
# Supporting Information

for *Macromol. Rapid Commun.*, DOI: 10.1002/marc.202000314

# On Demand Light-Degradable Polymers Based on 9,10-Dialkoxyanthracenes

Fabian Becker, Marvin Klaiber, Matthias Franzreb, Stefan Bräse, and Joerg Lahann*

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## Content

# 1 - General information

All reactions were carried out under argon using Schlenk techniques

## Materials:

All chemicals were purchased from VWR, Sigma-Aldrich, Alfa Aesar, ABCR or Merck and used as received unless otherwise mentioned.

Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60, $F_{254}$ plates. Flash column chromatography was performed using Merck silica gel (60, particle size 0.063-0.0200 mm). Visualization on TLC was achieved by use of UV light (254 nm), KMnO4 or iodine stain.

**Characterization:**

Nuclear Magnetic Resonance Spectroscopy (NMR). 1H-NMR spectra were recorded using a Bruker Avance 400 spectrometer operating at 400 MHz using DMSO-d6 with tetramethylsilane (TMS) as internal standard as solvent. 13C-NMR spectra were recorded using a Bruker 400 spectrometer operating at 100 MHz using DMSO-d6 with TMS as internal standard as solvent. Otherwise noted, standard experimental conditions and standard pulse sequences were used. For quantitative 1H-NMR, spectra were recorded over 64 scans at 298 K with interpulse delay D1 = 5 s. Chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for 1H NMR is recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplett), coupling constant (Hz), integration, assignment. Data for 13C NMR is reported in terms of chemical shift (δ, ppm) and assignment.

Mass spectrometric data was obtained using a Finnigan Mat 95 (EI / FAB) or Q Exactive Plus Orbitrap (ASAP) and is reported as m/z.

ATR-IR spectra were recorded using a Bruker ALPHA FT-IR spectrometer and are reported as cm-1.

UV/Vis spectra were recordet using an Agilent Cary 100 spectrometer.

**Gel Permeation Chromatography (GPC):**

Molecular weights and dispersities were determined by gel permeation chromatography on a Tosoh EcoSEC HLC-8320 SEC system with hexafluoro isopropanol (HFIP) containing 0.1 wt.% potassium trifluoroacetate as the solvent. The solvent flow was 0.40 mL/min at 30°C. The analysis was performed on a three column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10,000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). The system was calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, Mp 102 – 981 000 Da). Samples were prepared by dissolving the polymer at 1 w/v% and filtered through a PTFE syringe filter (0.2 µm pore size).

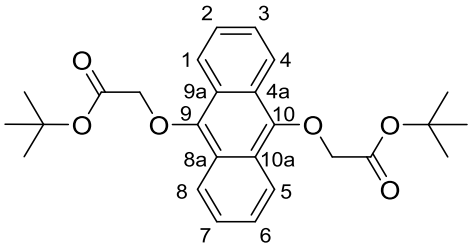
**Confocal Laser Scanning Microscopy (CLSM):**

CLSM images were recorded with TCS SP5 from LEICA MICROSYSTEMS. For the 3D reconstruction TCS SPE from LEICA MICROSYSTEMS was used. Parameters for the PAPA compartment: Excitation at 405 nm and emission at 420–480 nm. Parameters for the PLGA/PTDPV compartment: Excitation at 488 nm and emission at 500–620 nm.

## 2 - Synthesis and Polymerization

**Monomers**

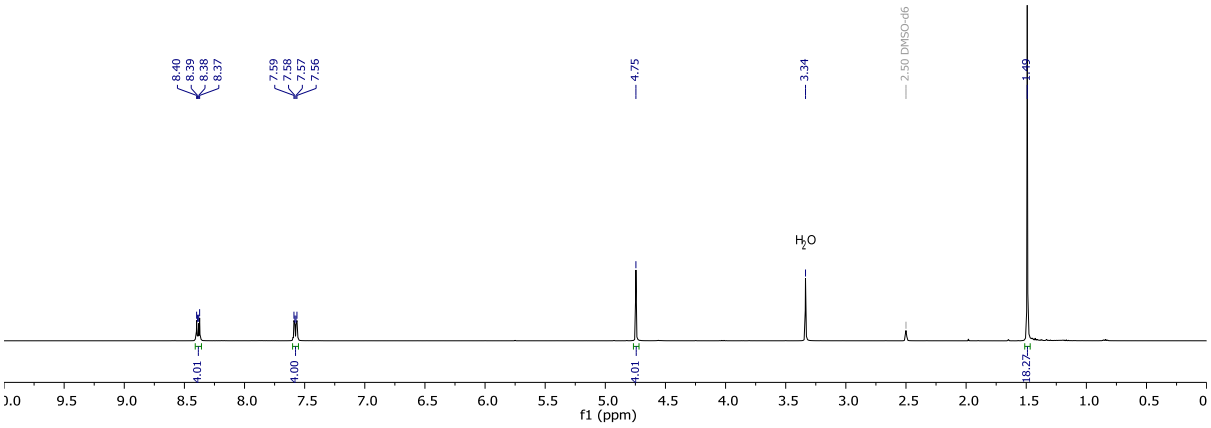
**Di-tert-butyl 2,2'-(anthracene-9,10-diylbis(oxy))diacetate - 6**




