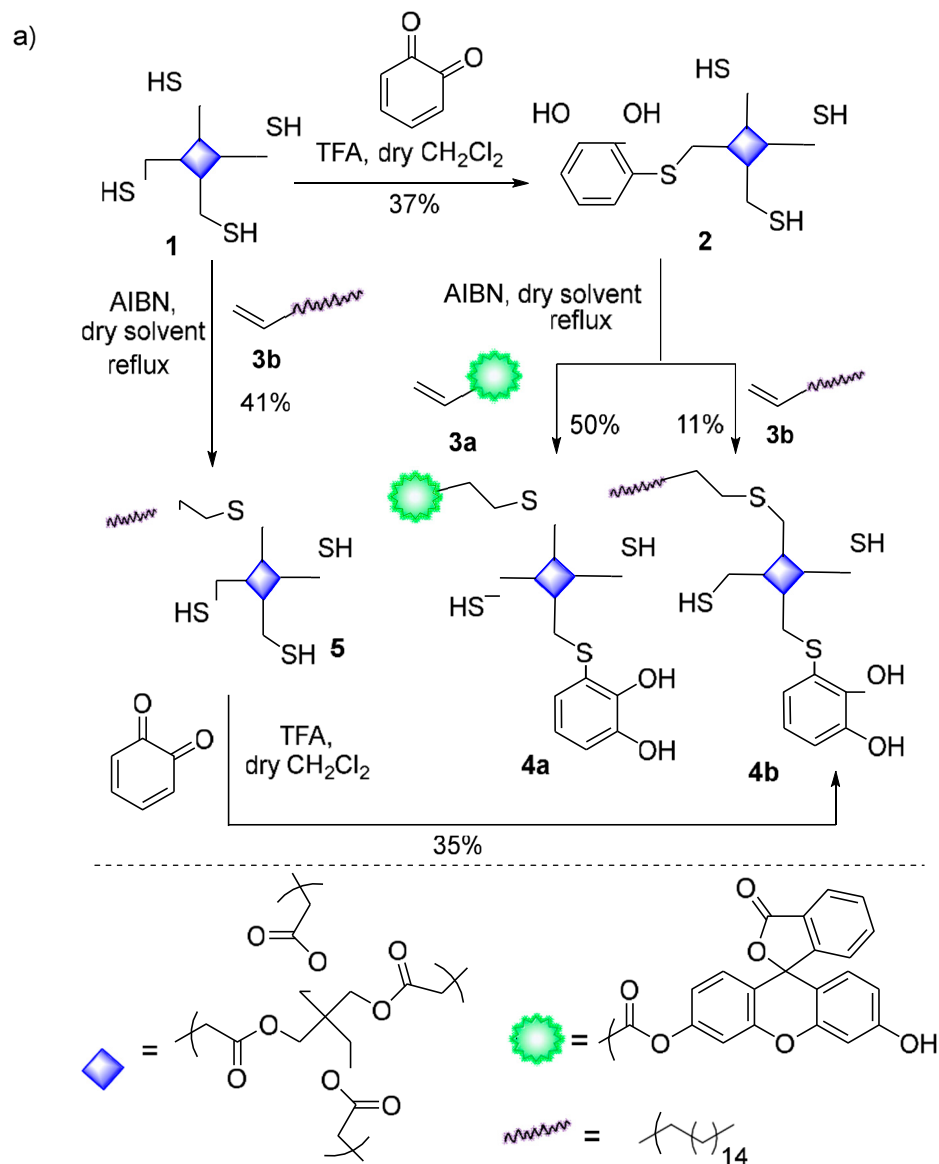


## Table of contents

S1. Synthesis of monomers <b>4a</b> and <b>4b</b> (Experimental part)	S3
S2. Synthesis of compounds <b>6a</b> and <b>6b</b> (Experimental part)	S6
S3. Polymerization of <b>4b</b> and <b>6b</b>	S9
S4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of new compounds	S10
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>2</b>	S10
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>4a</b>	S11
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>4b</b>	S12
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>5</b>	S13
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>6a</b>	S14
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>6b</b>	S15
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound <b>7</b>	S16
S5. IR spectra of polymeric materials	S17
IR spectrum of polymer <b>P4a</b>	S17
IR spectrum of polymer <b>P6a</b>	S17
IR spectrum of polymer <b>P4b</b>	S18
IR spectrum of polymer <b>P6b</b>	S18
S6. GPC spectra	S19
GPC spectra of building block <b>4b</b>	S19
GPC spectra of building block <b>6b</b>	S20
S7. Coating procedure	S21
S8. EDX spectra	S22
EDX of pristine and coated surfaces with <b>P4b</b> <i>via ex situ</i> polymerisation in solution	S22-S23
EDX of coated surfaces with <b>P4b</b> <i>via in situ</i> polymerisation	S24
S9. Characterization of coated textiles	S25

## S1. Synthesis of monomers 4a and 4b



Scheme 1

**3-[(3-sulfanylpropanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2,3-dihydroxyphenyl)sulfanyl]propanoate, 2.** A solution of pyrocatechol (571 mg, 5.21 mmol) in the minimum volume of Et<sub>2</sub>O was added to a solution of NaIO<sub>4</sub> (1.393 g, 6.51 mmol) in H<sub>2</sub>O (170 mL) cooled down to 0 °C. The final mixture was stirred for 10 min. The resulting *o*-benzoquinone was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 170 mL) in quantitative yield. The organic extracts were dried with Na<sub>2</sub>SO<sub>4</sub> anhydrous and filtered. In the meantime, a solution of pentaerythritol tetrakis(3-mercaptopropionate), **1**, (2.715 g, 5.53 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) with trifluoroacetic acid (TFA) (1 mL, 13.32 mmol) was prepared under N<sub>2</sub> atmosphere. Finally, the solution containing *o*-benzoquinone was added into the solution containing **1**. The resulting mixture was stirred at rt under Ar atmosphere for 8 h in the dark. After this time, the solvent and TFA were removed under vacuum. The resulting oil was purified by column chromatography using hexane:EtOAc 7:3 as eluent affording *S*-catechol tris-thiol **2** as an oil (1.221 g,

2.05 mmol, 37% yield):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.92 (dd,  $J = 7.7, 1.6$  Hz, 1H, H-6'), 6.87 (dd,  $J = 7.7, 1.6$  Hz, 1H, H-4'), 6.73 (t,  $J = 7.7$  Hz, 1H, H-5'), 4.16 (s, 8H, H-3'', H-1'', 2xH-1'''), 2.93 (t,  $J = 7.1$  Hz, 2H, H-3), 2.72 (m, 6H, H-H-3'', 2xH-3<sup>V</sup>), 2.64 (m, 6H, H-2''', 2xH-2<sup>V</sup>), 2.51 (t,  $J = 7.1$  Hz, 2H, H-2), 1.60 (t,  $J = 8.2$  Hz, 3H, -SH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6/171.5 (4xC=O), 144.7/144.2 (C-2'/C-3'), 126.4 (C-5'), 120.8 (C-6'), 117.7 (C-4'), 116.8 (C-1'), 62.0 (C-3'', C-1'', 2xC-1'''), 41.9 (C-2''), 38.1 (C-2''', 2xC-2<sup>V</sup>), 33.6 (C-2), 30.8 (C-3), 19.5 (C-3''', 2xC-3<sup>V</sup>). HRMS (HR-EI) calcd. for  $[\text{C}_{23}\text{H}_{32}\text{O}_{10}\text{S}_4\text{Na}]^+$ : 619.0777; found: 619.0776.

**3-({3-[(3-[[6-hydroxy-9H-spiro(3-oxo-isobenzofuran-1-yl)xanthen-3-yl]oxy}-3-oxopropyl)sulfanyl]propanoyl}oxy)-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2,3-dihydroxyphenyl)sulfanyl]propanoate, 4a.** To a solution of fluorescein *O*-acrylate (150 mg, 0.39 mmol) in dry  $\text{CH}_3\text{CN}$  (12 mL), AIBN (36 mg, 0.22 mmol) was added under  $\text{N}_2$  atmosphere. The mixture was heated at reflux temperature and a solution of *S*-catechol tris-thiol **2** (450 mg, 0.75 mmol) dry  $\text{CH}_3\text{CN}$  (5 mL) was added dropwise for 1 h. The reaction mixture was heated at reflux temperature overnight. The cooled reaction was concentrated under reduced pressure to afford an oil which was purified by column chromatography using a gradient of hexanes:EtOAc. The fraction of interest was crystallised with  $\text{Et}_2\text{O}$  to afford the final pure compound **4a** as an orange powder (192 mg, 0.19 mmol, 50% yield):  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  8.01 (m, 1H, H-Ar<sub>fluores</sub>), 7.79 (m, 1H, H-Ar<sub>fluores</sub>), 7.72 (m, 1H, H-Ar<sub>fluores</sub>), 7.32-7.17 (br. s, 3H, H-6', H-5', H-4'), 6.95-6.87 (br. s, 3H, H-Ar<sub>fluores</sub>), 6.79 (br. s, 1H, H-Ar<sub>fluores</sub>), 6.74 (s, 1H, H-Ar<sub>fluores</sub>), 6.66 (s, 1H, H-Ar<sub>fluores</sub>), 6.63 (br. s, 1H, H-Ar<sub>fluores</sub>), 4.26 (br. s, 8H, H-3'', H-1'', 2xH-1<sup>V</sup>), 3.17-2.61 (br.m, 20 H, H-2, H-3, H-2'', H-3'', 2xH-2''', 2xH-3''', H-2<sup>V</sup>, H-3<sup>V</sup>), 1.61 (m, 2H, SH).  $^{13}\text{C}$  NMR (100.6 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  170.8/171.5/171.3/171.1/170.8/168.8 (6xC=O), 159.9 (C-Ar<sub>fluores</sub>), 159.5 (C-Ar<sub>fluores</sub>), 153.1 (C-Ar<sub>fluores</sub>), 152.9 (C-Ar<sub>fluores</sub>), 152.4 (C-Ar<sub>fluores</sub>), 152.3 (C-Ar<sub>fluores</sub>), 152.1 (C-Ar<sub>fluores</sub>), 151.7 (C-Ar<sub>fluores</sub>), 135.4/135.1 (C-2'/C-3'/C-Ar<sub>fluores</sub>), 130.1 (C-Ar<sub>fluores</sub>), 129.2 (C-Ar<sub>fluores</sub>), 129.1 (C-Ar<sub>fluores</sub>), 126.6 (C-5'), 124.7/124.4/124.1 (C-1'/C-6'/C-Ar<sub>fluores</sub>), 117.8/112.8/112.3/110.7/110.3 (C-4'/4xC-Ar<sub>fluores</sub>), 102.5 (C-Ar<sub>fluores</sub>), 69.1/62.3/62.2 (C-3''/C-1''/C-1<sup>V</sup>), 43.4/33.7/27.6/25.7 (C-2/C-3/C-2'''/C-2'''), 25.7 (C-3''', C-3'''). HRMS (HR-EI) calcd. for  $[\text{C}_{46}\text{H}_{47}\text{O}_{16}\text{S}_4]^+$ : 983.1742; found: 983.1747.

**3-[(3-(octadecylsulfanyl)propanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl} propyl 3-[(2,3-dihydroxyphenyl)sulfanyl]propanoate, 4b.**

**Method A.** AIBN (31 mg, 0.19 mmol) and *S*-catechol tris-thiol **2** (535 mg, 0.90 mmol) were dissolved in dry toluene (10 mL), and 1-octadecene (291  $\mu\text{L}$ , 0.81 mmol) were added. The mixture was heated at reflux temperature under Ar atmosphere for 24 h. The cooled reaction was concentrated under reduced pressure to afford a yellow oil which was purified by column chromatography using a gradient of hexane:EtOAc as eluent. The final compound **4b** was obtained as a colourless oil (75 mg, 0.09 mmol, 11% yield).

**Method B.** Pentaerythritol tetrakis(3-mercaptopropionate) (2.541 g, 5.20 mmol) was dissolved in dry toluene (30 mL). Then, a solution of AIBN (180 mg, 1.10 mmol) in the minimum volume of dry toluene and 1-octadecene (1.8 mL, 5.03 mmol) were added. The mixture was heated at 80 °C under Ar atmosphere for 8 h. The cooled reaction was concentrated under reduced pressure to afford a yellow oil. The mixture was purified by column chromatography using a gradient of hexane:EtOAc as eluent to obtain compound **5**, 3-[(3-sulfanylpropanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-(octadecylsulfanyl)propanoate, as a colourless oil (1.519 g, 2.04 mmol, 41% yield).

A solution of pyrocatechol (110 mg, 1.00 mmol) in the minimum volume of Et<sub>2</sub>O was added to a solution of NaIO<sub>4</sub> (265 mg, 2.89 mmol) in H<sub>2</sub>O (34 mL) cooled down to 0 °C. The final mixture was stirred for 10 min. The resulting *o*-benzoquinone was extracted with dry CH<sub>2</sub>Cl<sub>2</sub> (3 x 34 mL) in quantitative yield. The organic extracts were dried with Na<sub>2</sub>SO<sub>4</sub> anhydrous and filtered. In the meantime, a solution of aliphatic chain precursor *S*-C<sub>18</sub>-functionalised tris-thiol **5** (693 mg, 0.93 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) with TFA (0.22 mL, 2.93 mmol) was prepared under an N<sub>2</sub> atmosphere. Then, the solution containing the *o*-benzoquinone was added, and the resulting mixture was stirred at rt under N<sub>2</sub> atmosphere for 8 h in the dark. After this time, the solvent and TFA were removed under vacuum. The resulting oil was purified by column chromatography using a gradient of hexane:EtOAc as eluent to afford *S,S'*-catechol-C<sub>18</sub>-bis-thiol **4b** as a colourless oil (268 mg, 0.32 mmol, 35% yield).

