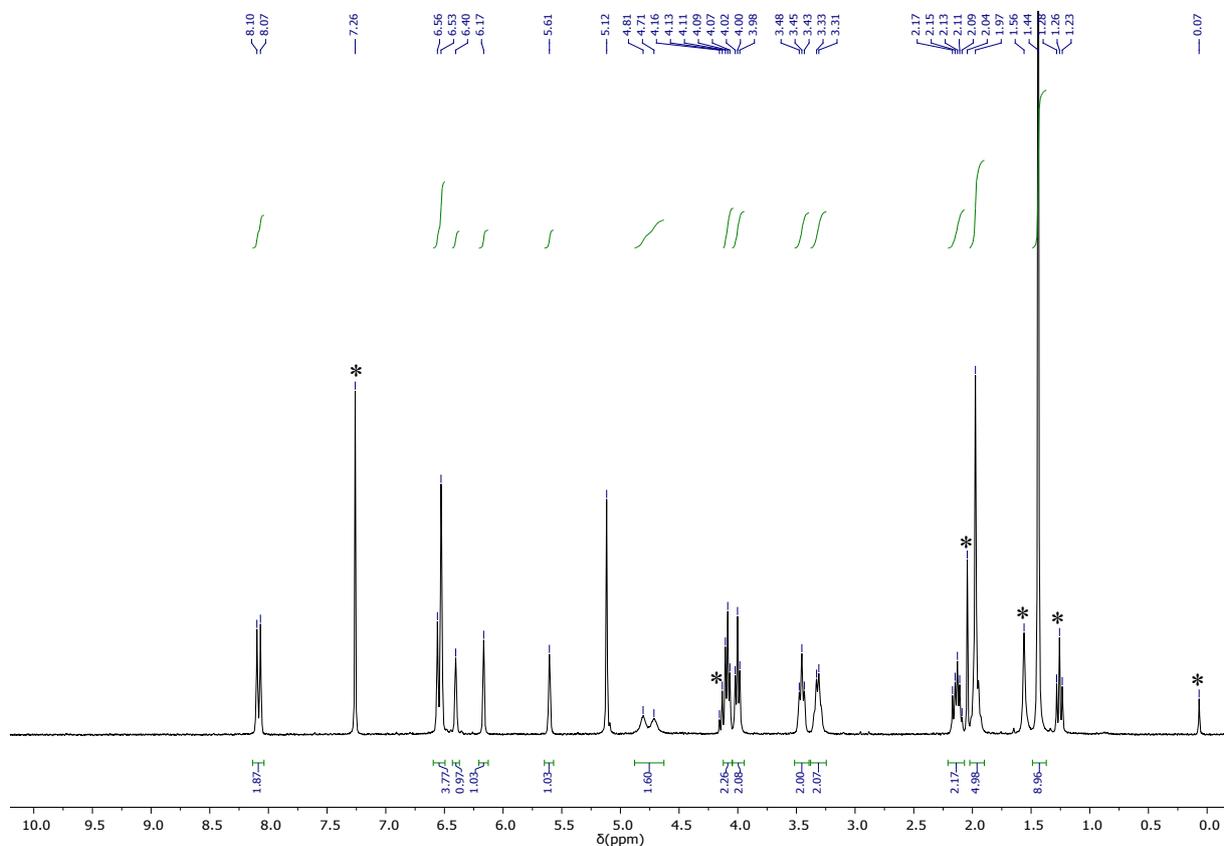


Figure S 16:  $^1\text{H-NMR}$  of **2b** in  $\text{CDCl}_3$  at 298 K.

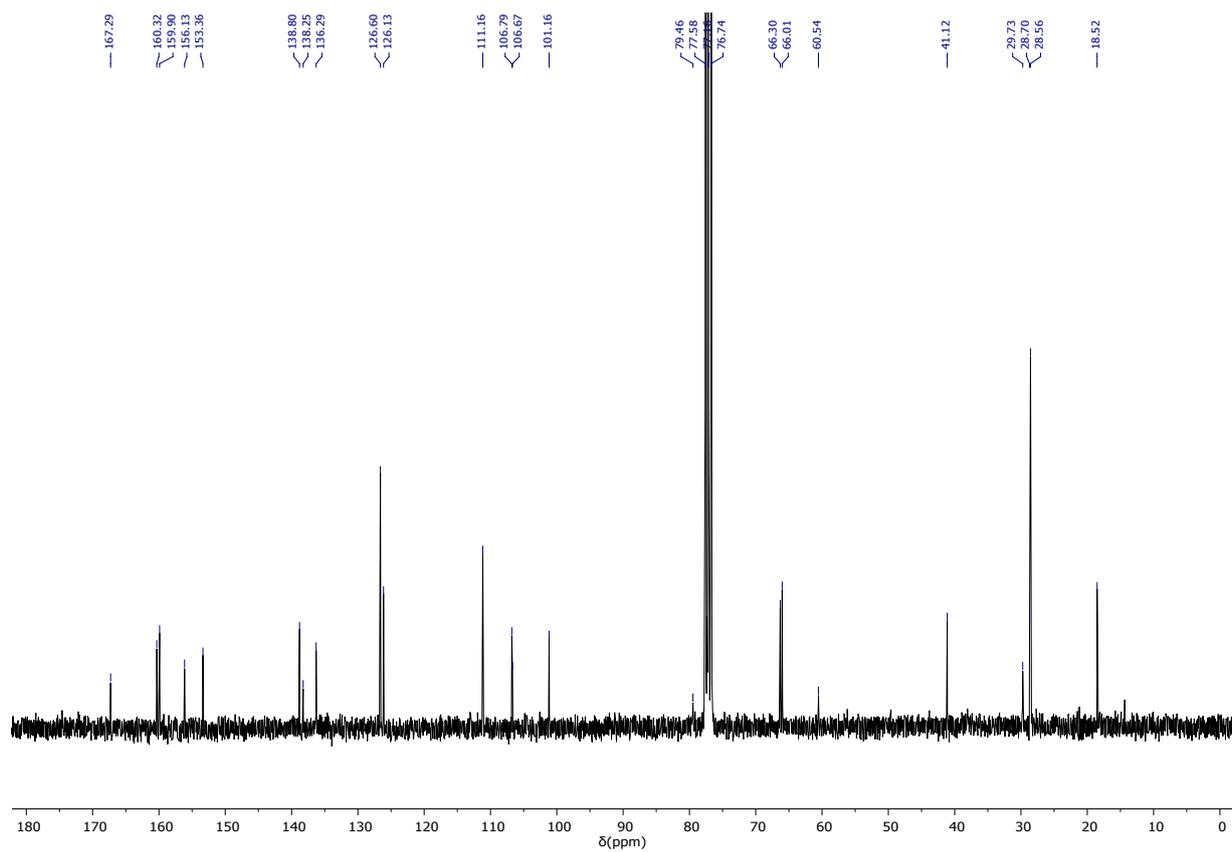


Figure S 17:  $^{13}\text{C}$ -NMR of **2b** in  $\text{CDCl}_3$  at 298 K.