$C_{26}H_{30}O_6$

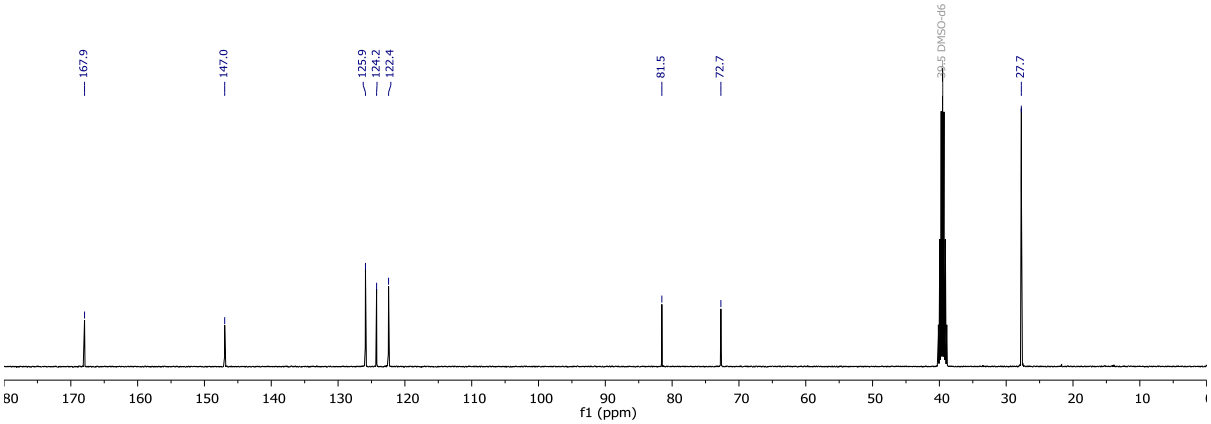
Di-tert-butyl 2,2'-(anthracene-9,10-diylbis(oxy))diacetate **6** was synthesized with a procedure similar to the one reported by KÖNIG.[a] To 9,10-anthraquinone (10.0 g, 48.1 mmol, 1.0 eq.) in a degassed mixture of dichlormethane and water (1:1 v:v, 500 ml) was added Adogen 464 (2.3 ml, 2.07 g, 4.96 mmol, 0.1 eq.) and $Na_2S_2O_4$ (19.9 g, 97.2 mmol, 2.0 eq.). After stirring for 10 min, NaOH (19.8 g, 491 mmol, 10.2 eq.) was added and the solution turned dark red. After 10 min, *tert*-butyl bromoacetate (37 ml, 49.2 g, 244.7 mmol, 5.0 eq.) was added over 30 min and the mixture was allowed to stir for 3 days. The phases were separated and the aqueous phase was washed with DCM (3 × 50 ml). The combined organic layers were washed with water (100 ml), 1M $Na_2CO_3$ (100 ml), brine (100 ml) and dried over $MgSO_4$. After filtration over silica (DCM:EE 6:1) the solvent was removed under reduced pressure and the residue was dried under high vacuum over night before it was triturated twice in pentane (2 × 30ml). The product was obtained as yellow solid (17.4 g, 39.7 mmol, 83 %).

**$^1$H-NMR** (400 MHz, DMSO-$d_6$) δ = 8.39 (dd, J = 6.7, 3.2 Hz, 4H, 1-H, 4-H, 5-H, 8-H), 7.58 (dd, J = 6.8, 3.2 Hz, 4H, 2-H, 3-H, 6-H, 7-H), 4.75 (s, 4H, OC***H*****$_2$**$CO_2$*t*Bu), 1.49 (s, 18H, $OCH_2CO_2$***tBu***) ppm.




[a] S. G. König, A. Mokhir, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 6544-6548.

**$^{13}$C-NMR** (101 MHz, DMSO-$d_6$) δ = 167.9 ($OCH_2\boldsymbol{C}O_2C(CH_3)_3$), 147.0 (C-9, C-10), 125.9 (C-2, C-3, C-6, C-7), 124.2 (C-4a, C-8a, C-9a, C-10a), 122.4 (C-1, C-4, C-5, C-8), 81.5 ($OCH_2CO_2\boldsymbol{C}(CH_3)_3$), 72.7 ($O\boldsymbol{C}H_2CO_2C(CH_3)_3$), 27.7 ($OCH_2CO_2C(\boldsymbol{C}H_3)_3$) ppm.

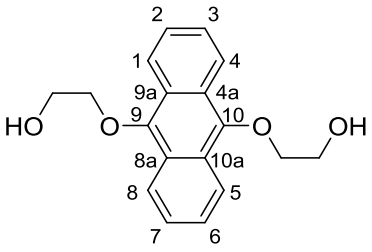



**IR** (ATR): ν = 2976.1, 2924.9, 1741.9, 1437.4, 1391.7, 1358.3, 1232.1, 1152.0, 1088.8, 1022.0, 776.8, 749.5, 670.7, 604.4, 435.9 $cm^{-1}$.

**HRMS** (ASAP): m/z = 438.2029 [$M^+$]; corresponds to the molecular formula $C_{26}H_{30}O_6$ (m/z = 438.2042).

The analytical properties match those reported in literature.[1]