Compound **5**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.16 (s, 8H, H-1',H-3',2xH-1'''), 2.73 (m, 6H, H-3'',2xH-3'''), 2.64 (m, 8H, H-2,H-2'',2xH-2'''), 2.48 (t, *J* = 7.1 Hz, 4H, H-3,H-1<sup>V</sup>), 1.60 (t, *J* = 7.8 Hz, 3H, -SH), 1.53 (q, *J* = 7.2 Hz, 2H, H-2<sup>V</sup>), 1.42-1.08 (br. s, 30H, H-3<sup>V</sup>-H-17<sup>V</sup>), 0.84 (t, *J* = 7.1 Hz, 3H, H-18<sup>V</sup>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.9/171.5/171.4/171.0 (C=O), 62.1 (C-1',C-3',2xC-1'''), 41.9 (C-2'), 38.3 (C-2,C-2'',2xC-2'''), 32.1 (C-1<sup>V</sup>,C-3), 29.7 (C-2<sup>V</sup>-C-16<sup>V</sup>), 26.9 (C-3<sup>V</sup>), 22.7 (C-17<sup>V</sup>), 19.7 (C-3'',2xC-3'''), 14.1 (C-18<sup>V</sup>). HRMS (HR-El) calcd. for [C<sub>35</sub>H<sub>64</sub>O<sub>8</sub>S<sub>4</sub>Na]<sup>+</sup>: 763.3379; found: 763.3382.

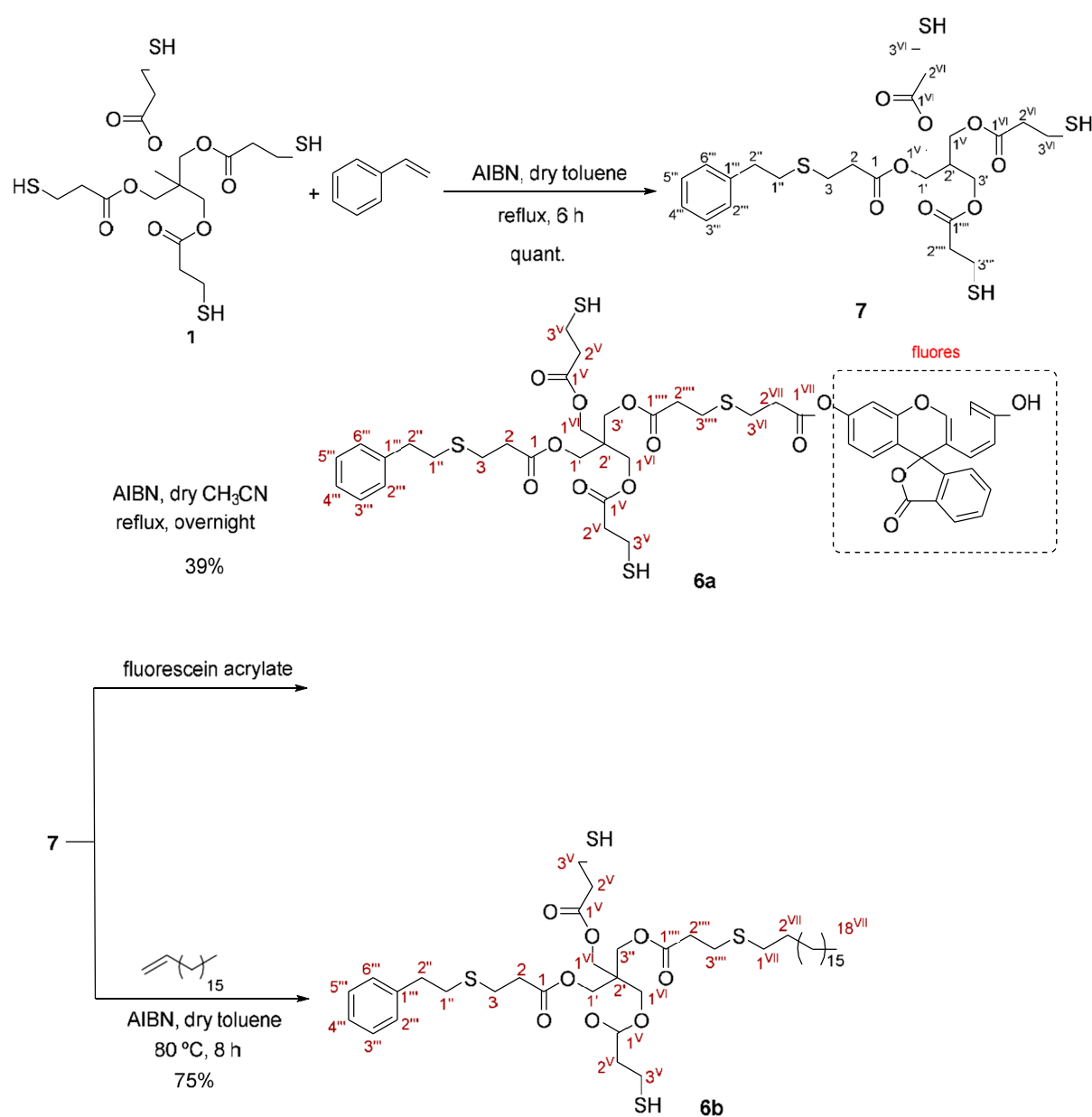
Compound **4b**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.00 (dd, *J* = 8.0, 1.6 Hz, 1H, H-6'), 6.95 (dd, *J* = 8.0, 1.6 Hz, 1H, H-4'), 6.81 (td, *J* = 8.0, 2.5 Hz, 1H, H-5'), 4.20 (s, 8H, H-1'',H-3'',2xH-1<sup>V</sup>), 3.03 (t, *J* = 7.1 Hz, 2H, H-3), 2.73 (m, 6H, H-3''',2xH-3'''), 2.64 (m, 6H, H-2''',2xH-2'''), 2.56 (t, *J* = 7.1 Hz, 4H, H-2, H-1<sup>VI</sup>), 1.66 (t, *J* = 8.3 Hz, 2H, -SH), 1.60 (q, *J* = 7.2 Hz, 2H, H-2<sup>VI</sup>), 1.43-1.18 (br. s, 30H, H-3<sup>VI</sup>-H-17<sup>VI</sup>), 0.90 (t, *J* = 7.2 Hz, 3H, H-18<sup>VI</sup>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.0/171.6/ 171.1/170.8 (C=O), 145.1/144.2 (C-2'/C-3'), 127.0 (C-5'), 126.0 (C-6'), 121.2 (C-1'), 117.2 (C-4'), 62.6/62.4 (C-1''/C-3''/C-1<sup>V</sup>), 42.5 (C-2''), 38.3 (C-2''',2xC-2'''), 31.9 (C-2,C-3,C-1<sup>VI</sup>), 29.7 (C-2<sup>VI</sup>-C-16<sup>VI</sup>), 26.9 (C-3'',2xC-3'''), 22.7 (C-17<sup>VI</sup>), 14.1 (C-18<sup>VI</sup>). HRMS (HR-El) calcd. for [C<sub>41</sub>H<sub>68</sub>O<sub>10</sub>S<sub>4</sub>Na]<sup>+</sup>: 872.3604; found: 872.3593.

### 3-({3-[(3-[[6-hydroxy-9*H*-spiro(3-oxo-isobenzofuran-1-yl)xanthen-3-yl]oxy}-3-

oxopropyl)sulfanyl]propanoyl}oxy)-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, **6a** (39% Yield). <sup>1</sup>H NMR (360 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) δ 8.01 (m, 2H, H-Ar<sub>fluores</sub>), 7.86-7.67 (br. m, 3H, H-Ar<sub>fluores</sub>), 7.38-7.12 (br. m, 5H, H-2''', H-3''', H-4''',H-5''',H-6'''), 6.96-6.82 (br. s, 2H, H-Ar<sub>fluores</sub>), 6.80 (br. s, 1H, H-Ar<sub>fluores</sub>), 6.74-6.62 (br. s, 2H, H-Ar<sub>fluores</sub>), 4.25 (br. s, 8H, H-1',H-3',2xH-1<sup>VI</sup>), 3.17-2.65 (br. m, 24H, H-2,H-3,H-1'',H-2'',H-2''',H-3''',2xH-2<sup>V</sup>,2xH-3<sup>V</sup>,H-2<sup>VII</sup>, H-3<sup>VII</sup>), 1.67 (t, *J* = 8.0 Hz, 2H, -SH). <sup>13</sup>C NMR (90.5 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) δ 172.0/171.5/171.3/171.1/170.8 (C=O), 168.8 (C-Ar<sub>fluores</sub>), 159.6 (C-Ar<sub>fluores</sub>), 153.1 (C-Ar<sub>fluores</sub>), 152.9 (C-Ar<sub>fluores</sub>), 152.5 (C-Ar<sub>fluores</sub>), 152.3 (C-Ar<sub>fluores</sub>), 152.2 (C-Ar<sub>fluores</sub>), 141.4 (C-1'''), 135.2 (C-3''',C-5'''), 130.7 (C-Ar<sub>fluores</sub>), 130.1 (C-Ar<sub>fluores</sub>), 129.8 (C-2''',C-6'''), 129.3 (C-Ar<sub>fluores</sub>), 129.1 (C-Ar<sub>fluores</sub>), 128.8 (C-4'''), 124.7 (C-Ar<sub>fluores</sub>), 112.8 (C-Ar<sub>fluores</sub>), 112.4 (C-Ar<sub>fluores</sub>), 110.8 (C-Ar<sub>fluores</sub>), 110.3 (C-Ar<sub>fluores</sub>), 102.5 (C-Ar<sub>fluores</sub>), 102.4 (C-Ar<sub>fluores</sub>), 82.4 (C-C<sub>fluores</sub>), 62.9 (C-1',C-3',2xC-1<sup>VI</sup>), 42.6 (C-2'), 38.5/36.5/35.1/34.9/33.9/33.6 (C-2/2xC-2<sup>V</sup>/C-2''''/C-2<sup>VII</sup>/C-1''/C-2''), 26.8/24.8/22.7/19.7 (C-3''''/2xC-3<sup>V</sup>/C-3<sup>VI</sup>/C-3). HRMS (HR-El) calcd. for [C<sub>48</sub>H<sub>51</sub>O<sub>14</sub>S<sub>4</sub>]<sup>+</sup>: 979.2141; found: 979.2161.

**3-[[3-(octadecylsulfanyl)propanoyl]oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl} propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, 6b** (75% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.31-7.16 (m, 5H, H-2''', H-6''', H-3''', H-5''', H-4'''), 4.15 (br. s, 8H, H-1', H-3'', 2xH-1<sup>VI</sup>), 2.87 (m, 6H, H-3, H-1'', H-2''), 2.75 (m, 8H, 2xH-3<sup>V</sup>, H-3''', H-1<sup>VII</sup>), 2.62 (m, 6H, H-2''', 2xH-2<sup>V</sup>), 2.50 (t,  $J = 7.2$  Hz, 2H, H-2), 1.65 (t,  $J = 8.3$  Hz, 2H, -SH), 1.56 (q,  $J = 7.0$  Hz, 2H, H-2<sup>VII</sup>), 1.30-1.17 (br. s, 30H, H-3<sup>VII</sup>-H-17<sup>VII</sup>), 0.87 (t,  $J = 7.0$  Hz, 3H, H-18<sup>VII</sup>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9/171.4/171.3/171.1 (C=O), 140.4 (C-1'''), 128.6/128.4 (C-2'''/C-6'''/C-3'''/C-5'''), 126.6 (C-4'), 62.6 (C-1', C-3', 2xC-1<sup>VI</sup>), 42.0 (C-2'), 38.5 (C-2), 36.2 (C-2''', 2xC-2<sup>V</sup>), 34.6/33.9 (C-1''/C-2''), 32.0 (C-1<sup>VII</sup>), 29.9/29.5 (C-2<sup>VII</sup>-C-16<sup>VII</sup>), 27.0 (C-3), 22.9 (C-3''', 2xC-3<sup>V</sup>), 20.0 (C-17<sup>VII</sup>), 14.5 (C-18<sup>VII</sup>). HRMS (HR-EI) calcd. for  $[\text{C}_{43}\text{H}_{72}\text{O}_8\text{S}_4]^+$ : 844.2897; found: 844.4110.

## S2. Synthesis of compounds 6a and 6b



Scheme 2

**3-[(3-sulfanylpropanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, 7.** A solution of pentaerythritol tetrakis(3-mercaptopropionate) (436 mg, 0.89 mmol) in dry toluene (5 mL) was added into a Schlenk containing AIBN (31 mg, 0.19 mmol). Afterwards, styrene (100  $\mu$ L, 0.87 mmol) was added. The mixture was heated at reflux temperature under Ar atmosphere. After 6 h, the cooled reaction was concentrated under reduced pressure to afford **7** as a colourless oil (513 mg, 0.87 mmol, quant.):  $^1\text{H}$  NMR (360 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.30-7.16 (m, 5H, H-2''', H-3''', H-4''', H-5''', H-6'''), 4.16 (br. s, 8H, H-3', H-1', 2xH-1<sup>V</sup>), 2.86 (t,  $J$  = 7.2 Hz, 2H, H-3), 2.72 (m, 10H, H-1'', H-2'', H-3'', 2xH-3<sup>V</sup>), 2.64 (m, 8H, H-2''', H-2, 2xH-2<sup>V</sup>), 1.66 (t,  $J$  = 8.2 Hz, 3H, -SH).  $^{13}\text{C}$  NMR (90.5 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  171.8/171.5/171.3/171.0 (C=O), 140.8 (C-1''), 128.5/128.4 (C-2'''/C-6'''/C-3'''/C-5'''), 126.3 (C-4'''), 62.6 (C-3', C-1', 2xC-1<sup>V</sup>), 41.9 (C-2'), 38.3 (C-2''', C-2<sup>V</sup>), 36.0 (C-2), 34.8/33.6 (C-1'/C-2'), 26.9 (C-3), 19.6 (C-3''', C-3<sup>V</sup>). HRMS (HR-El) calcd. for  $[\text{C}_{25}\text{H}_{38}\text{O}_9\text{S}_4]^+$ : 610.1335; found: 610.1399.