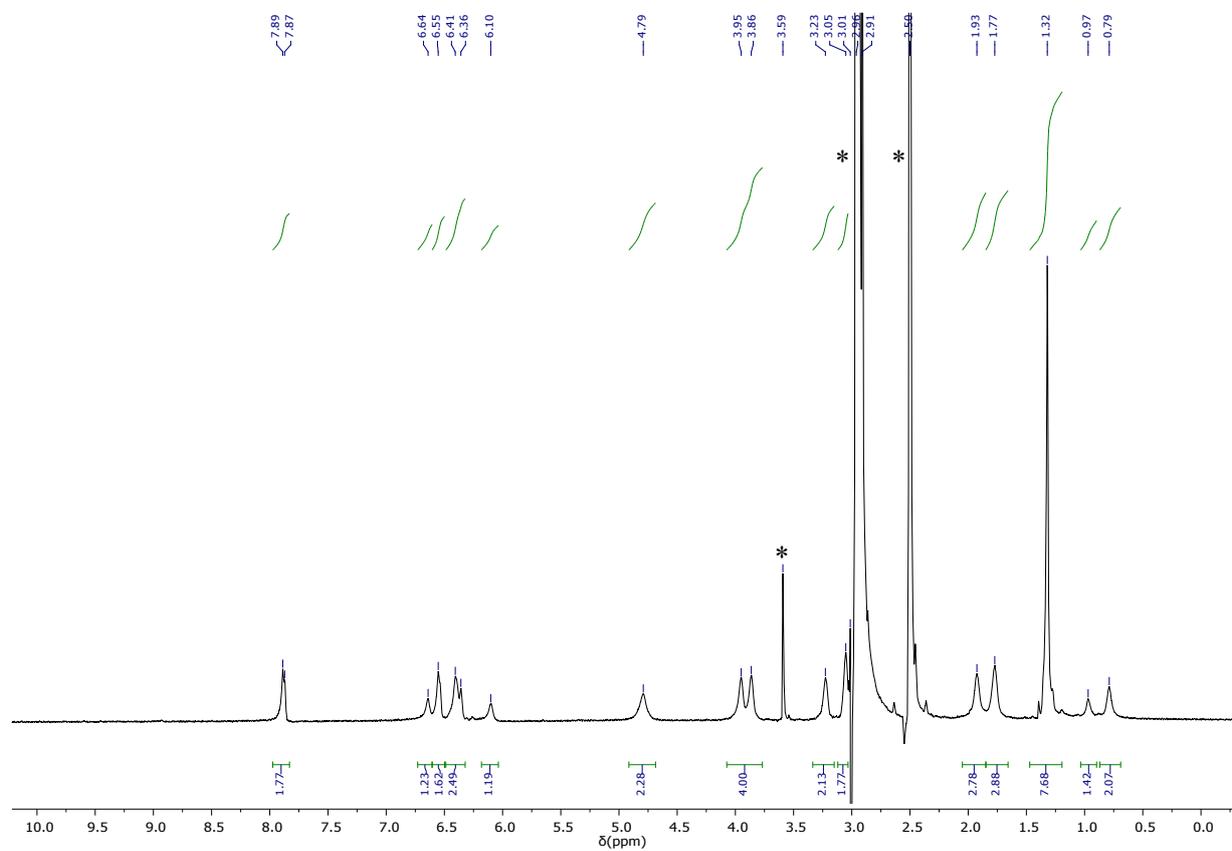


Figure S 18:  $^1\text{H}$ -NMR of *hs*-PG1 in  $\text{DMSO-}d_6$  at 373 K.

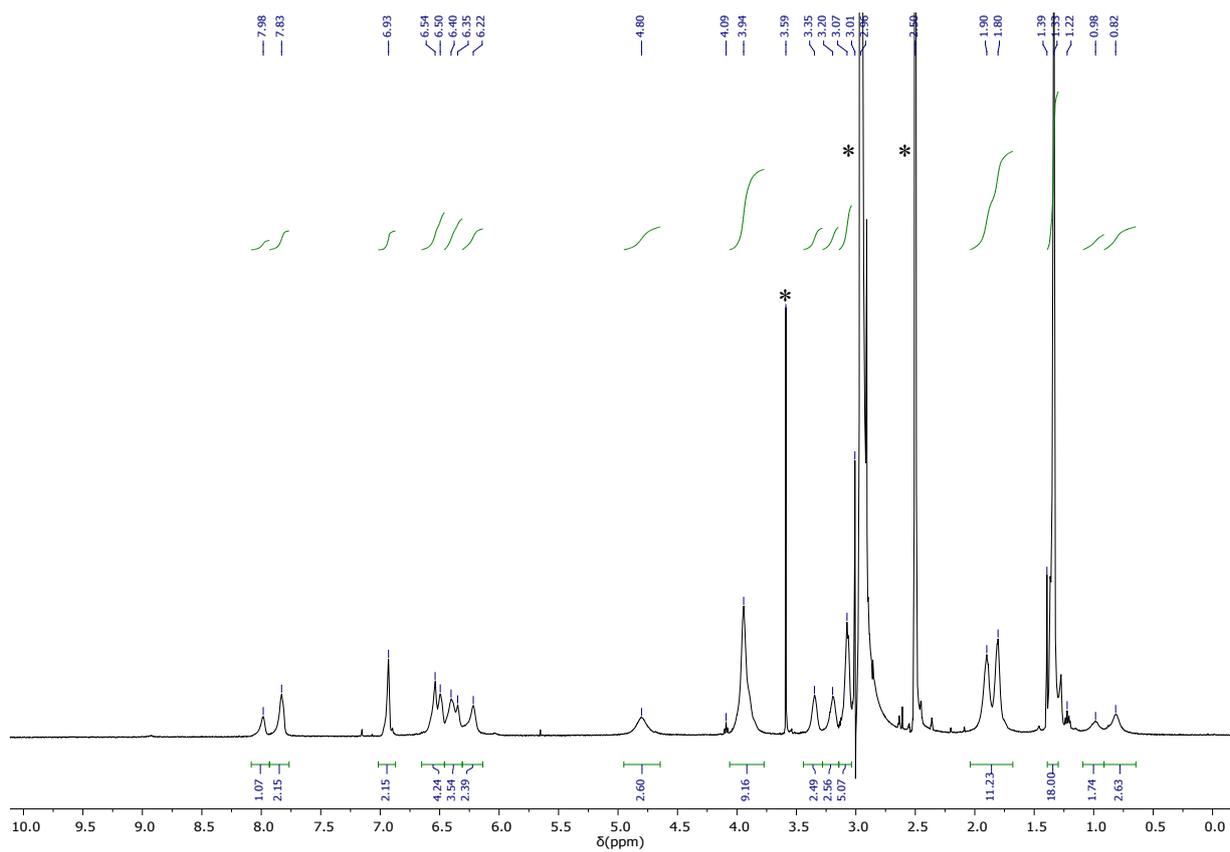


Figure S 19:  $^1\text{H-NMR}$  of *hs-PG2* in  $\text{DMSO-}d_6$  at 373 K.