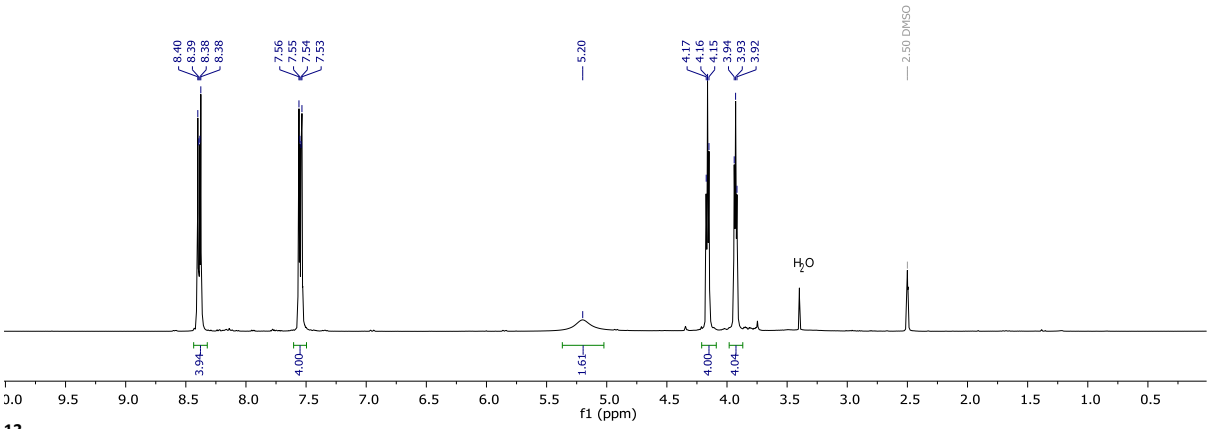
**2,2'-(Anthracene-9,10-diylbis(oxy))bis(ethan-1-ol) - 7**



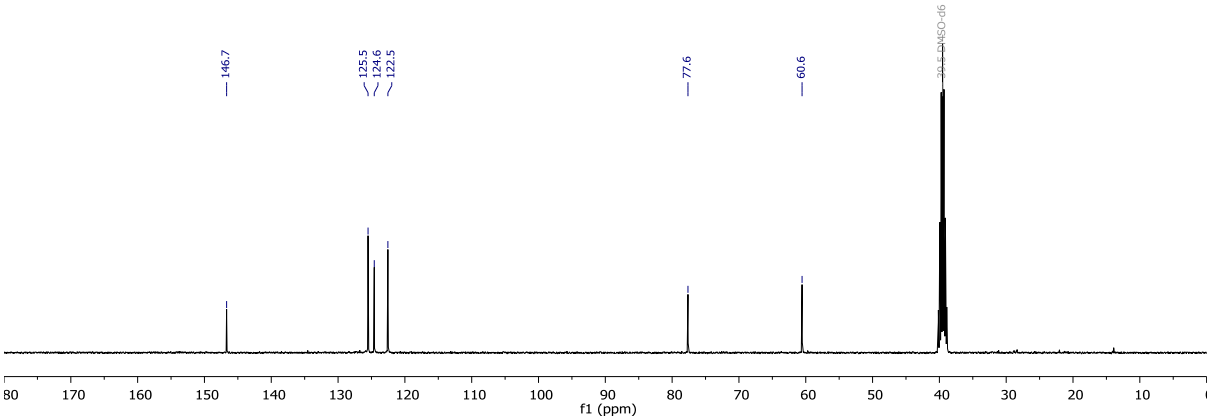

$C_{18}H_{18}O_4$

To Di-*tert*-butyl 2,2'-(anthracene-9,10-diylbis(oxy))diacetate **6** (5.17 g, 11.8 mmol, 1.0 eq.) in THF at 0°C (140 ml) was added $LiAlH_4$ (1.83 g, 47.3 mmol, 4.0 eq.). After 15 min the mixture was allowed to warm to room temperature and stirred for 3 h. Then, under ice cooling, excess $LiAlH_4$ was decomposed by addition of ethyl acetate (50 ml). The organic layer was washed with 2M HCl (2 × 100 ml), water (100 ml), brine (100 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was triturated in pentane (2 × 30 ml). The product was obtained as yellow solid (2.91 g, 9.75 mmol, 83 %).

**$^{1}$H-NMR** (400 MHz, DMSO-$d_6$) δ = 8.39 (dd, J = 6.7, 3.2 Hz, 4 H, 1-H, 4-H, 5-H, 8-H), 7.55 (dd, J = 6.7, 3.2 Hz, 4 H, 2-H, 3-H, 6-H, 7-H), 5.20 (br s, 1 H, O***H***), 4.16 (dd, J = 5.2, 4.1 Hz, 4 H, OC***H***$_2$CH$_2$OH), 3.93 (dt, J = 5.2 Hz, 4H, OCH$_2$C***H***$_2$OH) ppm.



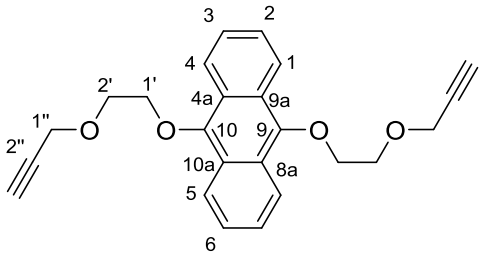

**$^{13}$C-NMR** (101 MHz, DMSO-$d_6$) δ = 146.7 (C-9, C-10), 125.5 (C-2, C-3, C-6, C-7), 124.6 (C-4a, C-8a, C-9a, C-10a), 122.5 (C-1, C-4, C-5, C-8), 77.6 (O***C***H$_2$CH$_2$OH), 60.6 (OCH$_2$***C***H$_2$OH) ppm.