**3-[(3-[(3-[(6-hydroxy-9H-spiro(3-oxo-isobenzofuran-1-yl)xanthen-3-yl]oxy)-3-oxopropyl)sulfanyl]propanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, 6a.** A solution of *S*-styrene tris-thiol **7** (152 mg, 0.26 mmol) in dry  $\text{CH}_3\text{CN}$  (1 mL) was added into a Schlenk containing AIBN (10 mg, 0.06 mmol). Then, a solution of fluorescein *O*-acrylate (100 mg, 0.26 mmol) in dry  $\text{CH}_3\text{CN}$  (2 mL) was added. The mixture was heated at reflux temperature under Ar atmosphere overnight. The cooled reaction was concentrated under reduced pressure to afford a yellow oil which was purified by column chromatography using a gradient of hexane:EtOAc as eluent to afford compound **6a** as an orange solid (99 mg, 0.10 mmol, 39% yield):  $^1\text{H}$  NMR (360 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  8.01 (m, 2H, H-Ar<sub>fluores</sub>), 7.86-7.67 (br. m, 3H, H-Ar<sub>fluores</sub>), 7.38-7.12 (br m, 5H, H-2''', H-3''', H-4''', H-5''', H-6'''), 6.96-6.82 (br. s, 2H, H-Ar<sub>fluores</sub>), 6.80 (sbr., 1H, H-Ar<sub>fluores</sub>), 6.74-6.62 (br. s, 2H, H-Ar<sub>fluores</sub>), 4.25 (br. s, 8H, H-1', H-3', 2xH-1<sup>V</sup>), 3.17-2.65 (br. m, 24H, H-2, H-3, H-1'', H-2'', H-2''', H-3''', 2xH-3<sup>V</sup>, 2xH-3<sup>V</sup>, H-2<sup>VII</sup>, H-3<sup>VII</sup>), 1.67 (t,  $J$  = 8.0 Hz, 2H, -SH).  $^{13}\text{C}$  NMR (90.5 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  172.0/171.5/171.3/171.1/170.8 (C=O), 168.8 (C-Ar<sub>fluores</sub>), 159.6 (C-Ar<sub>fluores</sub>), 153.1 (C-Ar<sub>fluores</sub>), 152.9 (C-Ar<sub>fluores</sub>), 152.5 (C-Ar<sub>fluores</sub>), 152.3 (C-Ar<sub>fluores</sub>), 152.2 (C-Ar<sub>fluores</sub>), 141.4 (C-1'''), 135.2 (C-3''', C-5'''), 130.7 (C-Ar<sub>fluores</sub>), 130.1 (C-Ar<sub>fluores</sub>), 129.8 (C-2''', C-6'''), 129.3 (C-Ar<sub>fluores</sub>), 129.1 (C-Ar<sub>fluores</sub>), 128.8 (C-4'''), 124.7 (C-Ar<sub>fluores</sub>), 112.8 (C-Ar<sub>fluores</sub>), 112.4 (C-Ar<sub>fluores</sub>), 110.8 (C-Ar<sub>fluores</sub>), 110.3 (C-Ar<sub>fluores</sub>), 102.5 (C-Ar<sub>fluores</sub>), 102.4 (C-Ar<sub>fluores</sub>), 82.4 (C-C<sub>fluores</sub>), 62.9 (C-1', C-3', 2xC-1<sup>V</sup>), 42.6 (C-2'), 38.5/36.5/35.1/34.9/33.9/33.6 (C-2/2xC-2<sup>V</sup>/C-2''''/C-2<sup>VII</sup>/C-1''/C-2''), 26.8/24.8/22.7/19.7 (C-3''''/2xC-3<sup>V</sup>/C-3<sup>V</sup>/C-3). HRMS (HR-El) calcd. for  $[\text{C}_{48}\text{H}_{51}\text{O}_{14}\text{S}_4]^+$ : 979.2141; found: 979.2161.

**3-[(3-(octadecylsulfanyl)propanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl} propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, 6b.** A solution of AIBN (48 mg, 0.29 mmol) in dry toluene (8 mL) and 1-octadecene (0.4 mL, 1.12 mmol) were added to a solution of *S*-styrene tris-thiol **7** (740 mg, 1.25 mmol) in dry toluene (5 mL). The reaction mixture was heated at 80 °C under Ar

atmosphere for 8 h. The cooled reaction was concentrated under reduced pressure to afford a yellowish oil which was purified by column chromatography using a gradient of hexanes:EtOAc as eluent to obtain compound **6b** as a colourless oil (696 mg, 0.82 mmol, 75% yield):  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.31-7.16 (m, 5H, H-2''', H-6''', H-3''', H-5''', H-4'''), 4.15 (br. s, 8H, H-1', H-3'', 2xH-1<sup>VI</sup>), 2.87 (m, 6H, H-3, H-1'', H-2''), 2.75 (m, 8H, 2xH-3<sup>V</sup>, H-3''', H-1<sup>VII</sup>), 2.62 (m, 6H, H-2''', 2xH-2<sup>V</sup>), 2.50 (t,  $J$  = 7.2 Hz, 2H, H-2), 1.65 (t,  $J$  = 8.3 Hz, 2H, -SH), 1.56 (q,  $J$  = 7.0 Hz, 2H, H-2<sup>VII</sup>), 1.30-1.17 (br. s, 30H, H-3<sup>VII</sup>-H-17<sup>VII</sup>), 0.87 (t,  $J$  = 7.0 Hz, 3H, H-18<sup>VII</sup>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9/171.4/171.3/171.1 (C=O), 140.4 (C-1'''), 128.6/128.4 (C-2'''/C-6'''/C-3'''/C-5'''), 126.6 (C-4'), 62.6 (C-1', C-3', 2xC-1<sup>VI</sup>), 42.0 (C-2'), 38.5 (C-2), 36.2 (C-2''', 2xC-2<sup>V</sup>), 34.6/33.9 (C-1''/C-2''), 32.0 (C-1<sup>VII</sup>), 29.9/29.5 (C-2<sup>VII</sup>-C-16<sup>VII</sup>), 27.0 (C-3), 22.9 (C-3''', 2xC-3<sup>V</sup>), 20.0 (C-17<sup>VII</sup>), 14.5 (C-18<sup>VII</sup>). HRMS (HR-ESI) calcd. for  $[\text{C}_{43}\text{H}_{72}\text{O}_8\text{S}_4]^+$ : 844.2897; found: 844.4110.

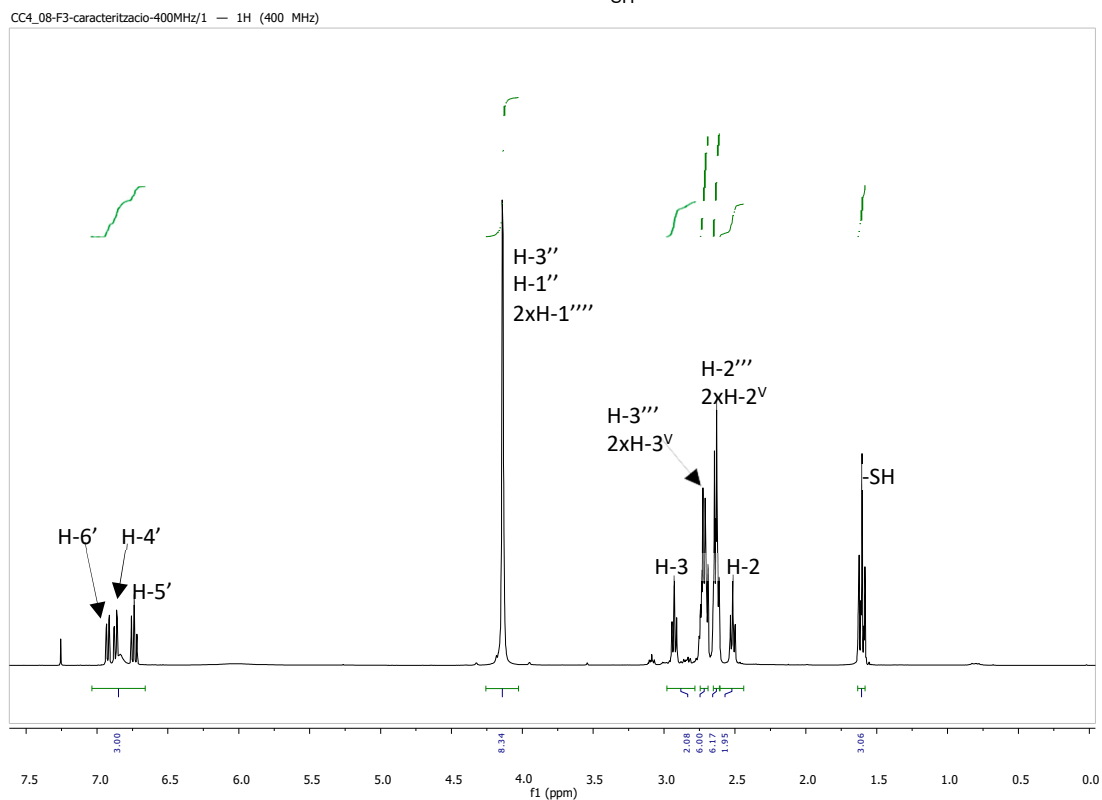
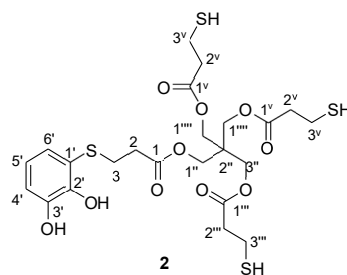
### S3. Polymerization of 4b and 6b

**Table S1.** Polymerization's degree of **P4b** and **P6b** obtained by  $^1\text{H}$  NMR, DOSY NMR experiments and GPC.

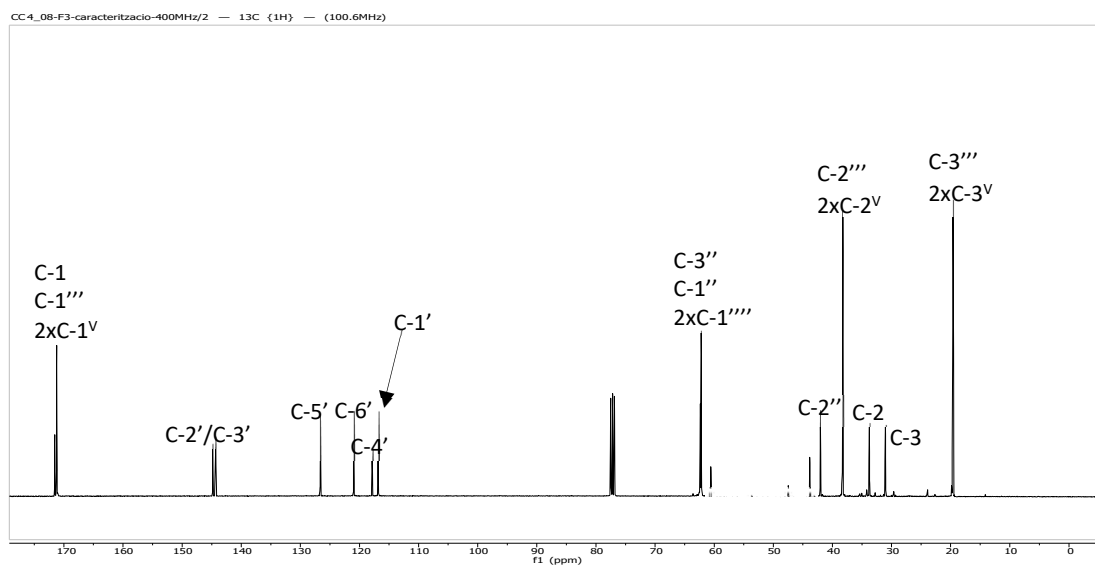
Derivative	$^1\text{H}$ NMR	DOSY	GPC			
<b>P4b</b>	2-4 units	6/7 units	IR		UV	
			Mn	Mw	Mn	Mw
			4017 Da	6013 Da	-	-
			4/5 units	7 units		
<b>P6b</b>	dimer-trimer	< 10 units	IR		UV	
			Mn	Mw	Mn	Mw
			3167 Da	3651 Da	3637 Da	4144
			tetramer	tetramer	tetramer	5 units

## S4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

**3-[(3-sulfany]propanoyl)oxy]-2,2-bis{[(3-sulfany]propanoyl)oxy]methyl}propyl 3-[(2,3-dihydroxyphenyl)sulfany]propanoate, 2**