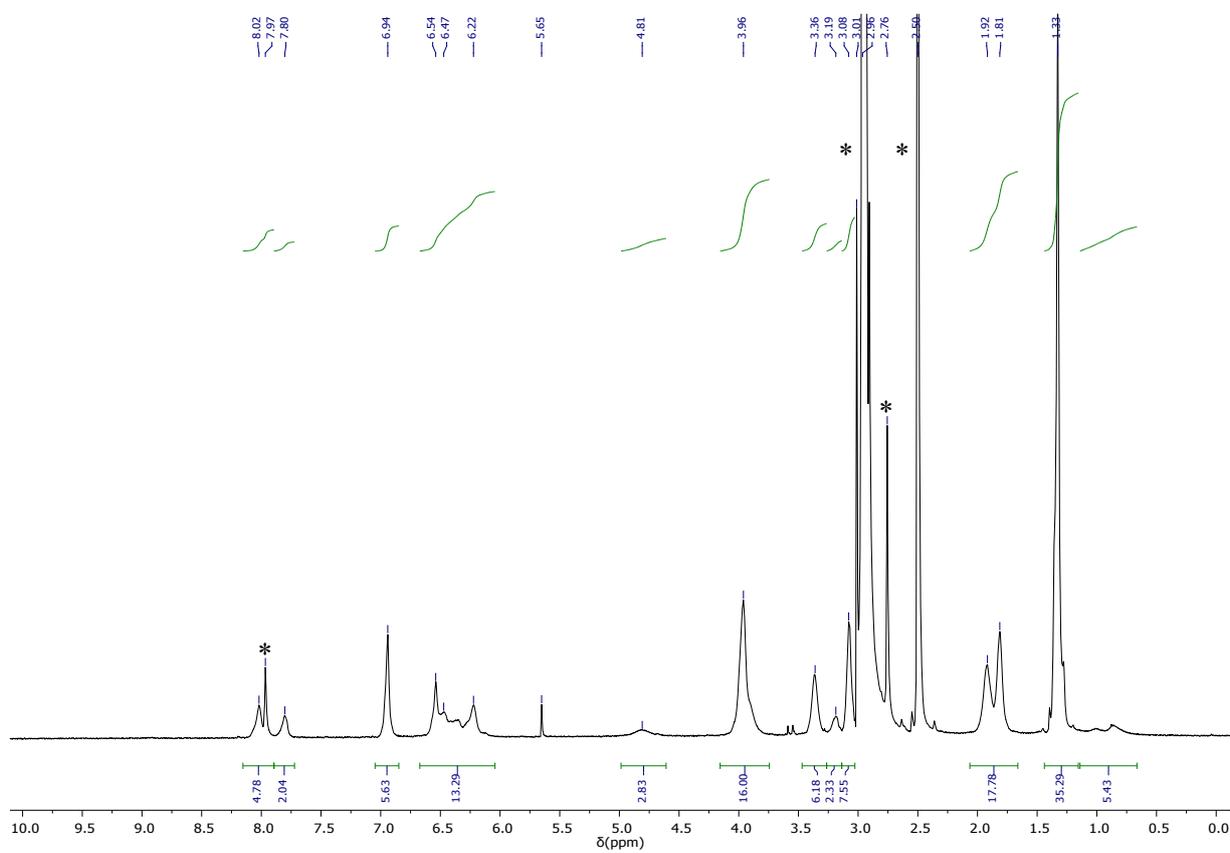


Figure S 20:  $^1\text{H-NMR}$  of *hs-PG3* in  $\text{DMSO-}d_6$  at 373 K.

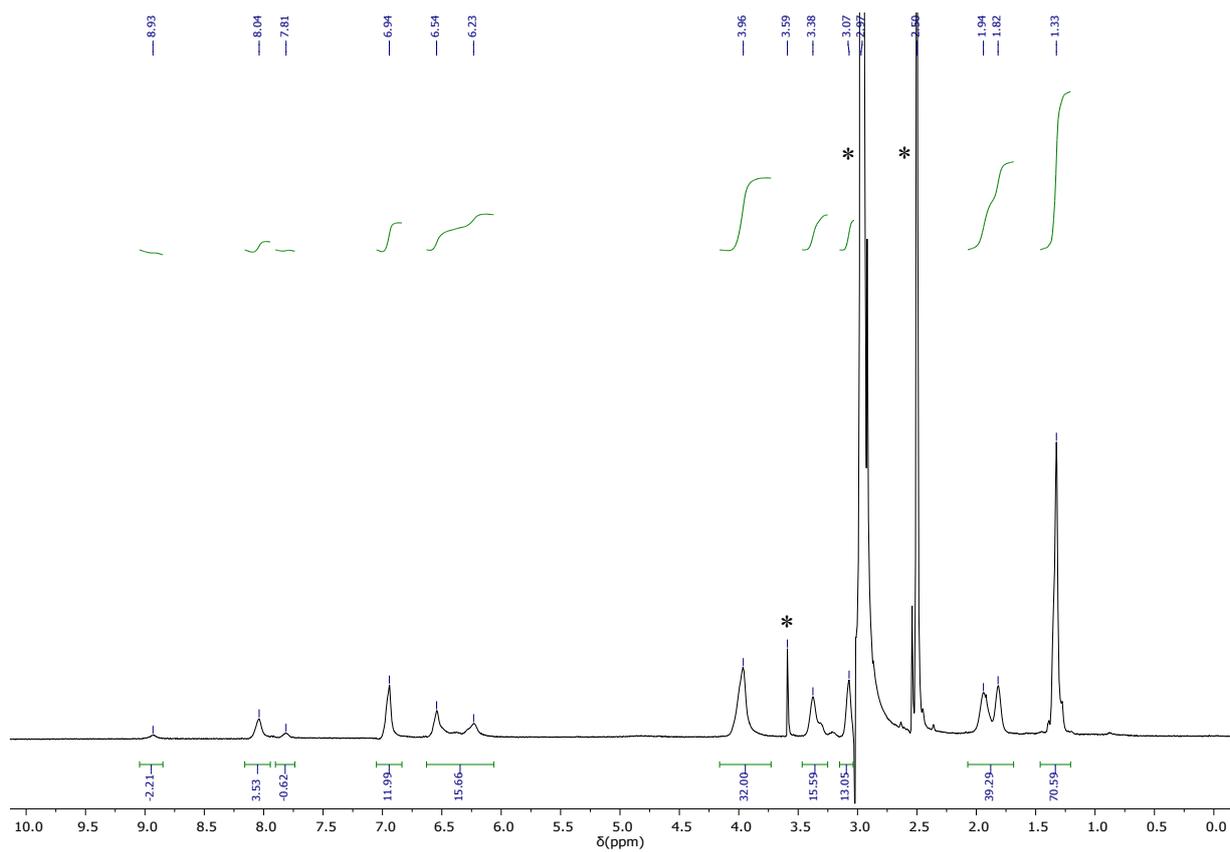


Figure S 21:  $^1\text{H-NMR}$  of *hs-PG4* in  $\text{DMSO-}d_6$  at 373 K.