**HRMS** (EI): m/z = 298.1206 [M$^+$]; corresponds to the molecular formula $C_{18}H_{18}O_4$ (m/z = 298.1205).

**IR** (ATR): ν = 3472.6, 2924.3, 1618.7, 1391.8, 1342.9, 1058.8, 1019.9, 877.4, 760.2, 676.9, 607.5, 416.4 cm$^{-1}$.

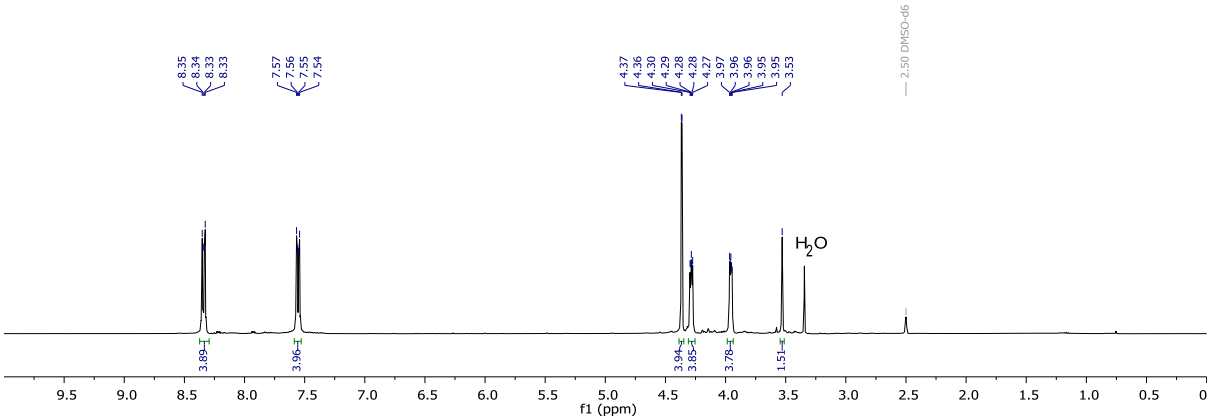
**9,10-Bis(2-(prop-2-yn-1-yloxy)ethoxy)anthracene - 8**



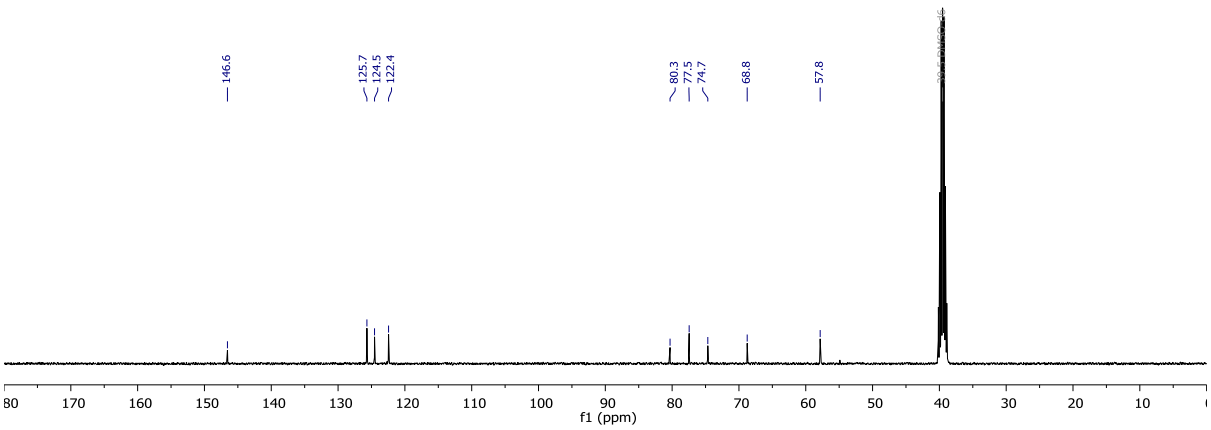

$C_{24}H_{22}O_4$

To a solution of 2,2'-(Anthracene-9,10-diylbis(oxy))bis(ethan-1-ol) **7** (3.22 g, 10.8 mmol, 1.0 eq.) in THF (100 ml) was cooled to 0°C and sodium hydride (60 wt% in mineral oil, 1.31 g corresponds to 0.79 g of pure NaH, 32.6 mmol, 3.0 eq.) was added. After 5 min Propargyl bromide (80 wt% in toluene, 6.0 ml, corresponds to 6.43 g Propargyl bromide, 53.9 mmol, 5.0 eq.) was added and the mixture was allowed to stir for three days at room temperature. The mixture was diluted with ethyl acetate (150 ml) and washed with water (2 × 50 ml). The solvent was removed under reduced pressure and the crude product purified by column chromatography on silica (hexanes/ethyl acetate 3:1, $R_f$ = 0.5)). The product was obtained as yellow solid (2.36 g, 6.29 mmol, 58 %).

**$^1$H-NMR** (400 MHz, $CDCl_3$) δ = 8.33 (dd, J = 6.8, 3.2 Hz, 1-***H***, 4-***H***, 5-***H***, 8-***H***, 4H), 7.56 (dd, J = 6.8, 3.2 Hz, 2-***H***, 3-***H***, 6-***H***, 7-***H***, 4H), 4.36 (d, J = 2.4 Hz, 1''-***H$_2$***, 4H), 4.30 – 4.27 (m, 1'-***H$_2$***, 4H), 3.97 – 3.94 (m, 2'-***H$_2$***, 4H), 3.53 (t, J = 2.4 Hz, 3''-***H***, 2H) ppm.



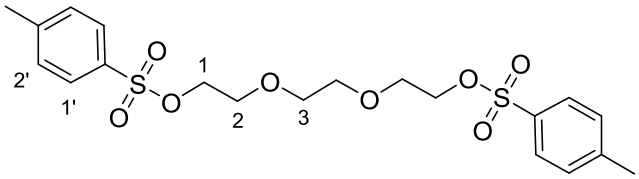

**$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 146.6 (C-9. C-10), 125.7 (C-2, C-3, C-6, C-7), 124.5 (C-4a, C-8a, C-9a, C-10a), 122.4 (C-1, C-4, C-5, C-8), 80.3 (C-2''), 77.5 (C-3''), 74.7 (C-1'), 68.8 (C-2'), 57.8 (C-1'') ppm.