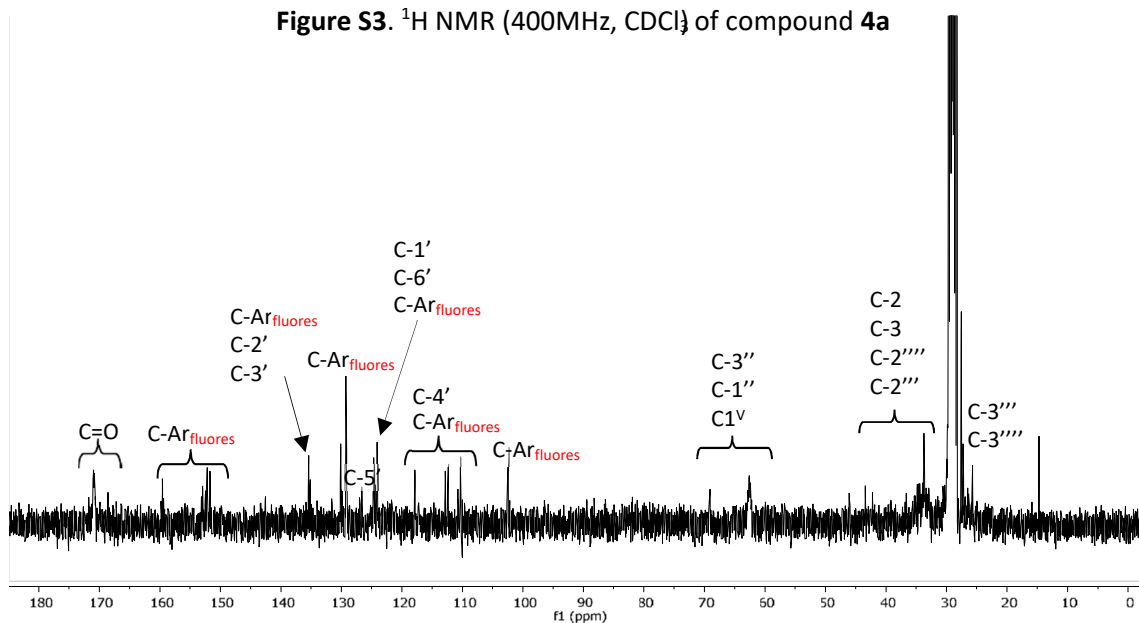
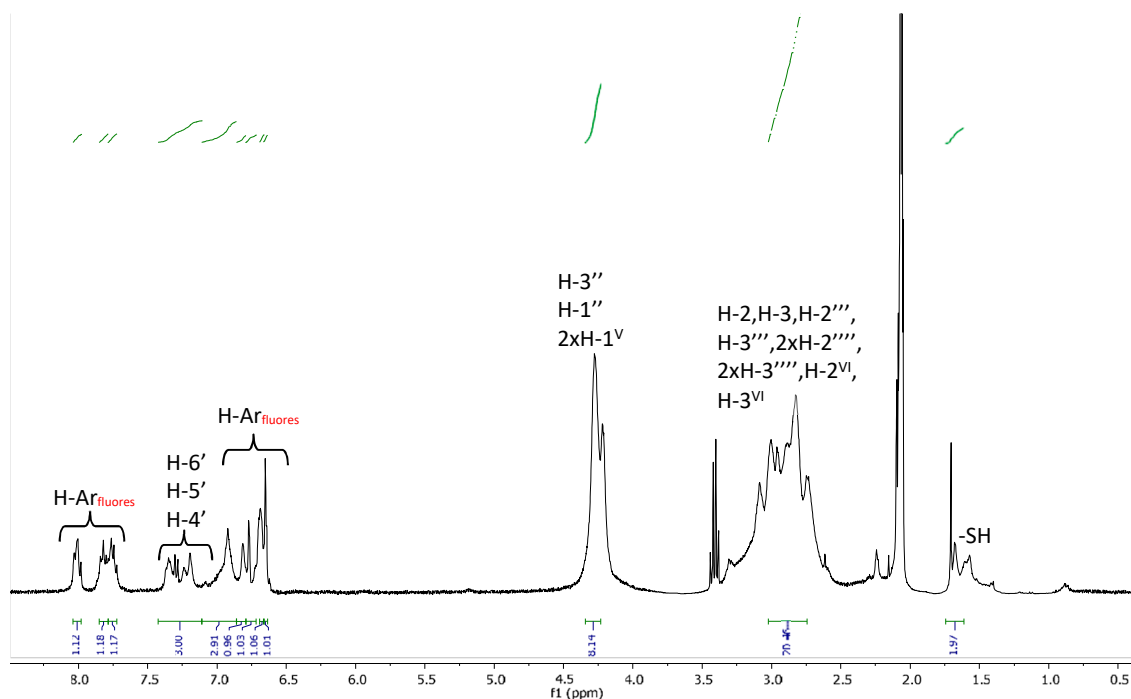
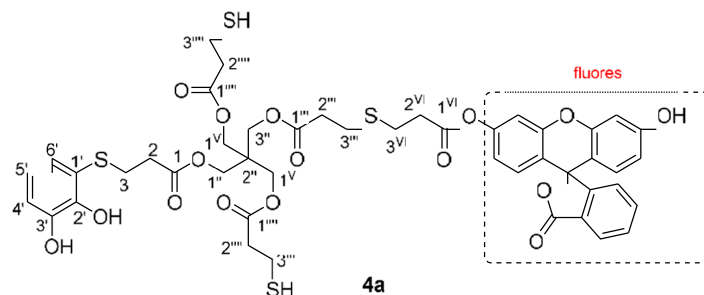
**Figure S1.**  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of compound 2



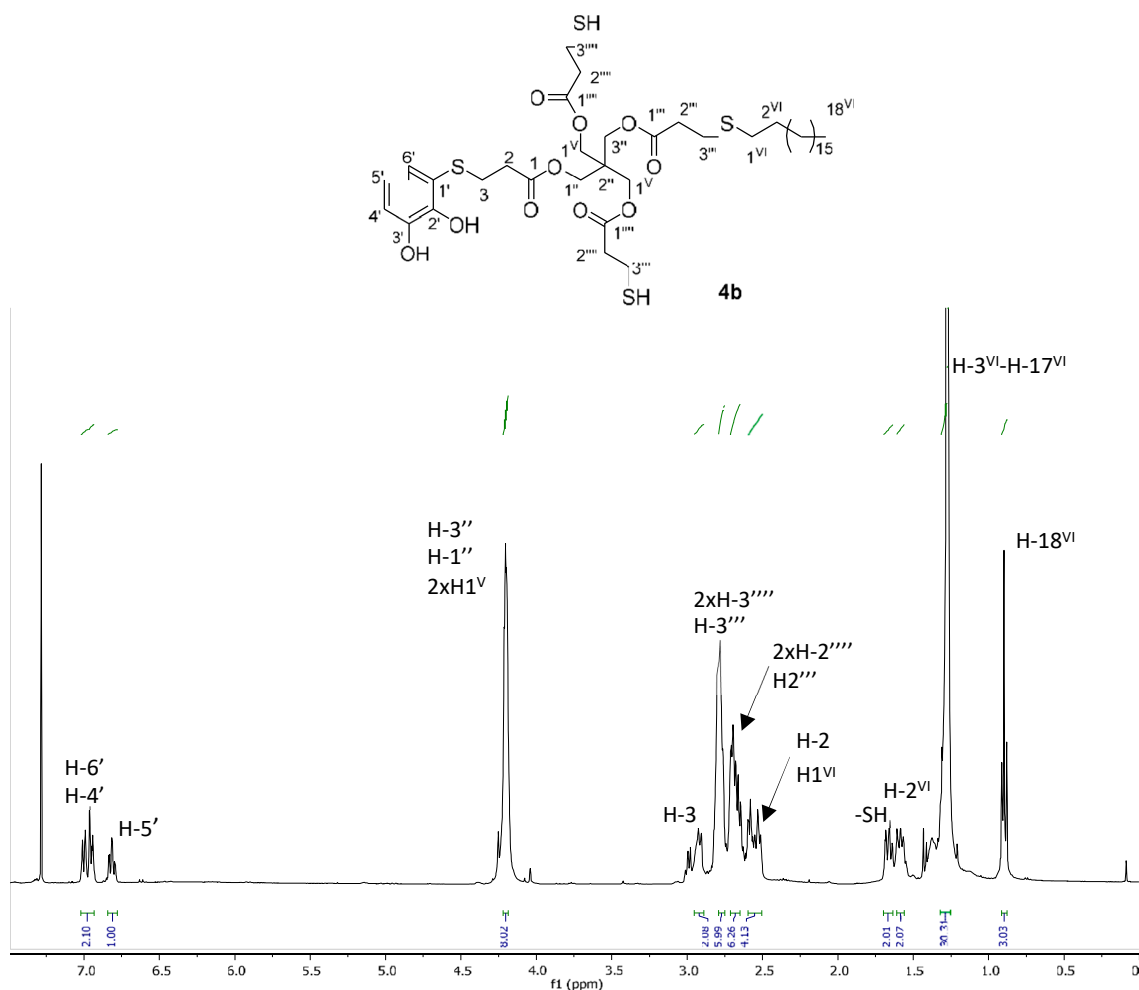
**Figure S2.**  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of compound 2



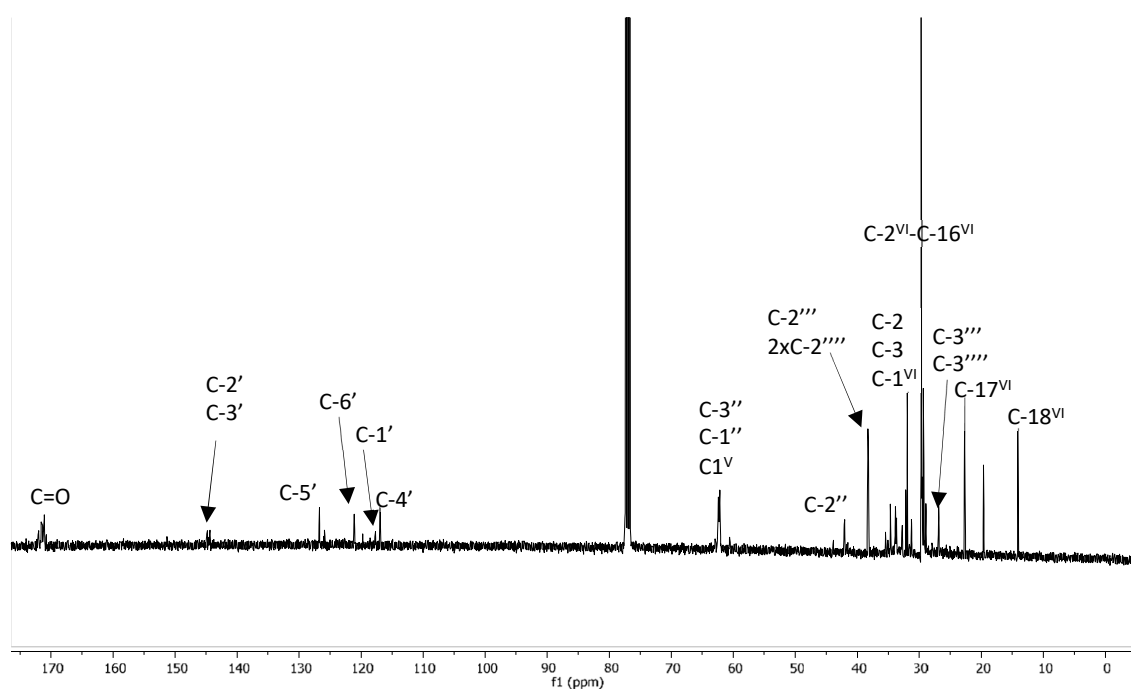
**3-({3-[(3-[[6-hydroxy-9H-spiro(3-oxo-isobenzofuran-1-yl)xanthen-3-yl]oxy}-3-oxopropyl)sulfanyl]propanoyl}oxy)-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2,3-dihydroxyphenyl)sulfanyl]propanoate, 4a**



**3-[[3-(octadecylsulfanyl)propanoyl]oxy]-2,2-bis[[3-(sulfanylpropanoyl)oxy]methyl] propyl 3-[(2,3-dihydroxyphenyl)sulfanyl]propanoate, 4b**

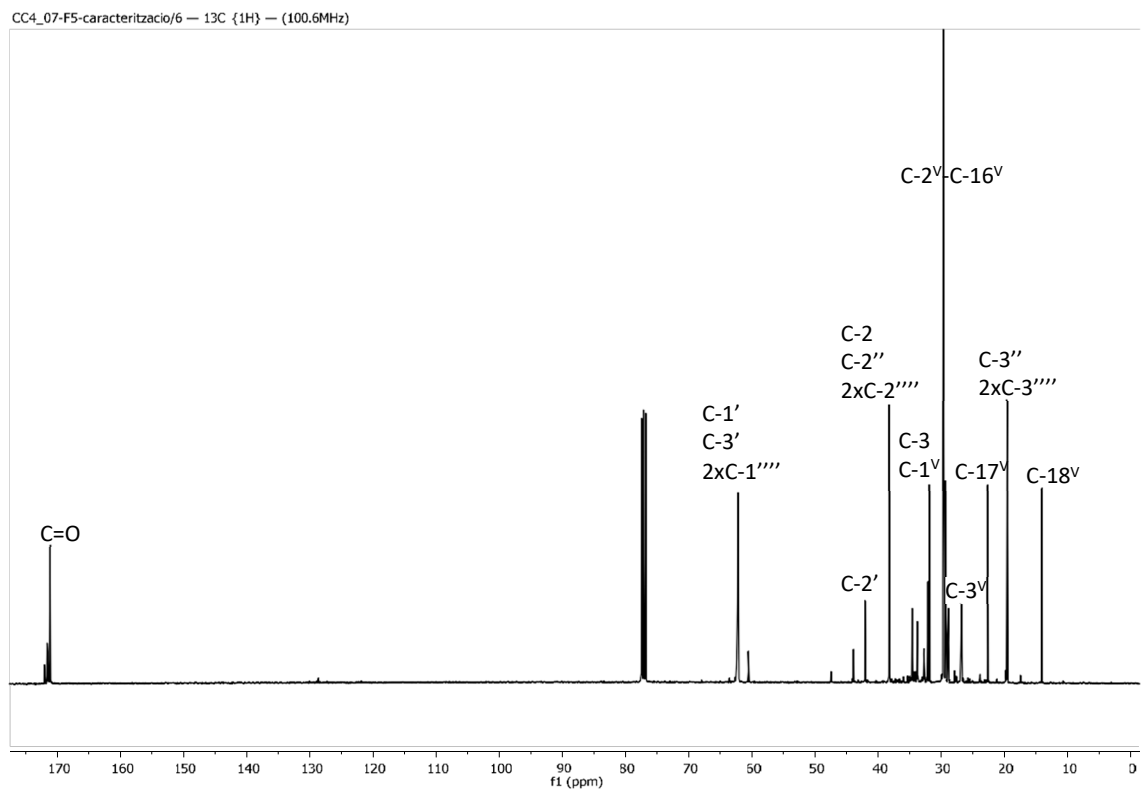
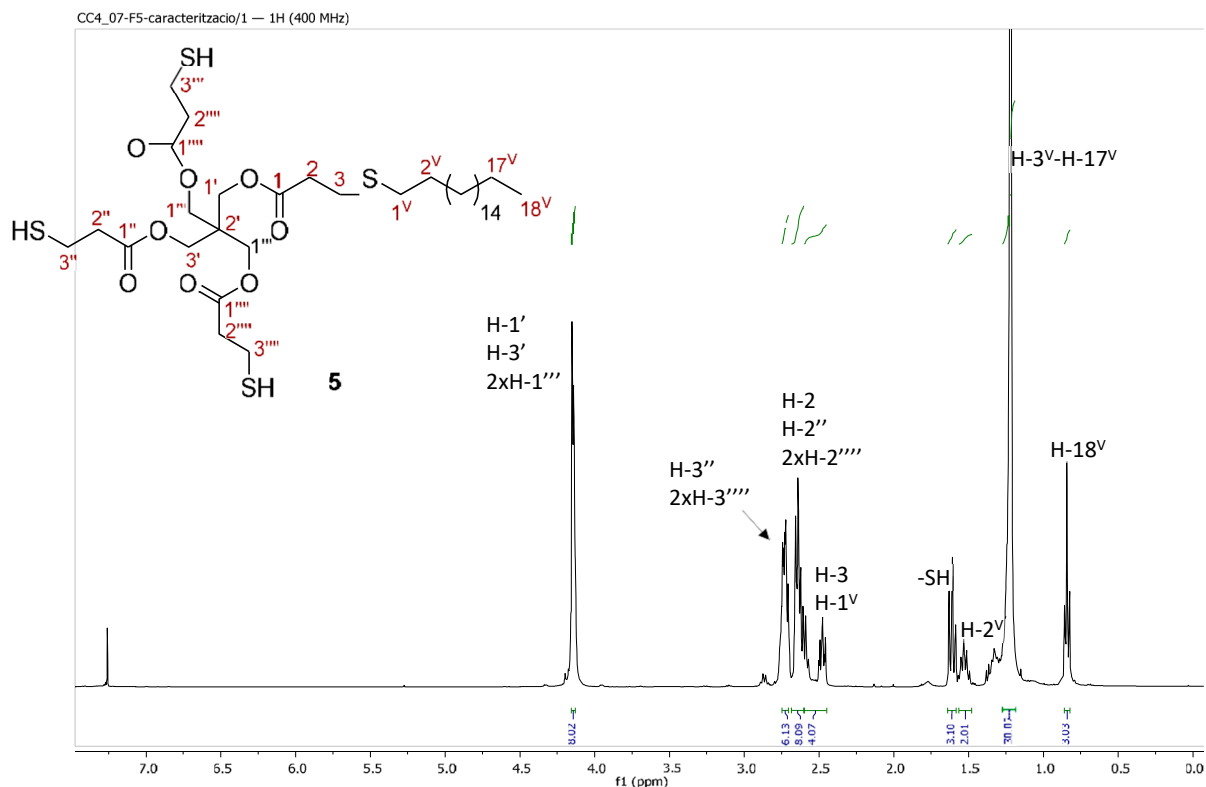