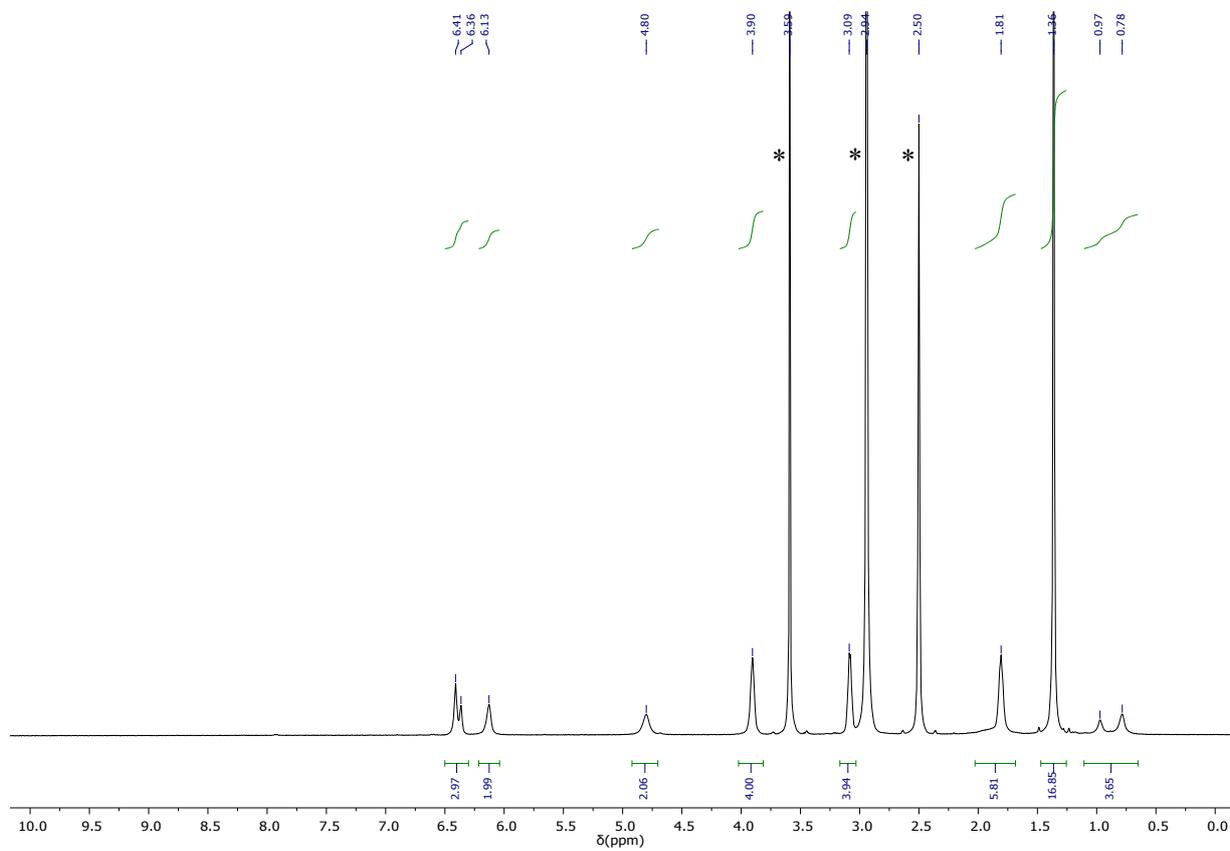


Figure S 22:  $^1\text{H-NMR}$  of *ls-PG1* in  $\text{DMSO-}d_6$  at 373 K.

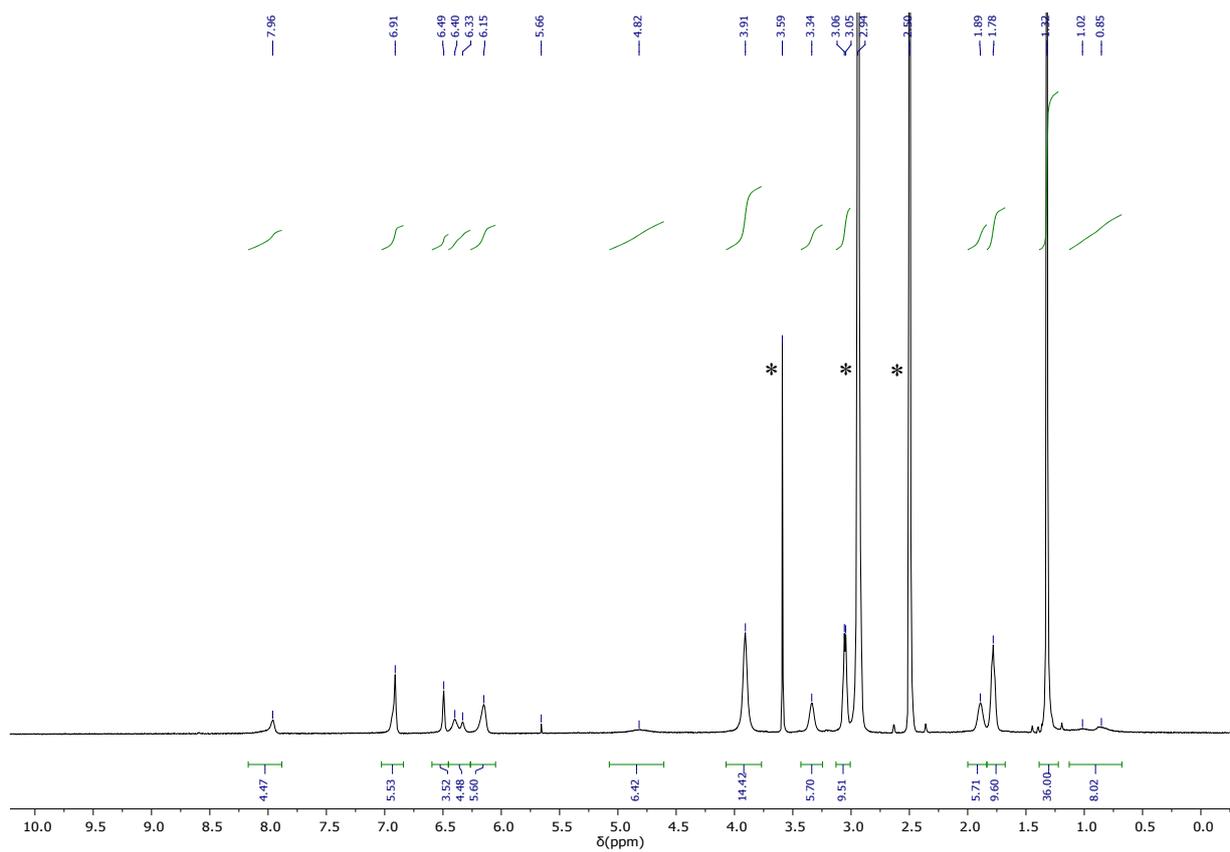


Figure S 23:  $^1\text{H-NMR}$  of *ls-PG2* in  $\text{DMSO-}d_6$  at 373 K.