**HRMS** (EI): m/z = 374.1517 [$M^+$]; corresponds to the molecular formula $C_{24}H_{24}O_4$ (m/z = 374.1518).

**IR** (ATR): ν = 3245.2, 2940.1, 1391.4, 1344.5, 1102.0, 1055.0, 1027.6, 891.0, 758.6, 677.0, 471.2 $cm^{-1}$.

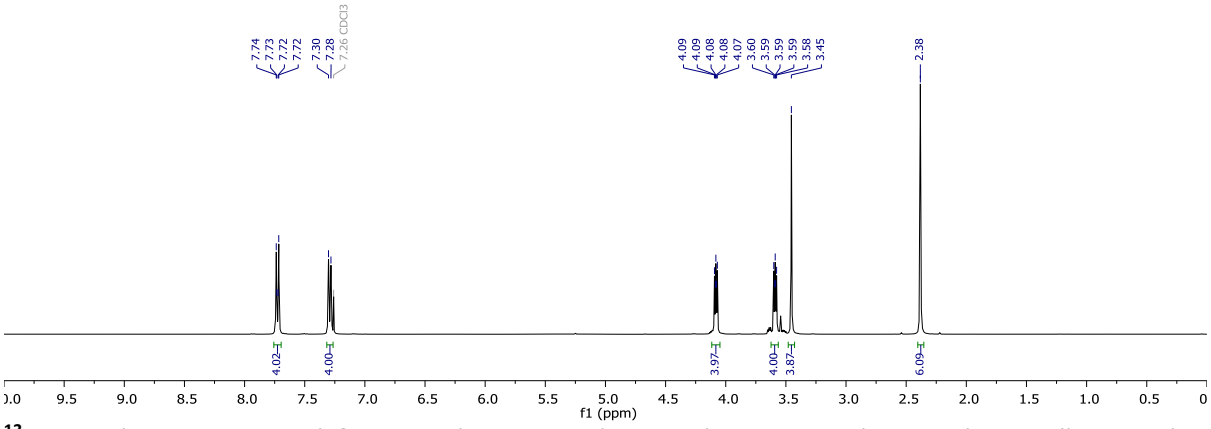
**1,2-Bis(2-tosylethoxy)ethane**



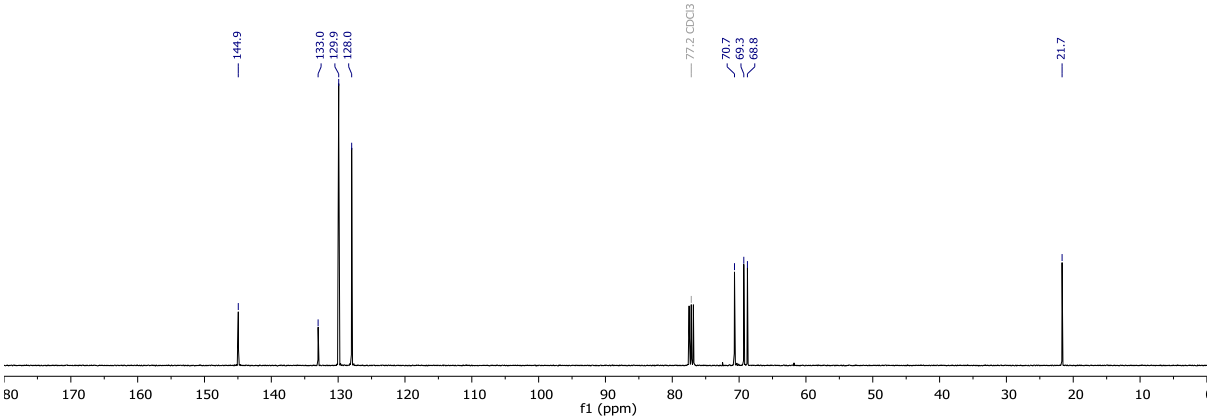

$C_{20}H_{26}O_8S_2$

To Triethylene glcyol **9** (14.6 ml, 16.4 g, 109 mmol, 1.0 eq.) and 4-toluenesulfonyl chloride (43.8 g, 230 mmol, 2.1 eq.) in DCM (190 ml) was slowly added freshly powdered KOH (49.2 g, 877 mmol, 8.0 eq.) at 0°C. The mixture was stirred for 3 h at 0°C before ice water (200 ml) was added. The phases were separated and the organic layer was washed with water (100 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was obtained as colorless solid (50.0 g, 109 mmol, quant.).

**$^1$H-NMR** (400 MHz, $CDCl_3$) δ =7.72 (d, J = 8.1 Hz, 4H, 4 × 1'-H), 7.29 (d, J = 8.1 Hz, 4H, 4 × 2'-H), 4.08 (t, J = 4.8 Hz, 4H, 1-$H_2$, 6-$H_2$), 3.59 (t, J = 4.8 Hz, 4H, 2-$H_2$, 5-$H_2$), 3.45 (s, 4H, 3-$H_2$, 4-$H_2$), 2.38 (s, 6H, 2 × Ar-C***$H_3$***) ppm.




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 144.9 (2 × ***C***$_{AR}$-$CH_3$), 133.0 (2 × ***C***$_{AR}$-$SO_3R$), 129.9 (4 × C-1'), 128.0 (4 × C-2'), 70.7 (C-3, C-4), 69.3 (C-2, C-5), 68.8 (C-1, C-6), 21.7 (Ar-***C***$H_3$) ppm.