**Figure S5.** <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) of compound 4b

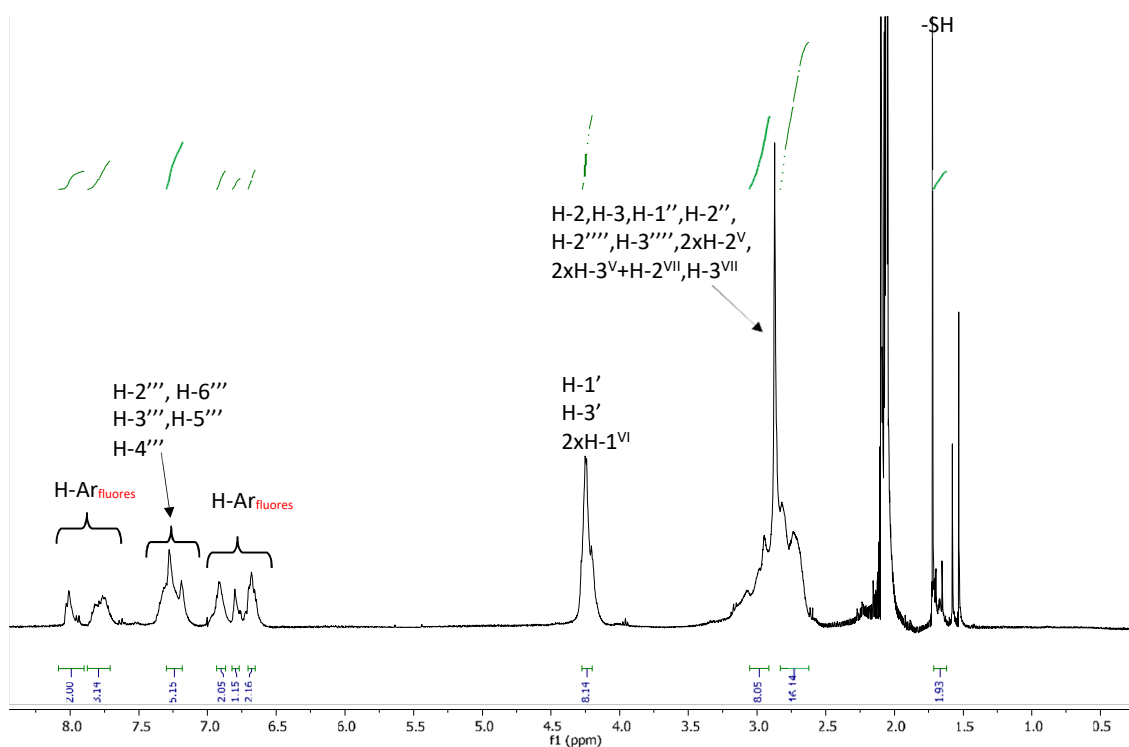
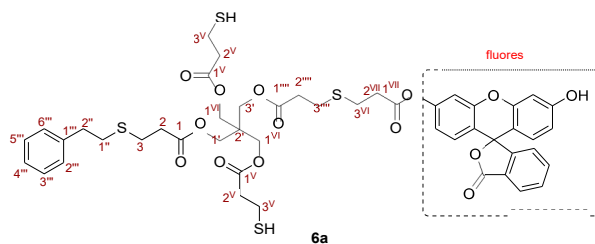


**Figure S6.** <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) of compound 4b

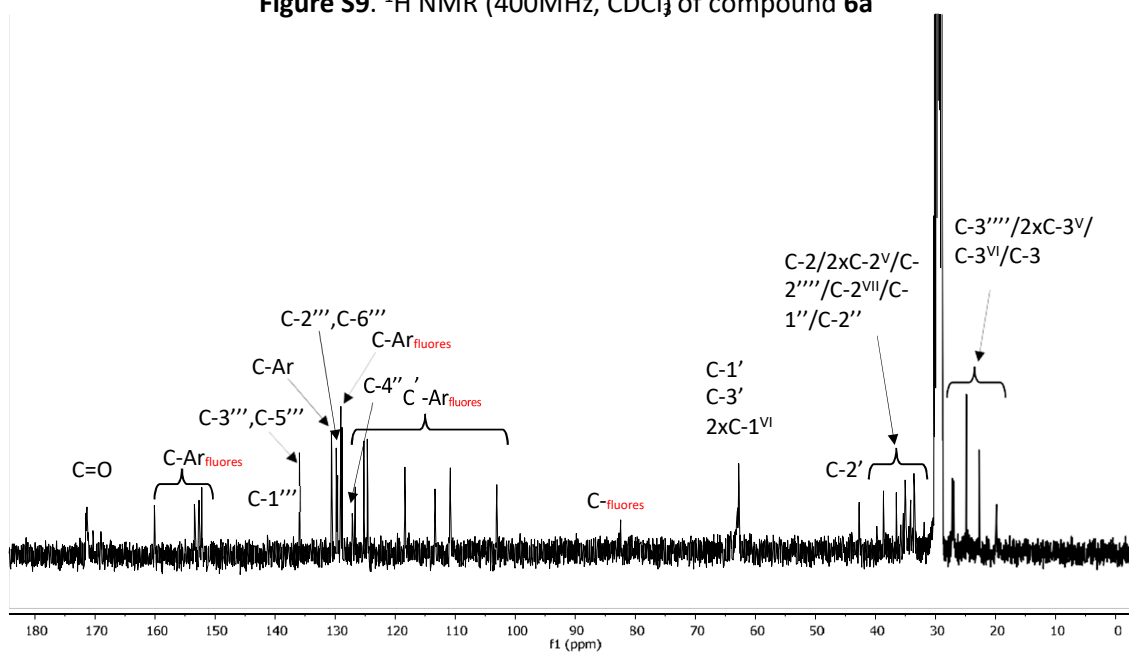
**3-[(3-sulfanylpropanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-(octadecylsulfanyl)propanoate, 5**



**3-({3-[(3-[[6-hydroxy-9H-spiro(3-oxo-isobenzofuran-1-yl)xanthen-3-yl]oxy]-3-oxopropyl)sulfanyl]propanoyl}oxy)-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2-phenylethenyl)sulfanyl]propanoate 6a**

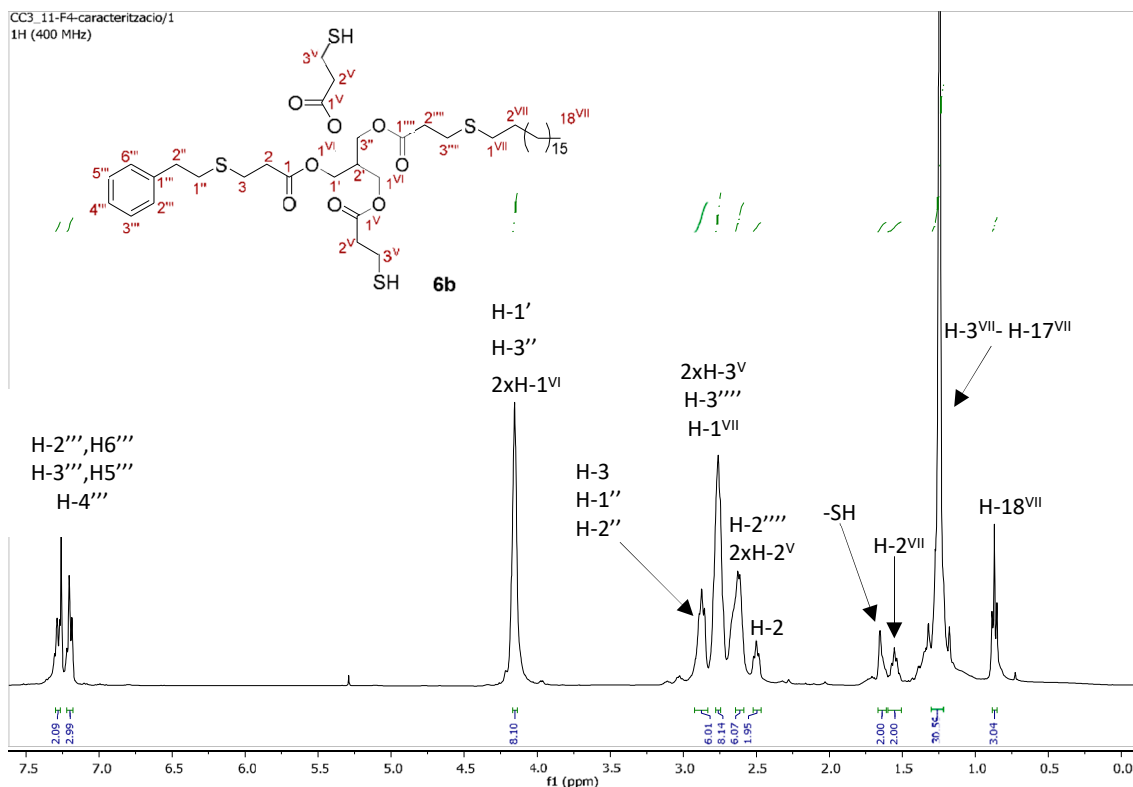


**Figure S9.**  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) of compound **6a**

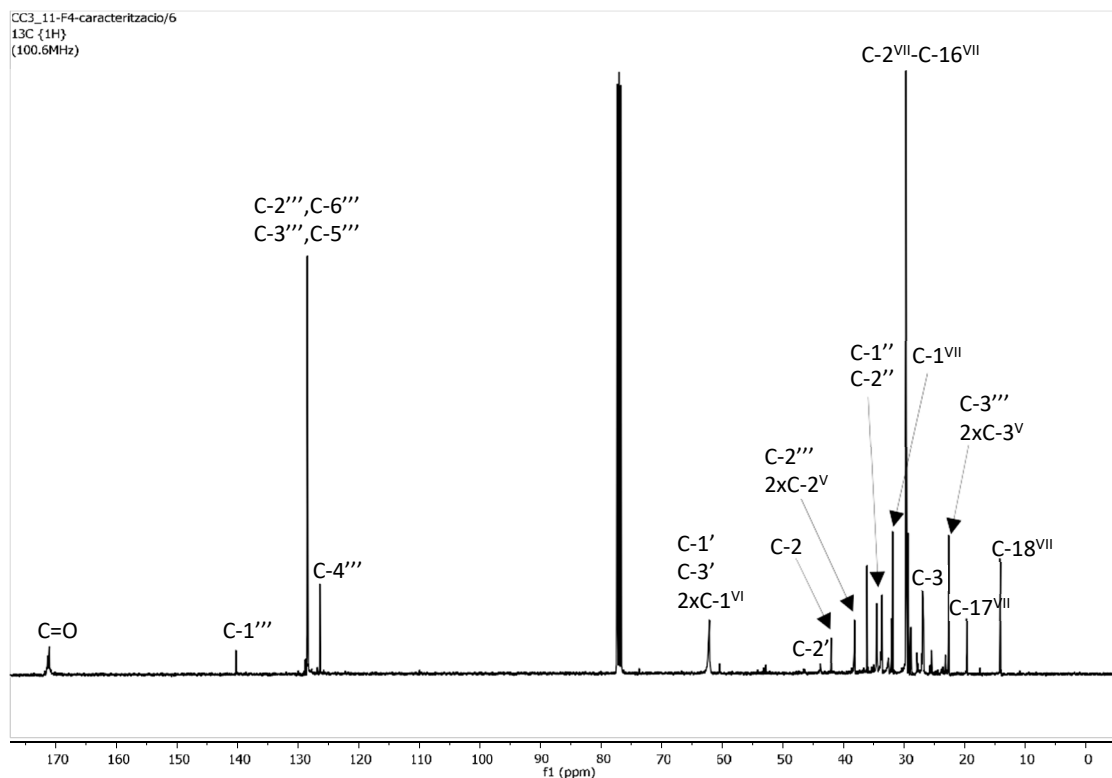


**Figure S10.**  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) of compound **6a**

**3-[[3-(octadecylsulfanyl)propanoyl]oxy]-2,2-bis[[3-(3-sulfanylpropanoyl)oxy]methyl] propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, 6b**