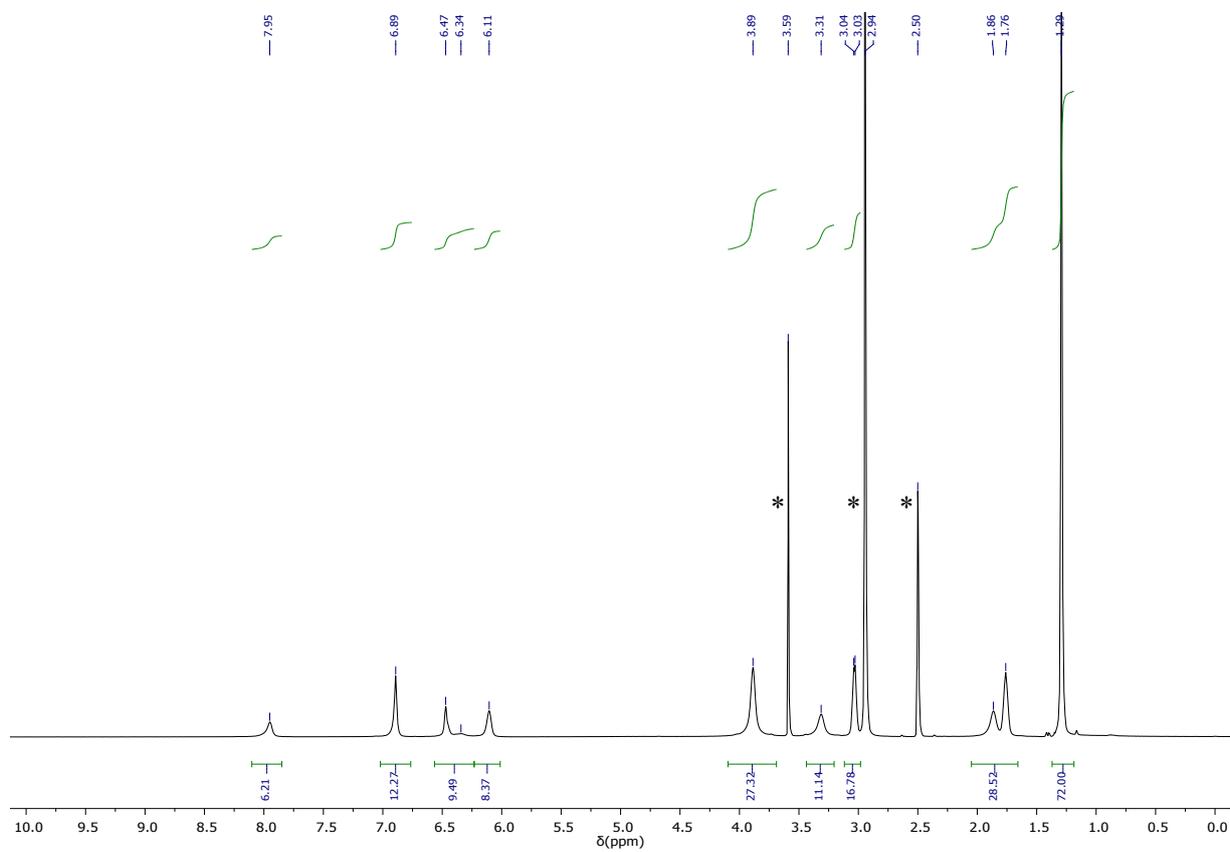


Figure S 24:  $^1\text{H-NMR}$  of *ls-PG3* in  $\text{DMSO-}d_6$  at 373 K.

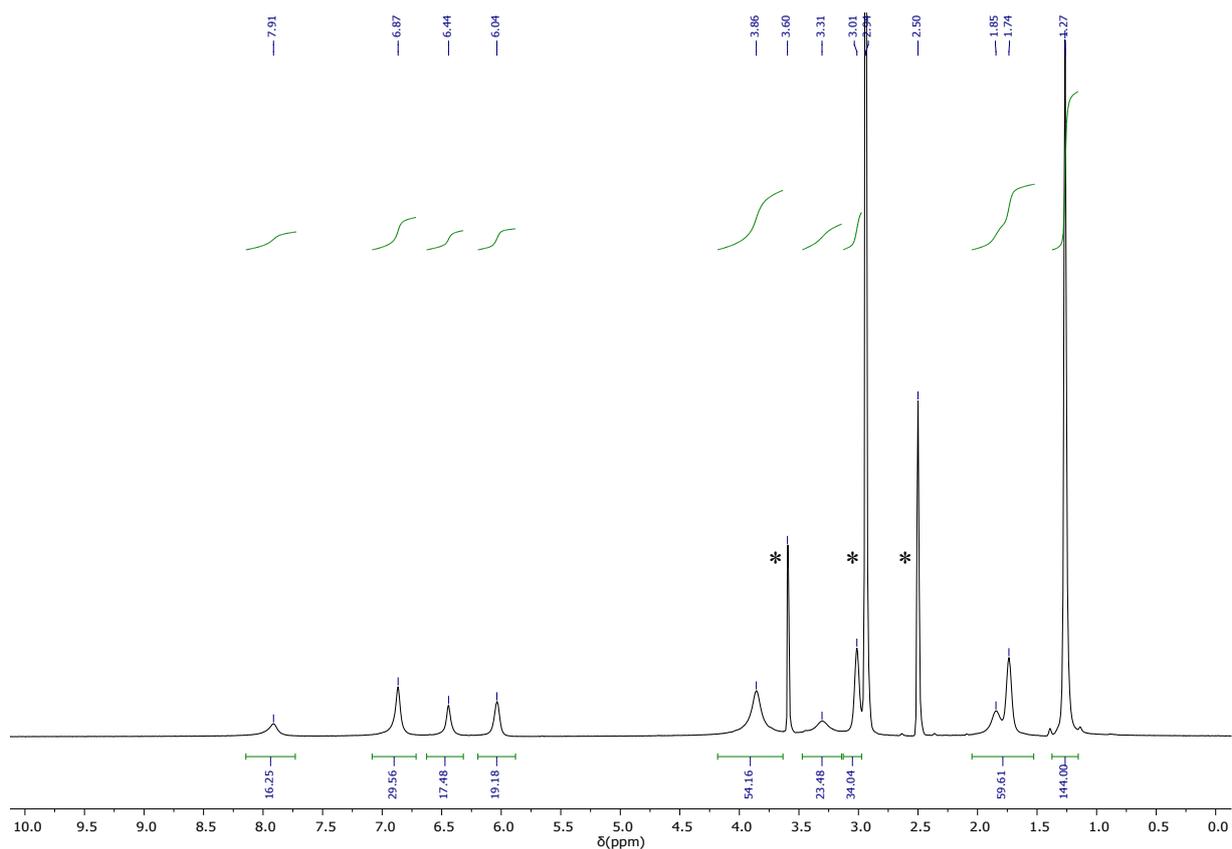


Figure S 25:  $^1\text{H-NMR}$  of *ls*-PG4 in  $\text{DMSO-}d_6$  at 373 K.

2.8. GPC spectra:

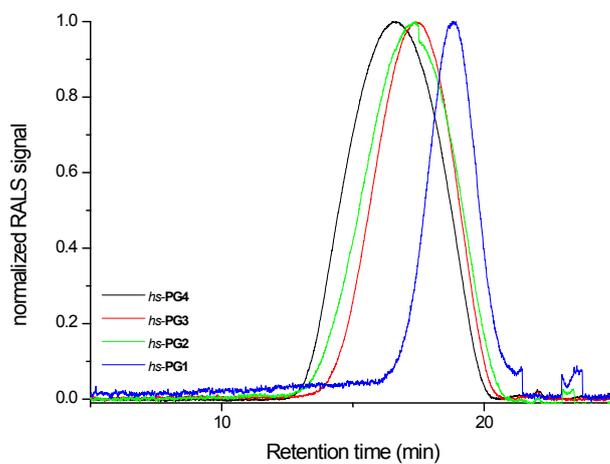


Figure S 26: GPC elution curves of *hs*-PG1-4. Detection by RALS.