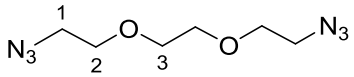



**HRMS** (ASAP): m/z = 459.113 $[M + H]^+$; corresponds to the molecular formula ($C_{20}H_{26}O_8S_2$ + H) = $C_{20}H_{27}O_8S_2$ (m/z = 459.115).

The analytical properties match those reported in the literature.[b]

[b] E. M. D. Keegstra, J. W. Zwikker, M. R. Roest, L. W. Jenneskens, *J. Org. Chem.* **1992**, *57*, 6678-6680.

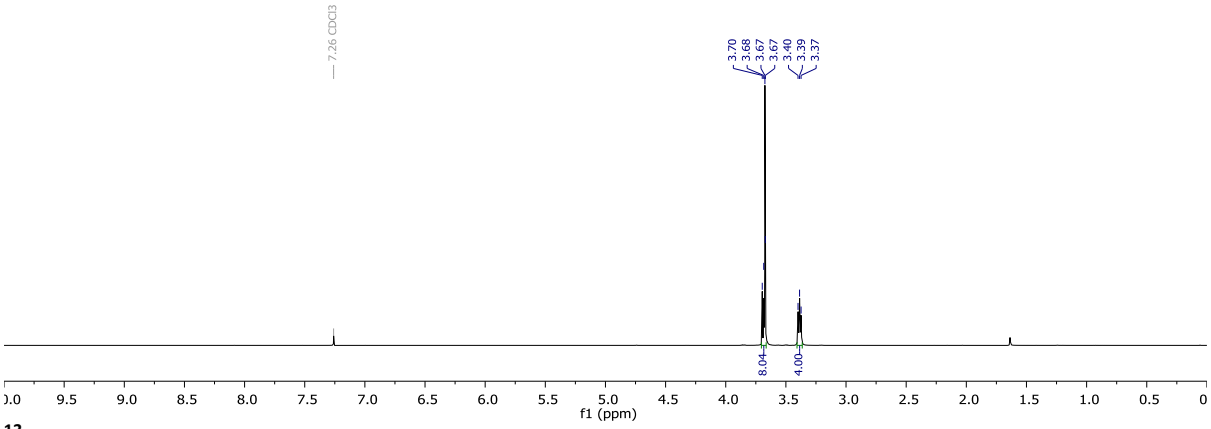
**1,2-Bis(2-azidoethoxy)ethane - 10**



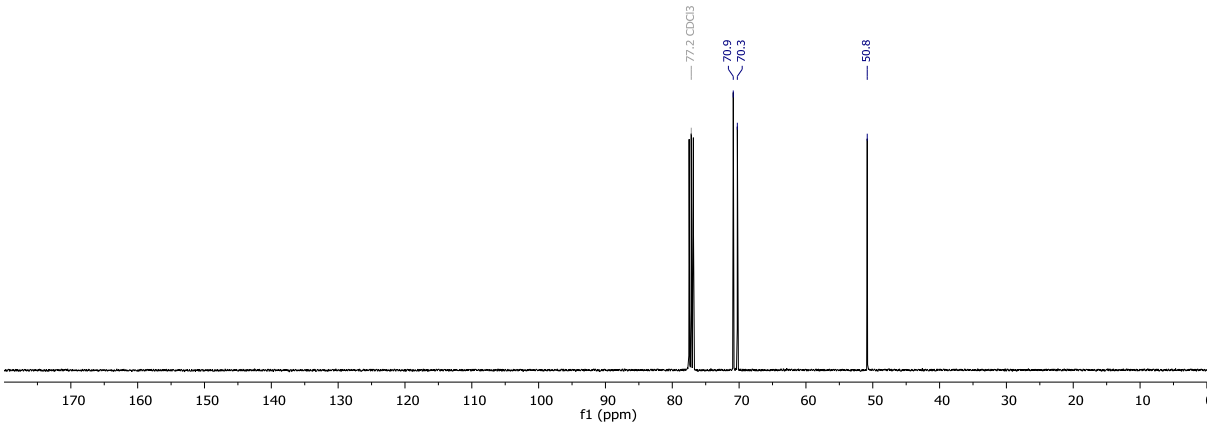

$C_6H_{12}N_6O_2$

1,2-Bis(2-azidoethoxy)ethane **10** was synthesized according to a procedure by CHANG.[c] To 1,2-Bis(2-tosylethoxy)ethan (20.5 g, 44.8 mmol, 1.0 eq.) in DMF (230 ml) was added $NaN_3$ (14.7 g, 226 mmol, 5.1 eq.). The mixture was heated to 80°C for 20 h. The mixture was concentrated to about 20 ml and diluted with ethyl acetate (300 ml) and water (200 ml). The phases were separated and the organic layer was washed with water (6 × 100 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was obtained as colorless oil (7.73 g, 38.6 mmol, 86 %).

**$^1$H-NMR** (400 MHz, $CDCl_3$) δ = 3.67 (s, 4H, 3-$H_2$, 4-$H_2$), 3.63 (d, J = 5.6, 4.3 Hz, 4H, 1-$H_2$, 6-$H_2$), 3.39 (dd, J = 5.6, 4.3 Hz, 4H, 2-$H_2$, 5-$H_2$) ppm.