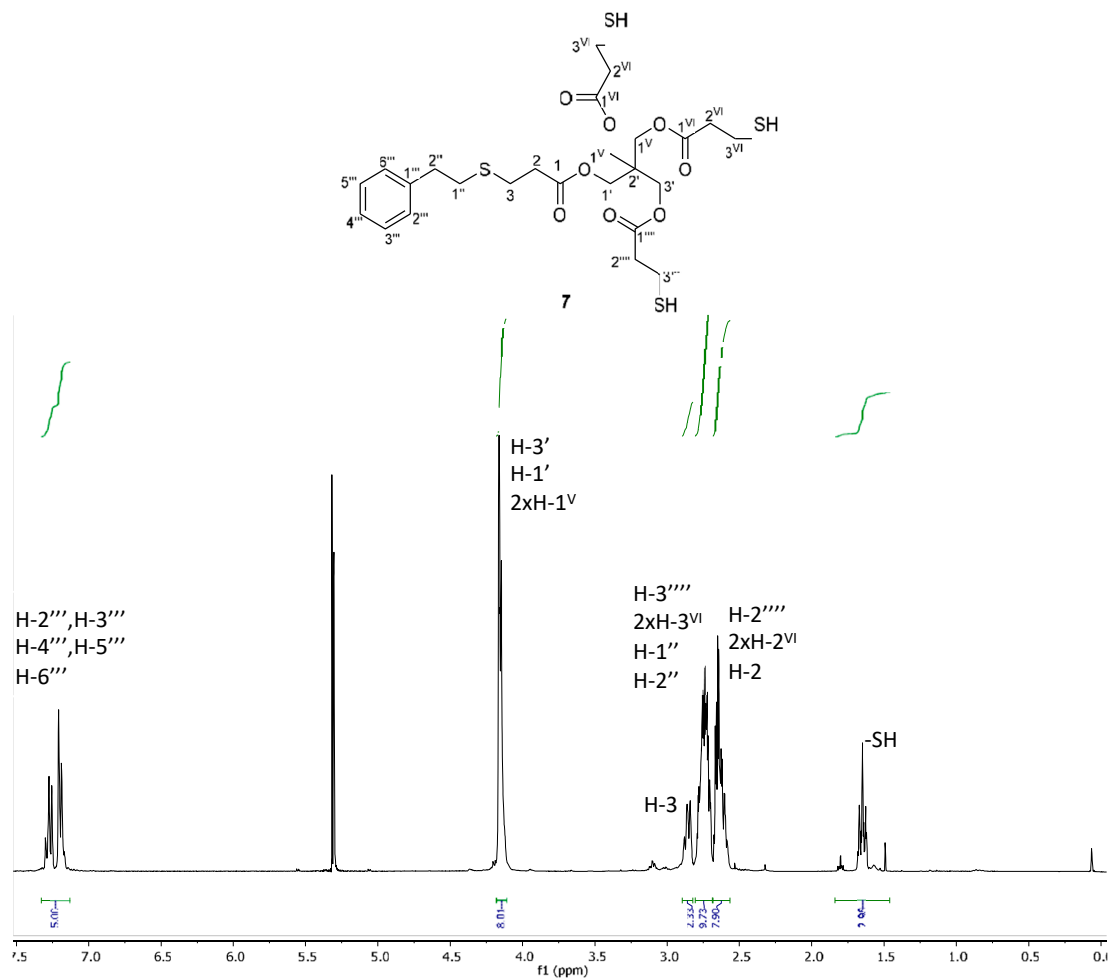


**Figure S10.** <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) of compound **6b**

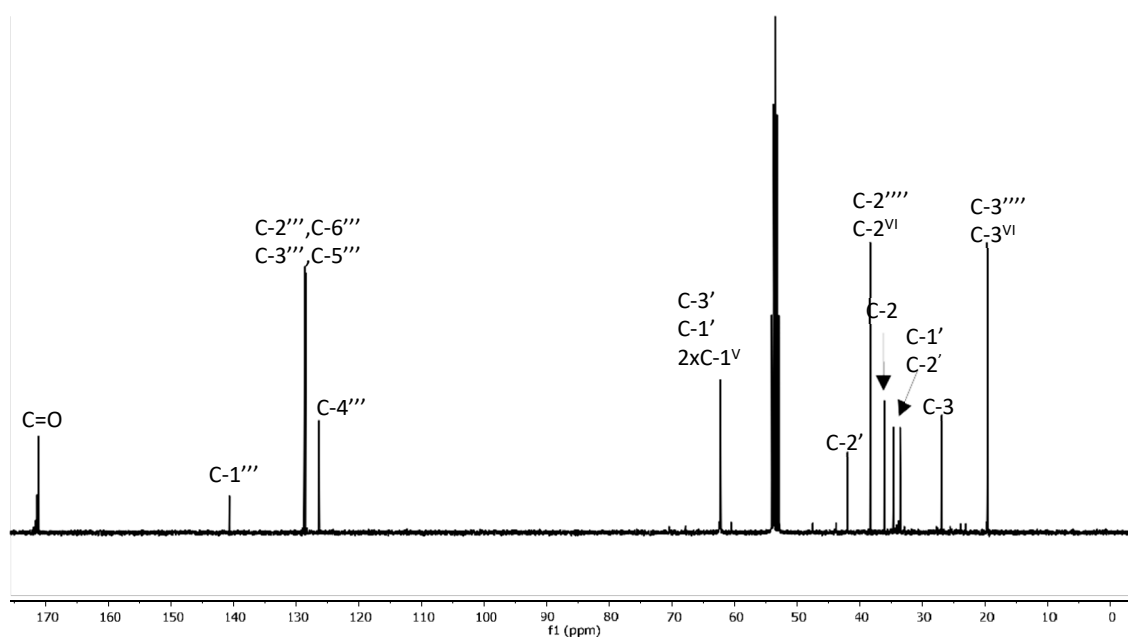


**Figure S11.** <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) of compound **6b**

**3-[(3-sulfanylpropanoyl)oxy]-2,2-bis{[(3-sulfanylpropanoyl)oxy]methyl}propyl 3-[(2-phenylethenyl)sulfanyl]propanoate, 7**

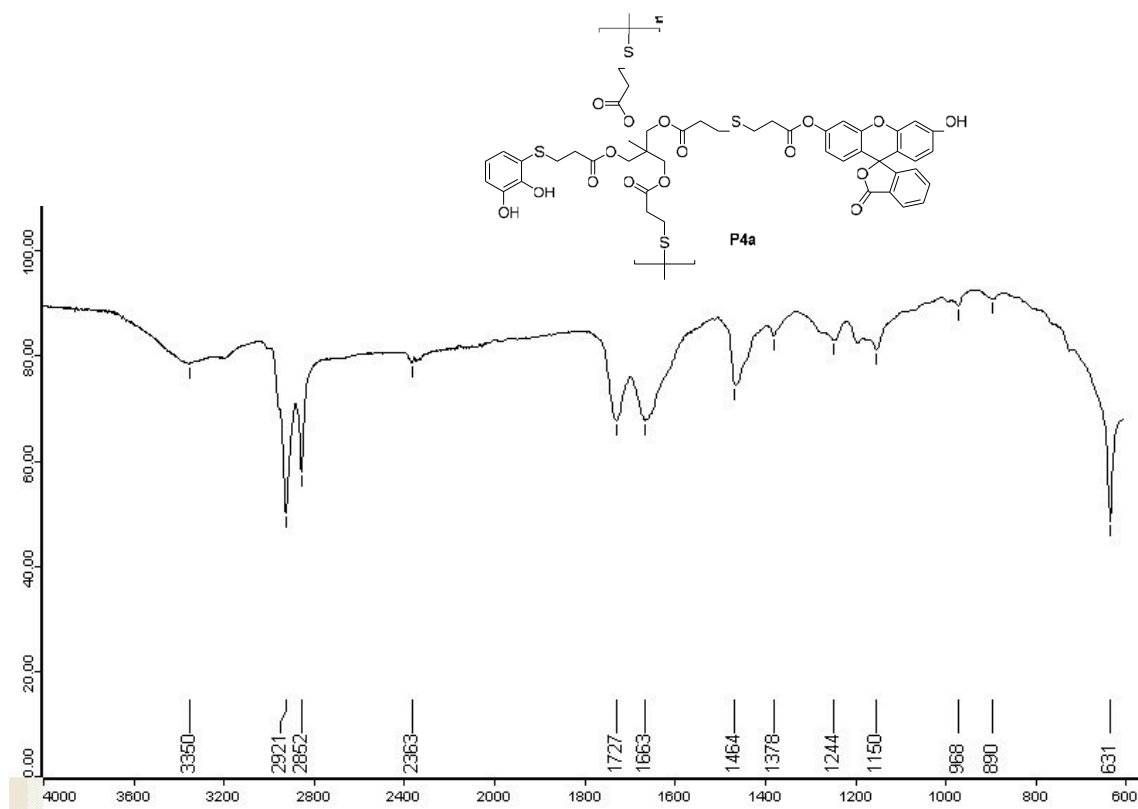


**Figure S11.** <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) of compound 7

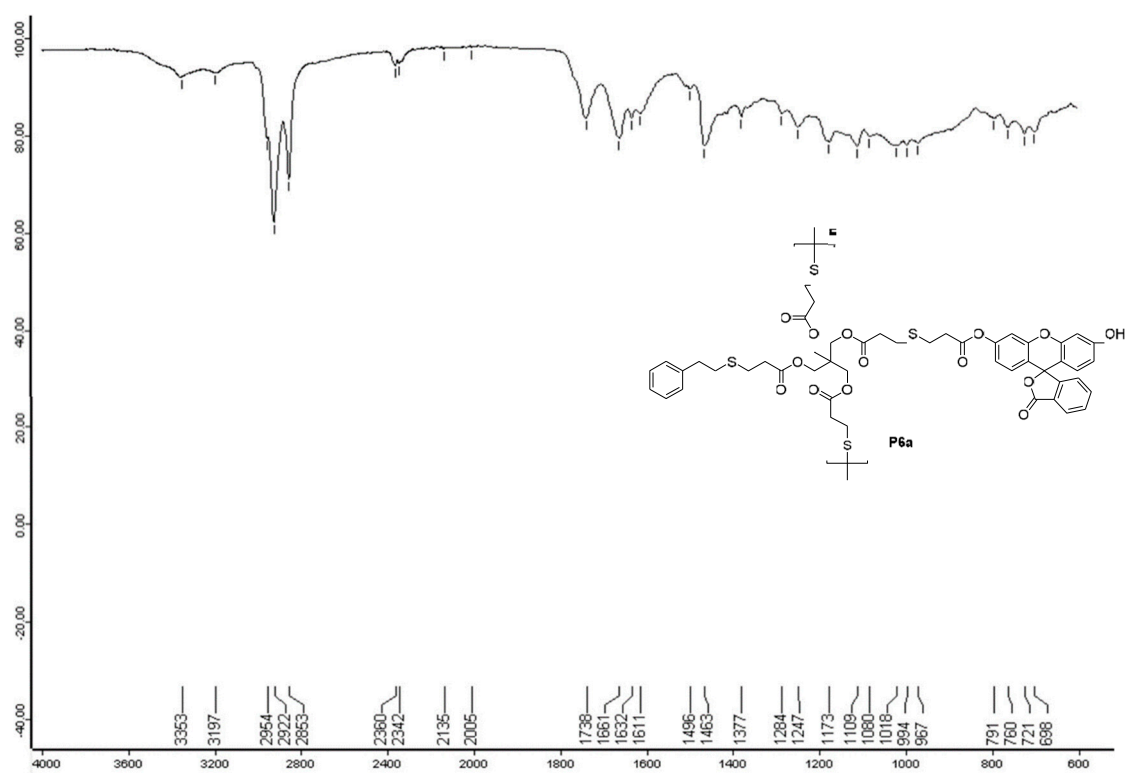


**Figure S12.** <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) of compound 7

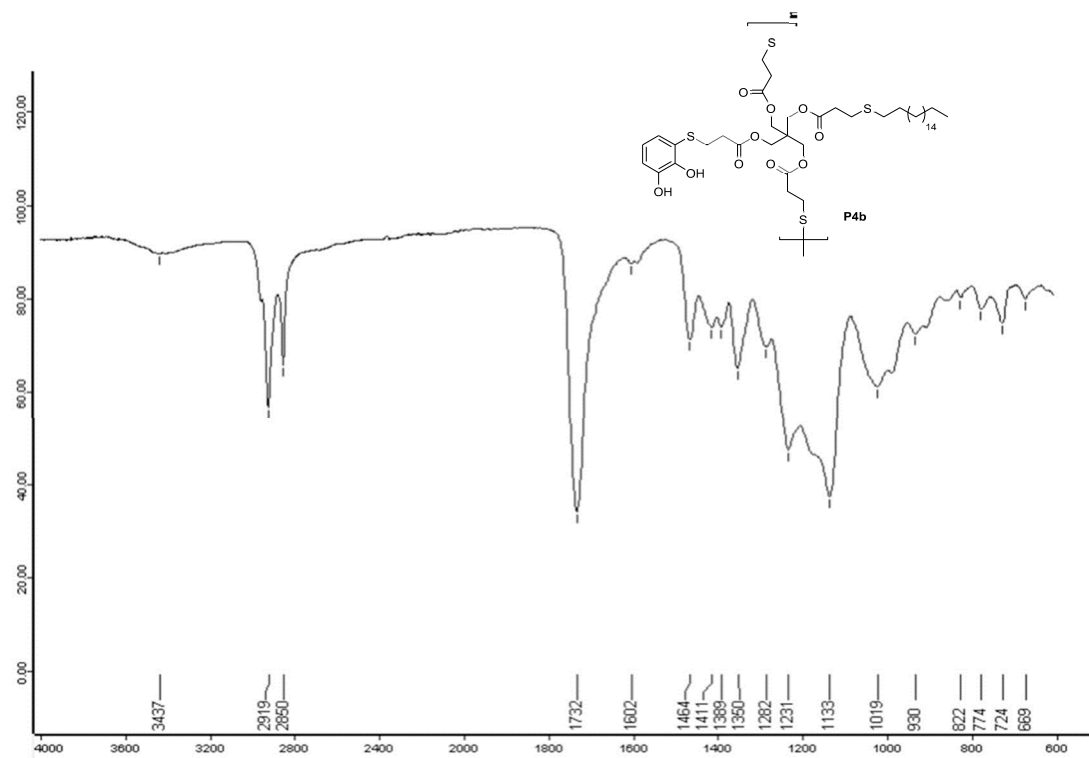
### S5. IR spectra of polymerization reaction products