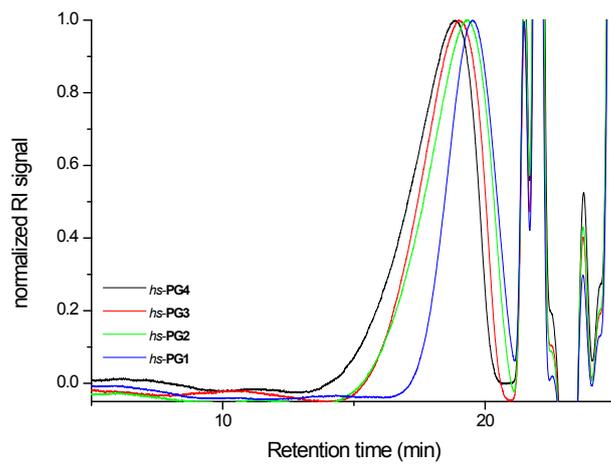


Figure S 27: GPC elution curves of *hs-PG1-4*. Detection by RI.

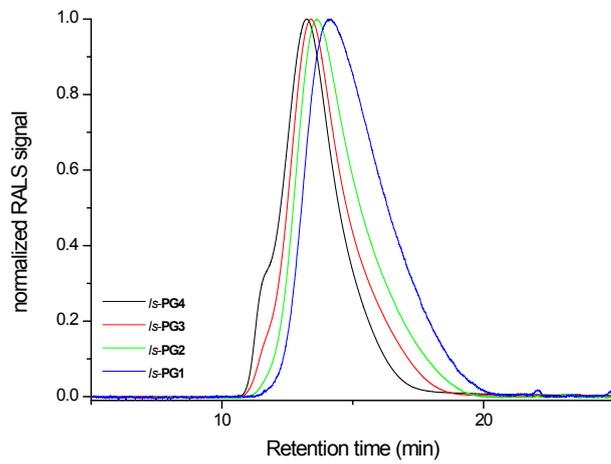


Figure S 28: GPC elution curves of *ls-PG1-4*. Detection by RALS.

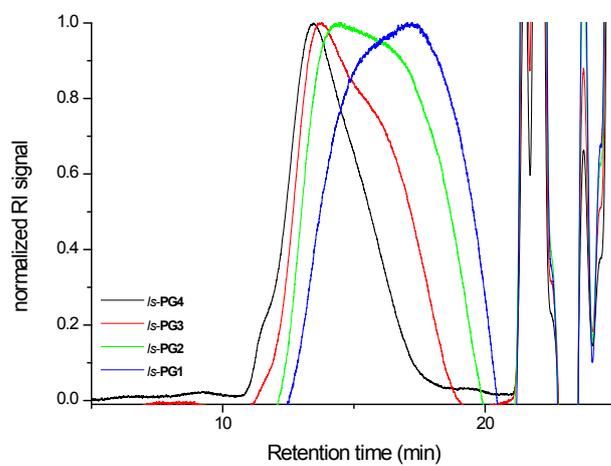


Figure S 29: GPC elution curves of *ls-PG1-4*. Detection by RI.

## 2.9. TGA spectra

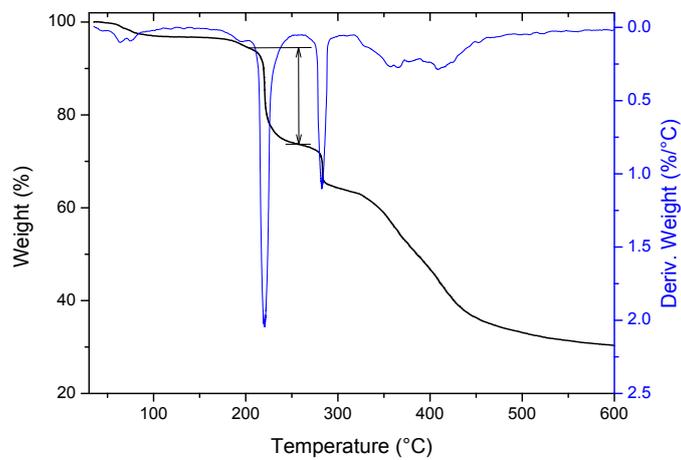


Figure S 30: Thermogram of *hs-PG2*.

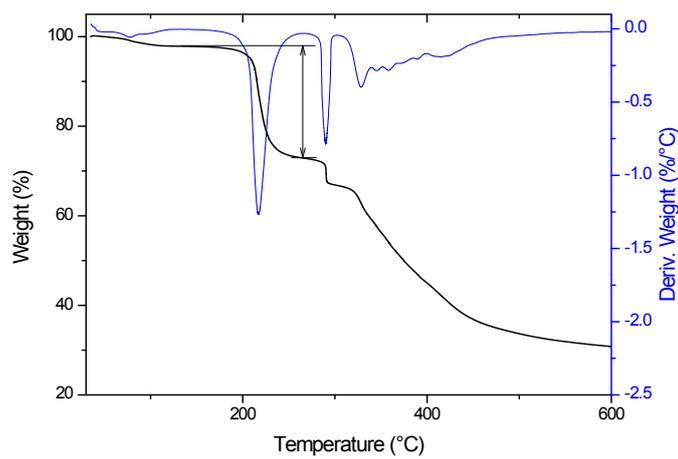


Figure S 31: Thermogram of *hs-PG3*.

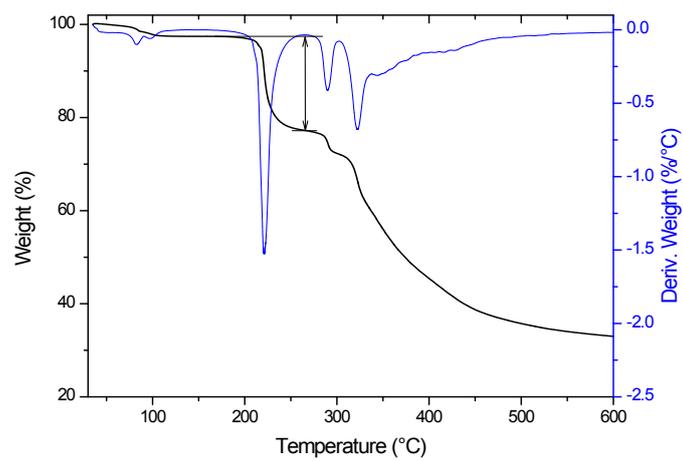


Figure S 32: Thermogram of *hs-PG4*.

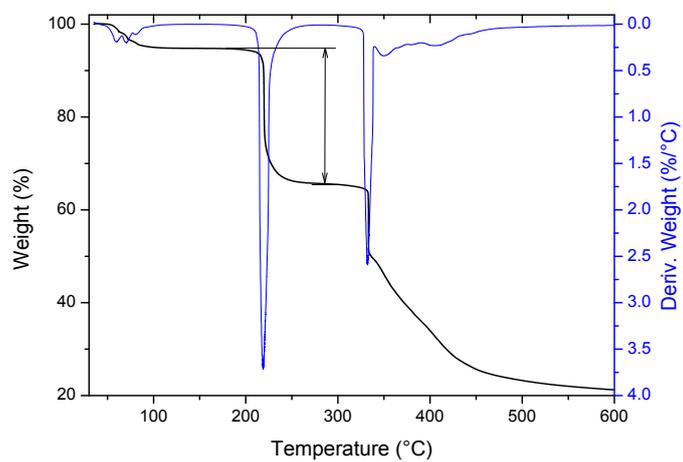


Figure S 33: Thermogram of *ls-PG2*.