**$^{13}$C-NMR** (101 MHz, $CDCl_3$) δ = 70.9 (C-2, C-6), 70.3 (C-4, C-4), 50.8 (C-1, C-8) ppm.



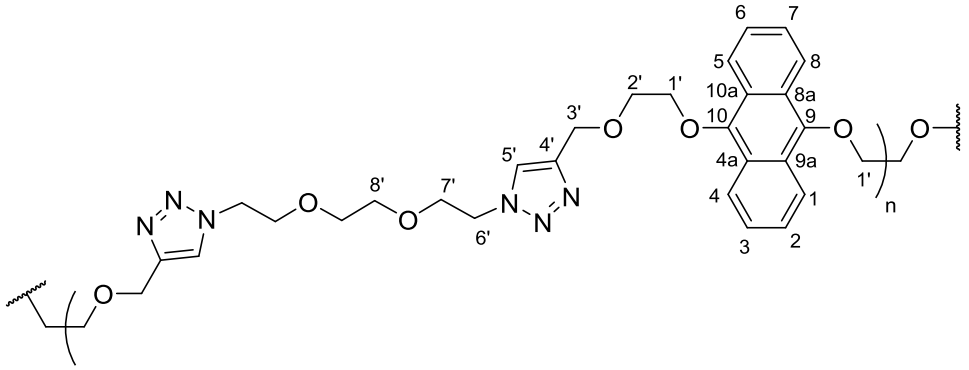

**HRMS** (ASAP): m/z = 173.103 $[M - N_2 + H]^+$; corresponds to the molecular formula ($C_6H_{12}N_6O_2 - N_2 + H$) = $C_6H_{13}N_4O_2$ (m/z = 173.104).

[c] K. N. More, J. Y. Lee, D.-Y. Kim, N.-C. Cho, A. Pyo, M. Yun, H. S. Kim, H. Kim, K. Ko, J.-H. Park, D.-J. Chang, *Bioorg. Med. Chem. Lett.* **2018**, *28*, 915-921.

The analytical properties match those reported in the literature.[e]