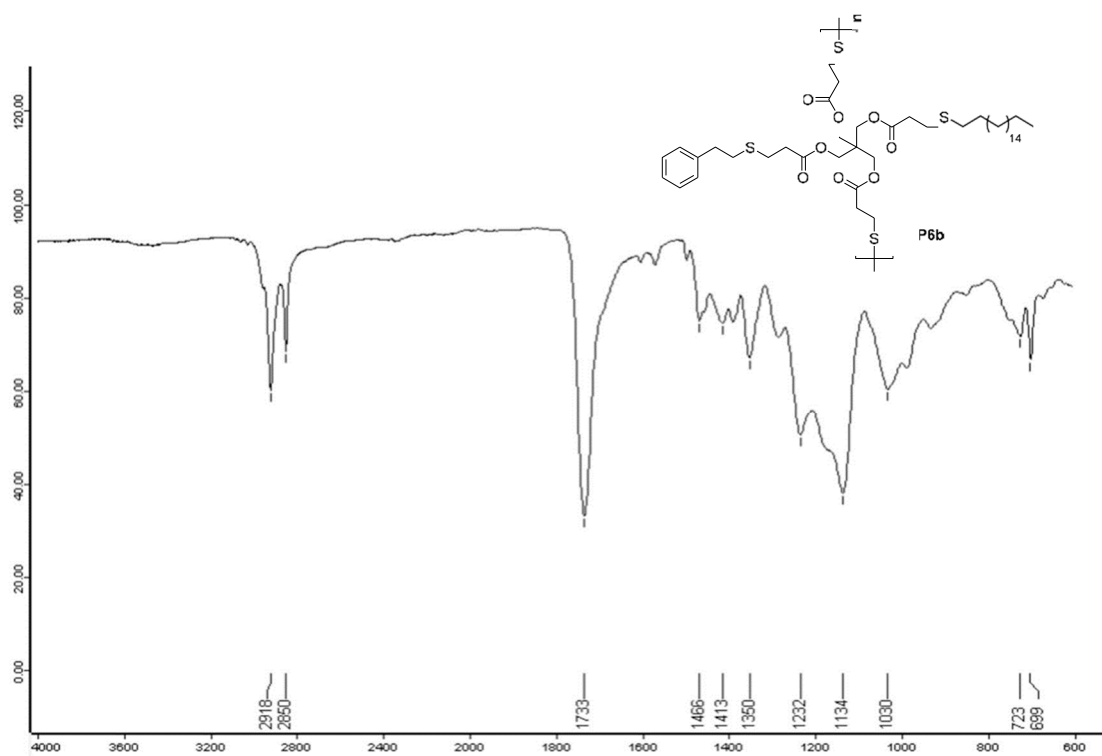
**Figure S13.** FT-IR spectrum of **P4a**



**Figure S14.** FT-IR spectrum of P6a



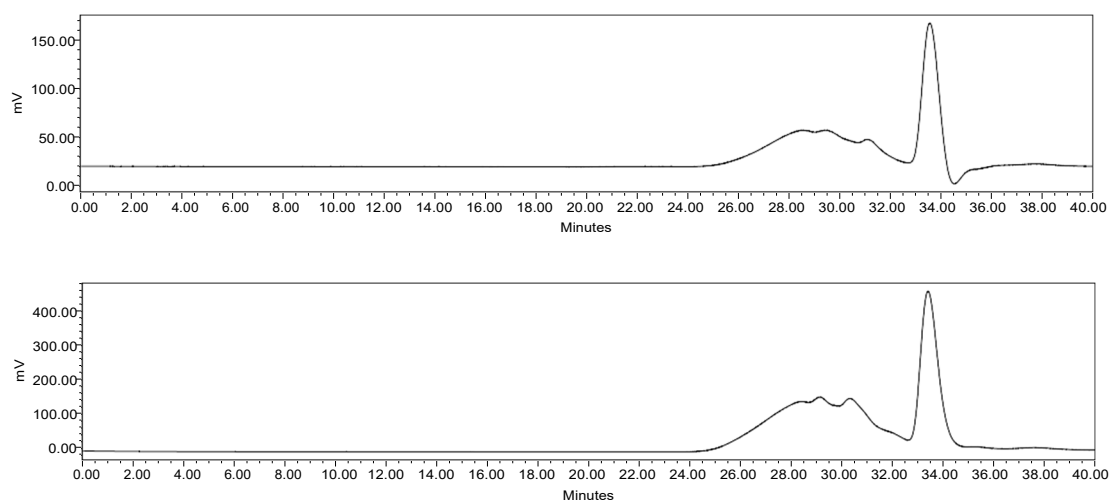
**Figure S14.** FT-IR spectrum of **P4b**



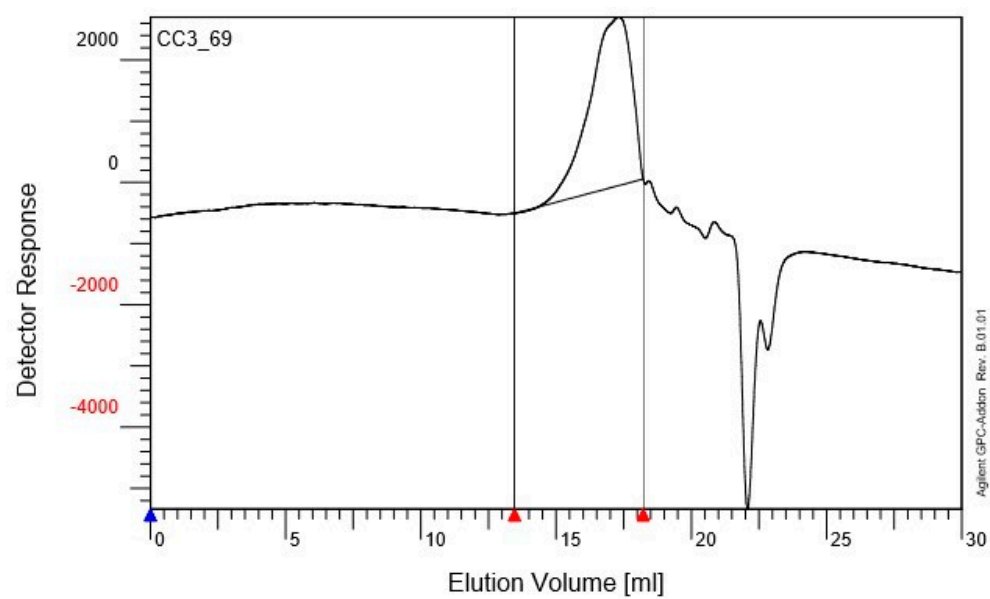
**Figure S15.** FT-IR spectrum of **P6b**



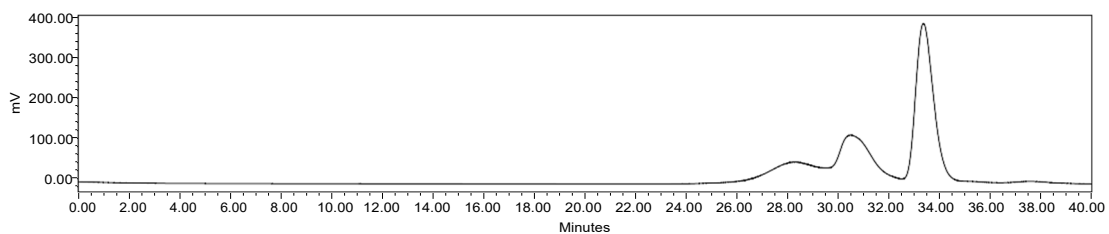
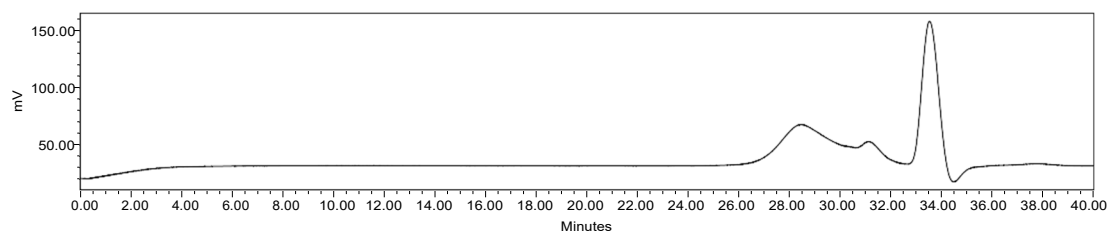
## S6. GPC SPECTRA



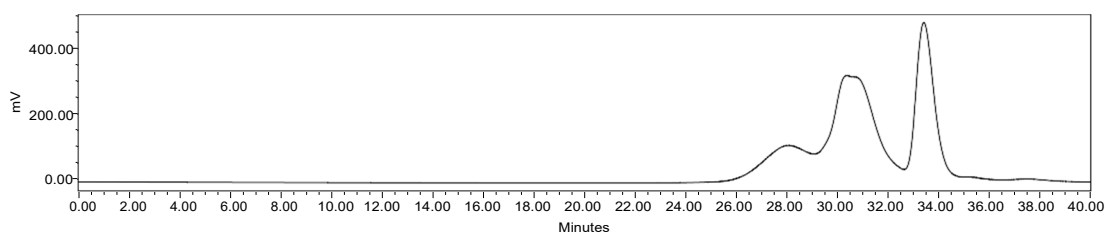
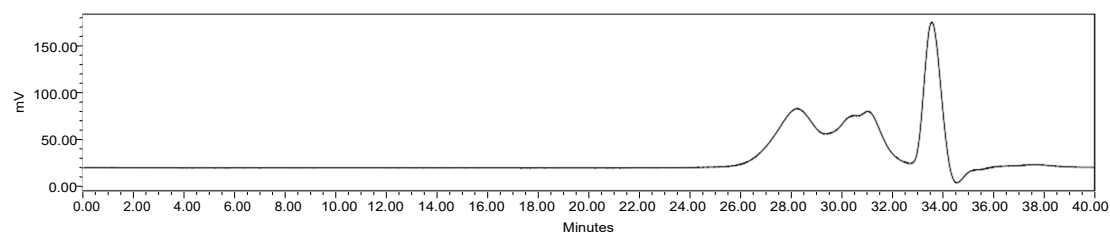
**Figure S16.** GPC spectra with both IR (top) and UV (bottom) detectors of building block **4b**