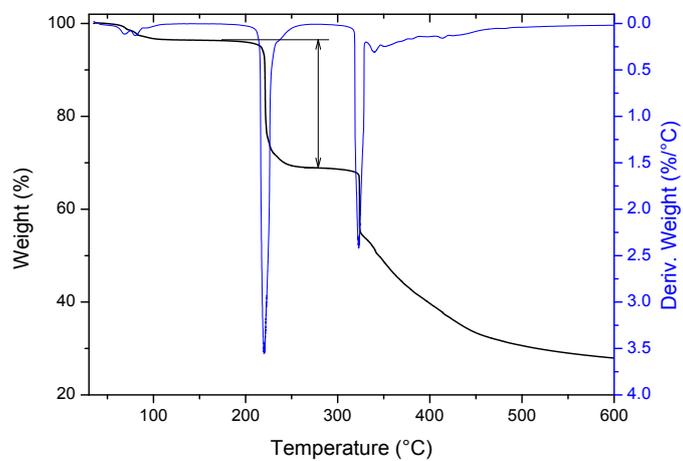


Figure S 34: Thermogram of *ls-PG3*.

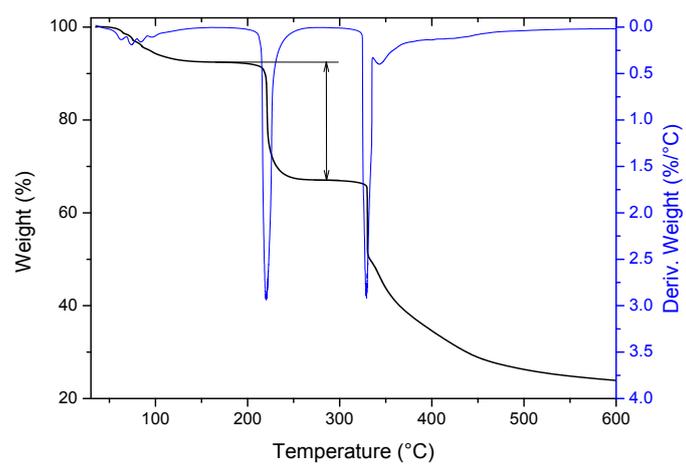


Figure S 35: Thermogram of *ls*-PG4.

2.10. Fluorescence spectra:

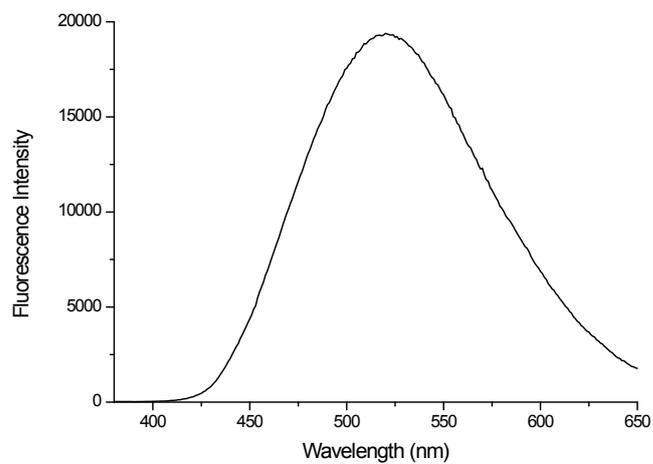


Figure S 36: Fluorescence spectrum of *hs-PG4*.

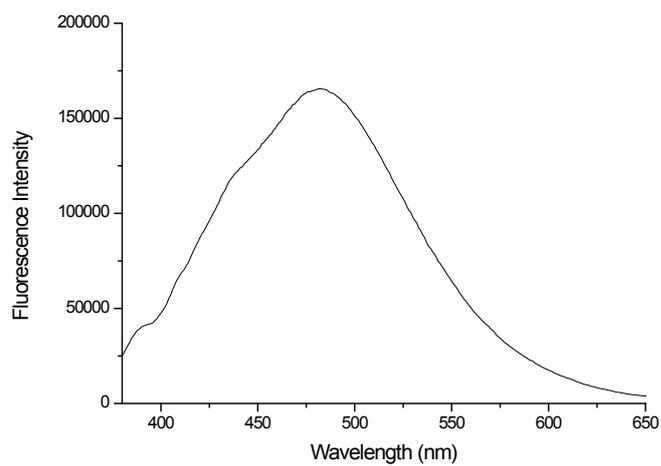


Figure S 37: Fluorescence spectrum of *ls-PG4*.

2.11. AFM image:

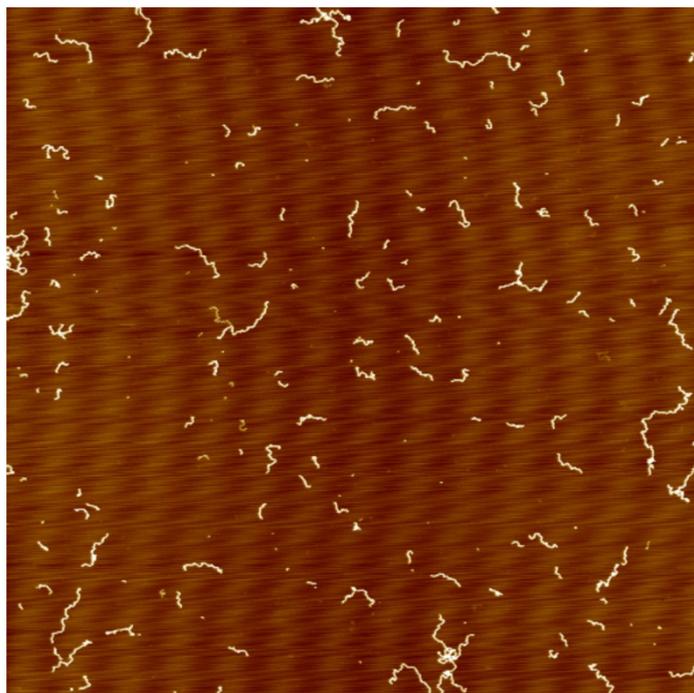


Figure S 38: AFM image of *ls*-**PG4** (5  $\mu\text{m}$  x 5  $\mu\text{m}$ ) showing that the degree of main chain branching is negligible if there is any.

### 3. Synthesis and characterization of *ls*-PG5:

TFA (5 mL) was slowly added to *ls*-PG4 (0.5 g, 0.093 mmol) while being kept at -5 °C. After 24 h the reaction was quenched by addition of MeOH. Addition and removal of MeOH was repeated three times. The product was freeze dried from H<sub>2</sub>O (~100% yield). Then, the product was dissolved in DMF (10 mL). Et<sub>3</sub>N (0.465 mL, 3.20 mmol) and DMAP (0.08 g, cat.) were added. The solution was cooled to -10°C and **1d** (2.26 g, 4.00 mmol) was added slowly. Then, the ice bath was removed and the reaction solution was stirred for ten days. Then again **1d** (1.13 g, 2.00 mmol) was added at -10 °C. After ten more days **1d** (1.13 g, 2.00 mmol) was added at -10 °C. After ten further days the solvent was removed and the product was precipitated into cold Et<sub>2</sub>O. The product was purified by a short column (eluent: DCM), then freeze dried from dioxane and obtained as a yellow powder (0.47 g, 48% yield).

<sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>, 373 K): δ= 1.27 (s, 288 H, *t*Bu), 1.75, 1.87 (2 x br, 124 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 3.02, 3.33 (2 x br, 124 H, CH<sub>2</sub>NH), 3.87 (br, 124 H, OCH<sub>2</sub>), 6.03 (br, 34 H, NH), 6.45, 6.88 (2 x br, 93 H, Ph), 7.95 (br, 30 H, NH).

TGA: 26% (28% theor.)

Fluorescence Quantification: 99.77%

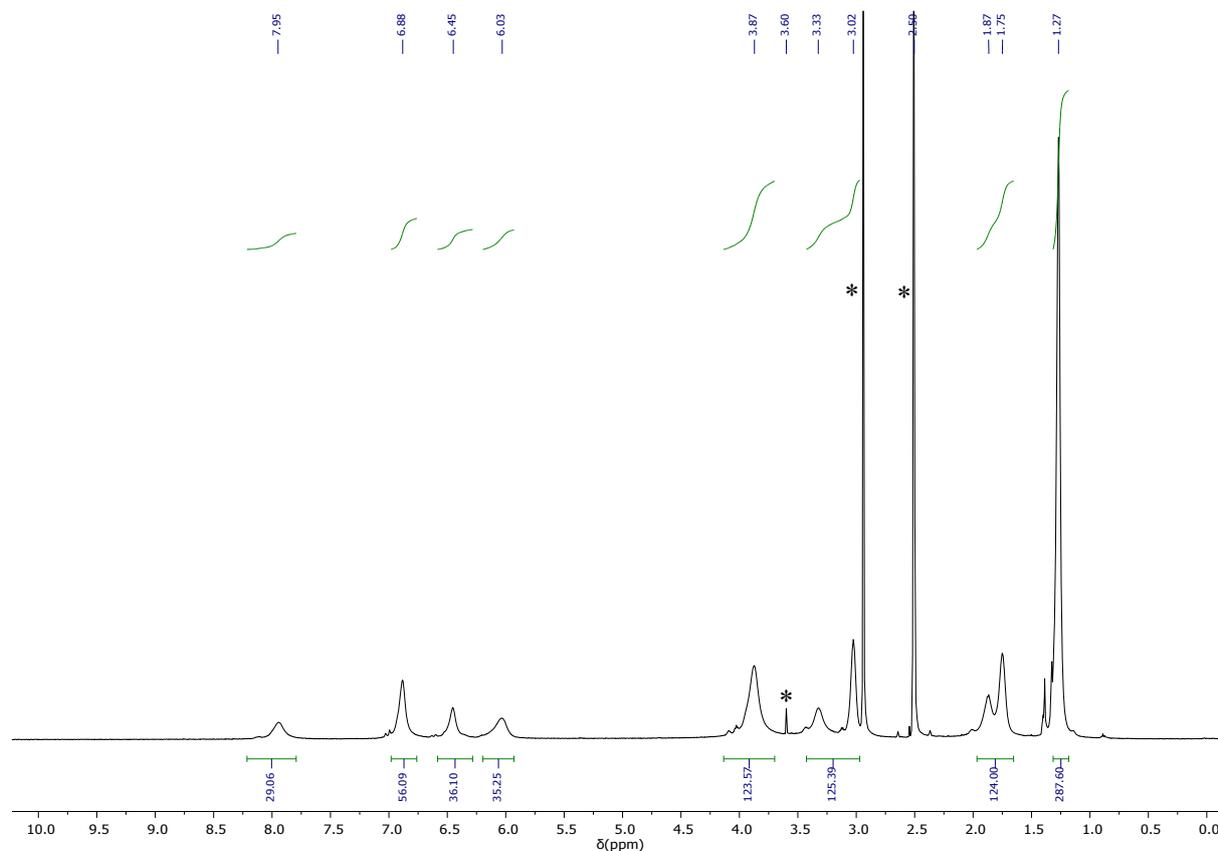


Figure S 39: <sup>1</sup>H-NMR of *ls*-PG5 in DMSO-*d*<sub>6</sub> at 373 K.

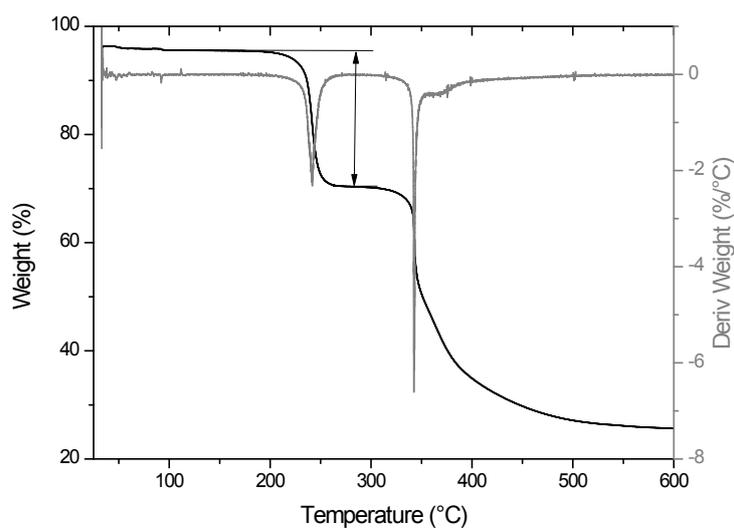


Figure S 40: Thermogram of *ls*-PG5.

UV-Vis spectra of *ls*-PG5 showed strong scattering effects in most solvents, also at elevated temperatures. A mathematical fit in order to subtract scattering could not be found. Therefore, meaningful  $\lambda_{\text{max}}$  value could not be extracted from the spectra.

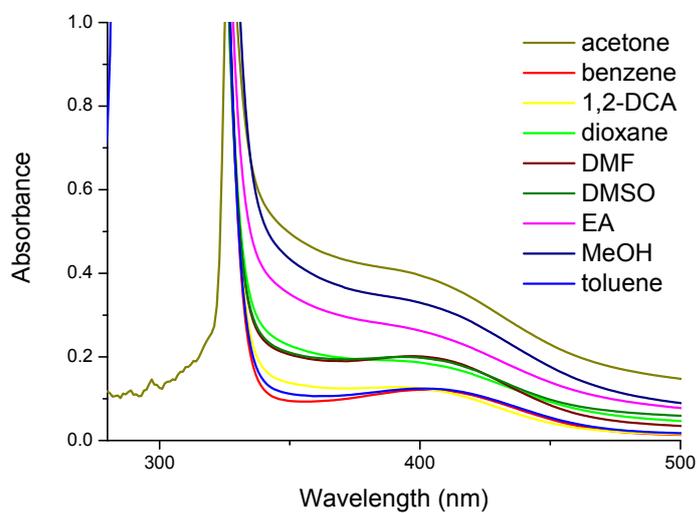


Figure S 41: UV-Vis spectra of *ls*-PG5 in all solvents at 25 °C.

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