**Figure S17.** GPC spectrum with IR detector of **P4b**

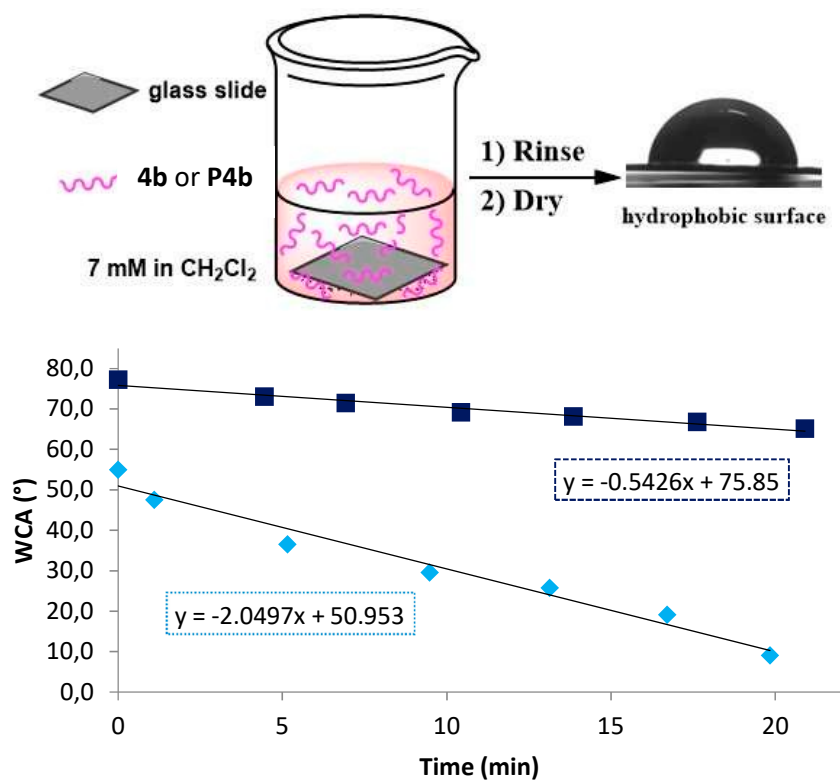


**Figure S18.** GPC spectra with both IR (top) and UV (bottom) detectors of building block **6b**



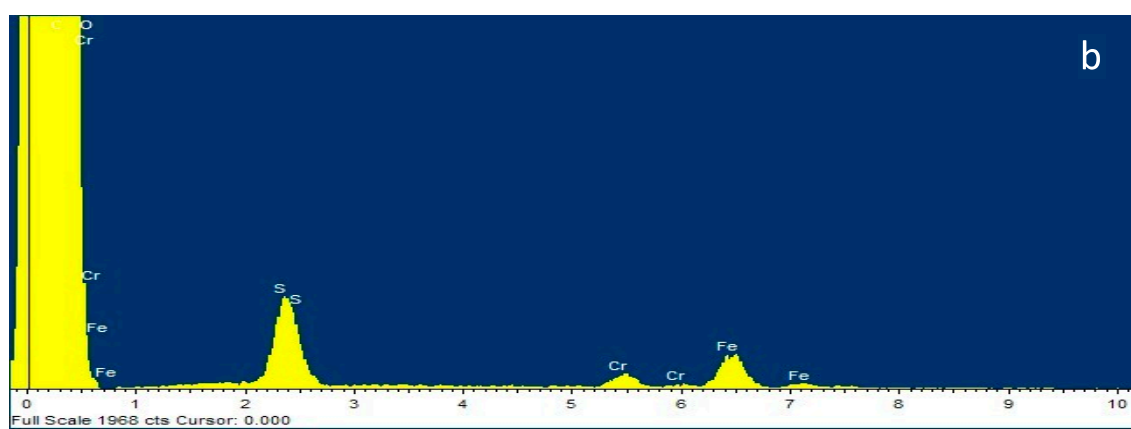
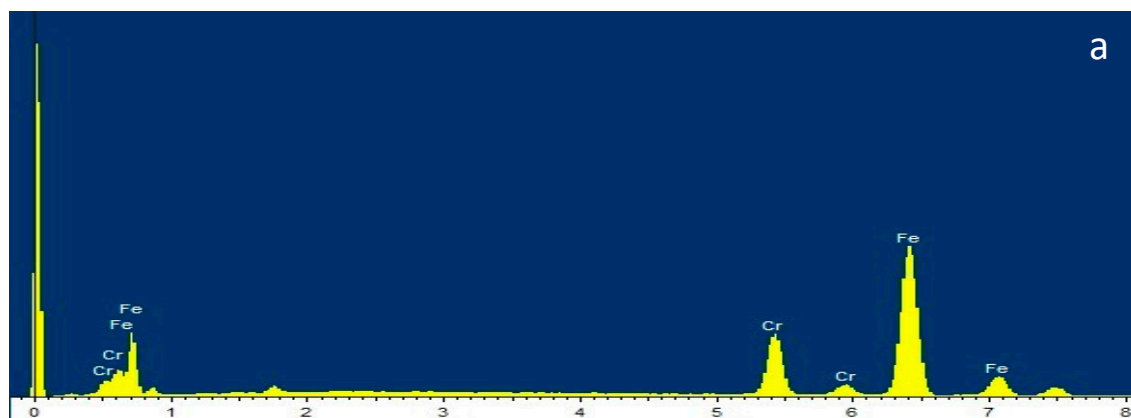
**Figure S19.** GPC spectra with both IR (top) and UV (bottom) detectors of building block **P6b**

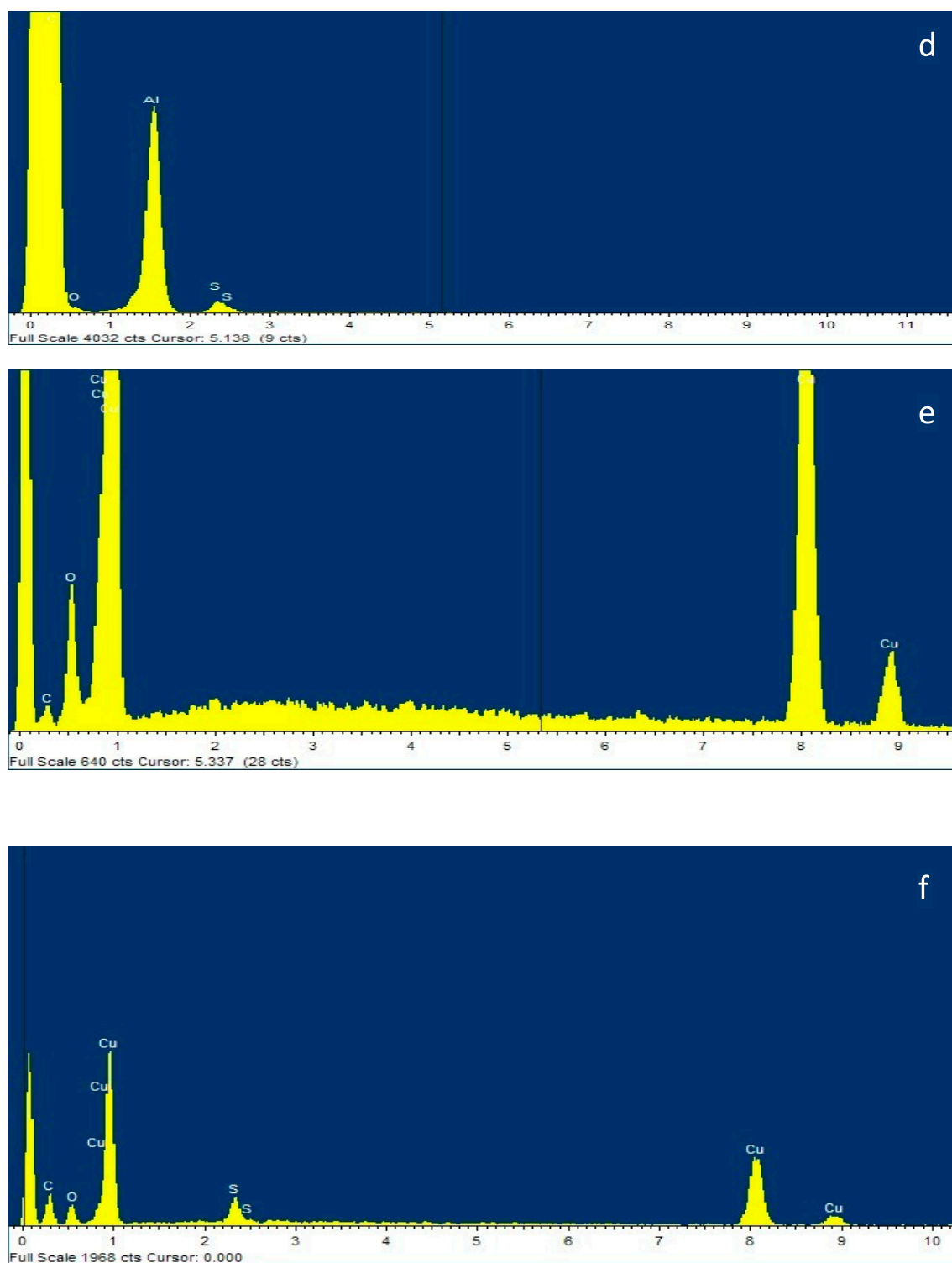
## S7. Coating procedure



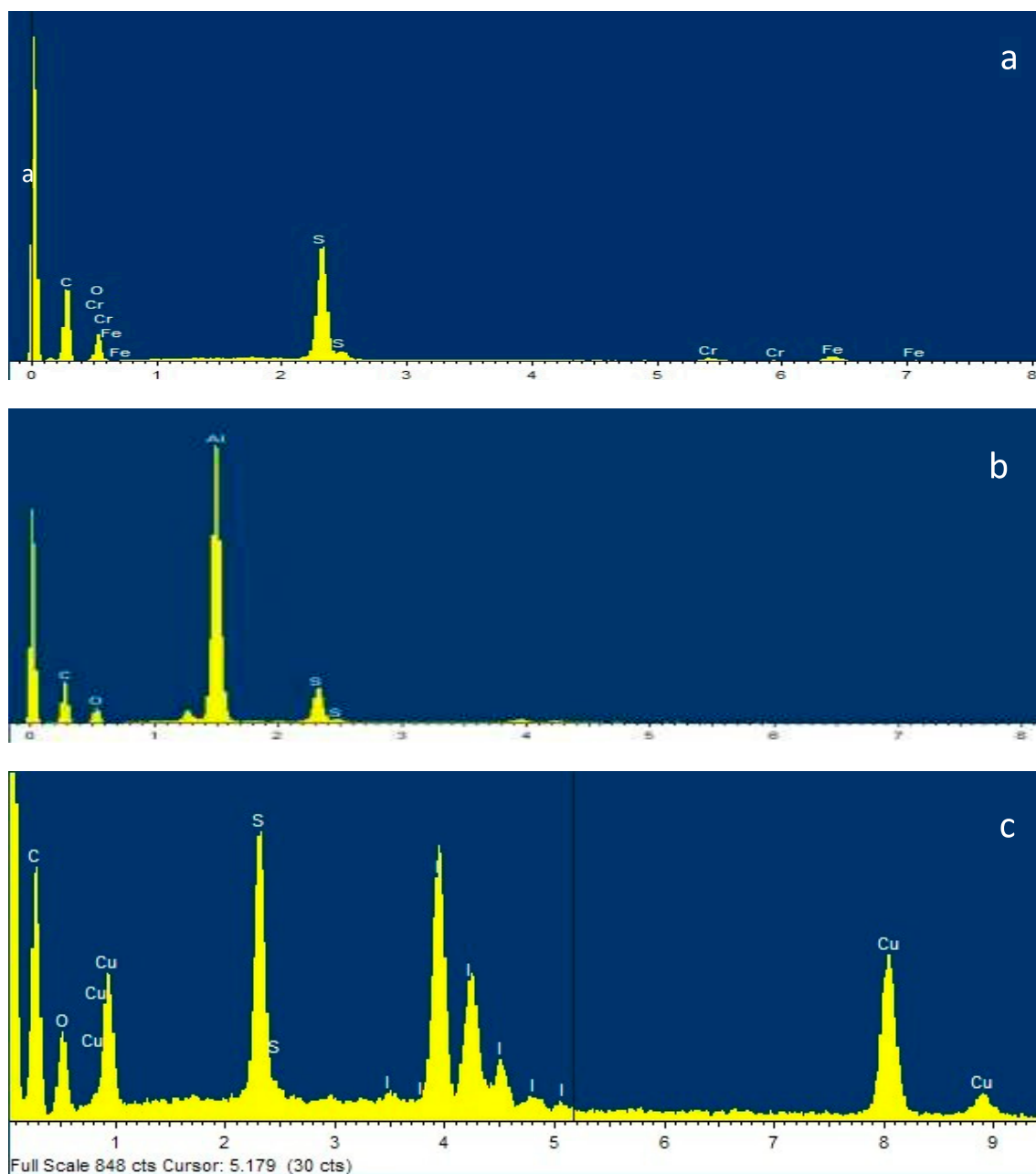
**Figure S20.** Schematic representation of coating procedure. The glass slide is submerged into the solution for at least 4 h, washed and dried before measuring WCAs. WCA values vs. time of **4b**-coated glass slide (light blue) and **P4b**-coated glass slide (dark blue).

## S8. EDX SPECTRA



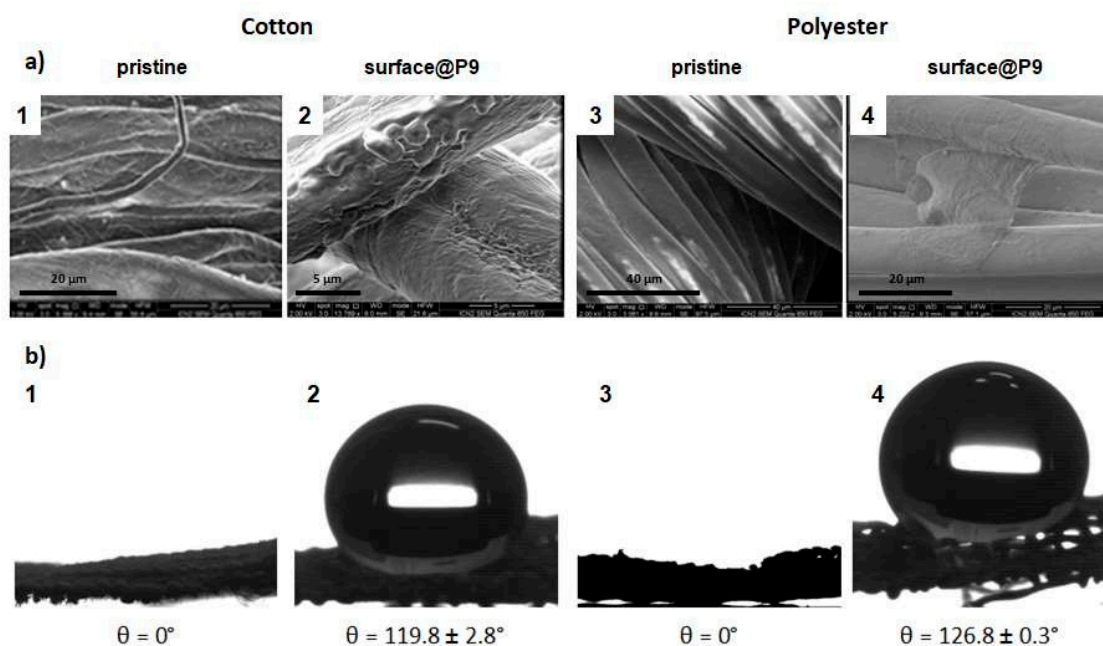


**Figure S21.** Images from EDX experiments of pristine and coated surfaces with P4b *via ex situ* polymerisation in solution: a) pristine stainless steel (SS), b) SS@P4b, c) pristine aluminium, d) Al@P4b, e) pristine copper and f) Cu@P4b.



**Figure S22.** Images from EDX experiments of coated surfaces with P4b *via in situ* polymerisation: (a)SS@P4b, b) Al@P4b and c) Cu@P4b.)

## S9. Characterization of coated textiles



**Figure S.23.** a) SEM images of pristine fibres (1 and 3), and **P4b**-coated textiles (2 and 4). b) Images from water droplets onto pristine fibres (1 and 3) and **P4b**-coated textiles (2 and 4).