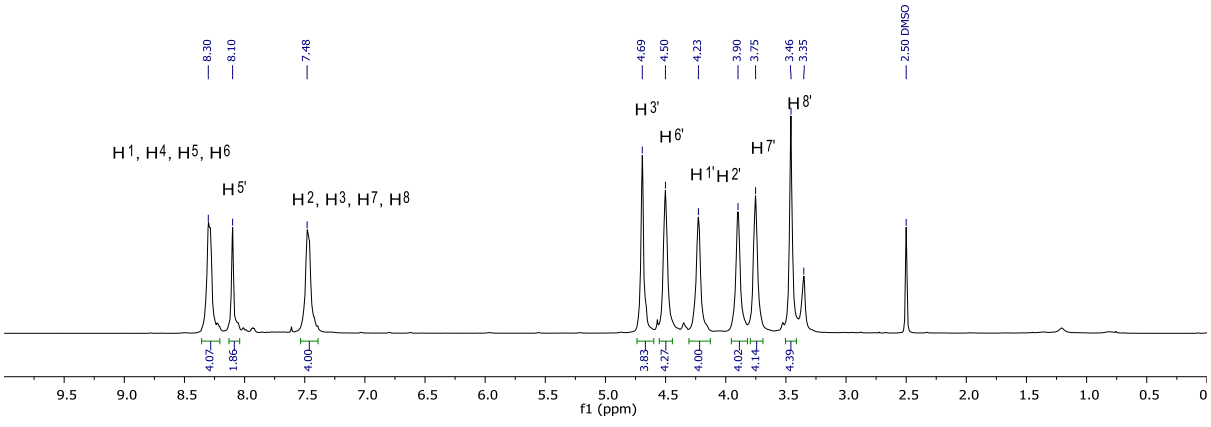
**Polymerization**

**Poly-[(1,2-bis(2-azidoethoxy)ethane)-*alt*-(9,10-bis(2-(prop-2-yn-1-yloxy)ethoxy)anthracene)] - PAPA**

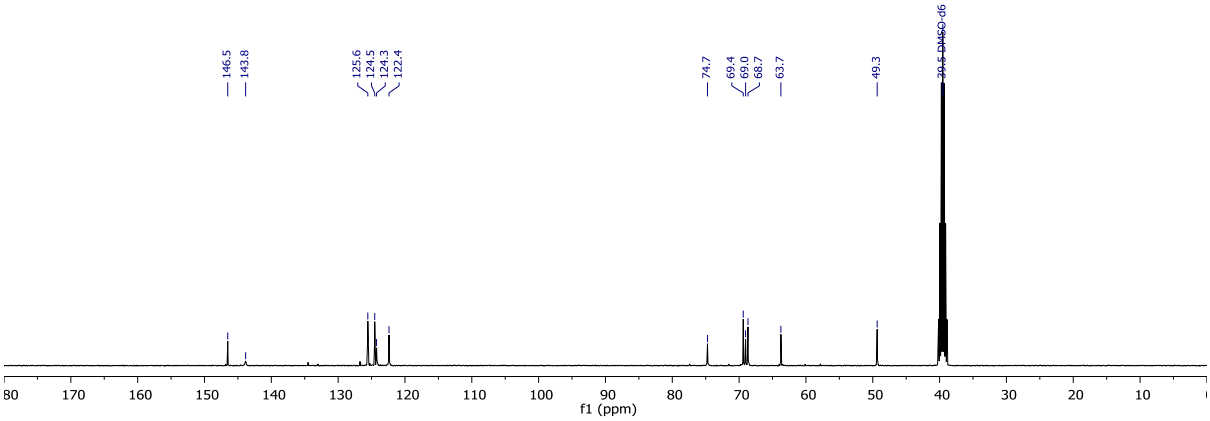



9,10-Bis(2-(prop-2-yn-1-yloxy)ethoxy)anthracene **8** (674 mg, 1.80 mmol, 1.0 eq.), 1,2-Bis(2-azidoethoxy)ethane **10** (360 mg, 1.80 mmol, 1.0 eq.), $CuSO_4 \cdot 5H_2O$ (10.8 mg, 43.3 µmol, 2 mol%) and 6.0 mL DMF were charged in a 20 mL vial. This vial was capped with a teflon septum and bubbled with argon for 50min, followed by quick addition of sodium ascorbate (32.7 mg, 0.17 mmol, 9 mol%). The mixture was then allowed to stir at room temperature for 2.5 d before it was diluted with DCM (150 ml) and washed with water (6 × 40 ml). The solvent was removed under reduced pressure and the residue was triturated in acetone (3 × 10 ml). After drying under high vacuum, the product was obtained as brown solid (927 mg, 90%, Mn (1H-NMR): 14800 g/mol, GPC in HFIP Mn: 12700 g/mol, Mw: 22000 g/mol Mz: 35400 g/mol Đ: 1.74.).

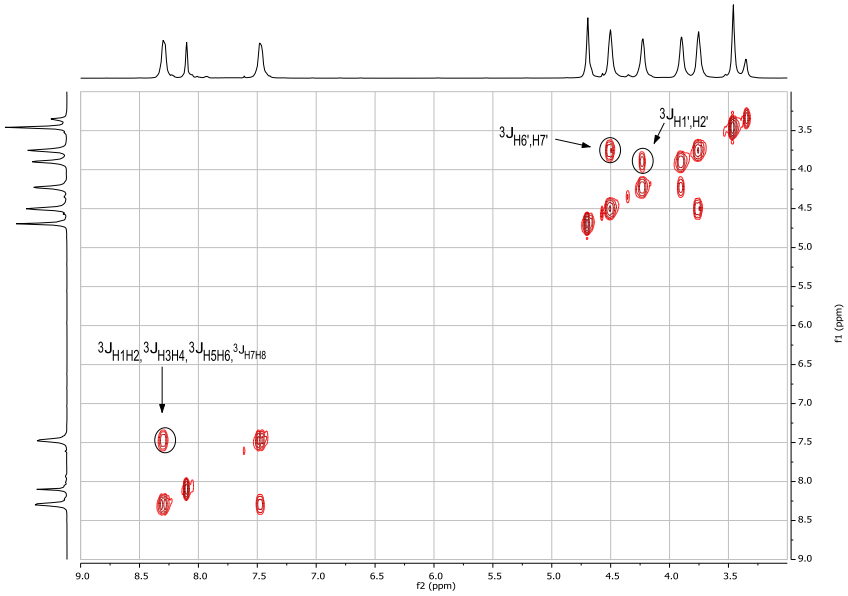
**$^1$H-NMR** (400 MHz, DMSO-$d_6$) δ = 8.30 (1-H, 4-H, 5-H, 8-H), 8.10 (5‘-H), 7.48 (2-H, 3-H, 6-H, 7-H), 4.69 (3’-H), 4.50 (6‘-H, assigned via HMBC cross peak with C-5‘), 4.23 (1’-H), 3.90 (2’-H), 3.75 (7‘-H), 3.46 (8‘-H) ppm.



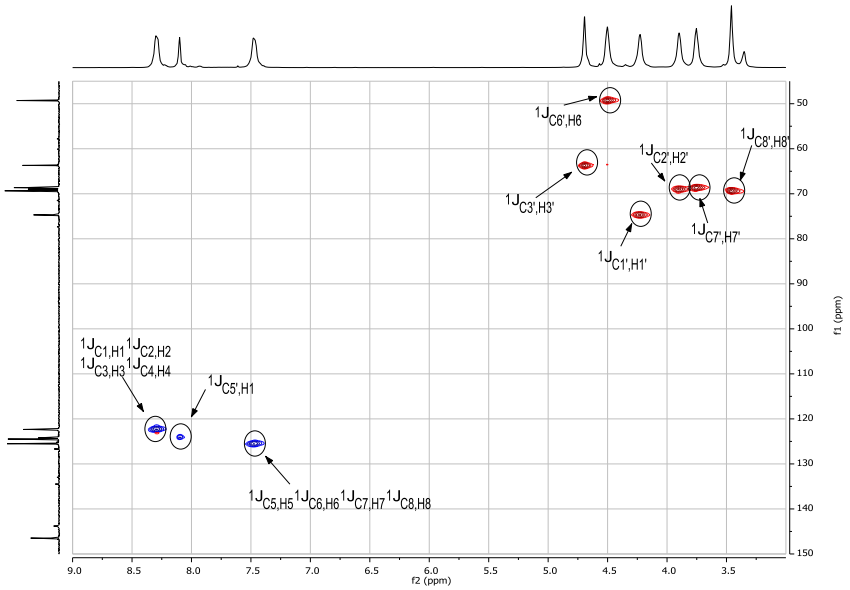
**$^{13}$C-NMR** (101 MHz, DMSO-$d_6$) δ = 146.5 (C-4a, C-8a, C-9a, C-10a), 143.8 (C-4‘), 125.6 (C-2, C-3, C-6, C-7), 124.3 (C-5‘), 122.4 (C-1, C-4, C-5, C-8), 74.7 (C-1’), 69.4 (C-8’), 69.0 (C-2’), 124.5 (C-9, C-10), 68.7 (C-7’), 63.8 (C-3’), 49.3 (C-6’) ppm.



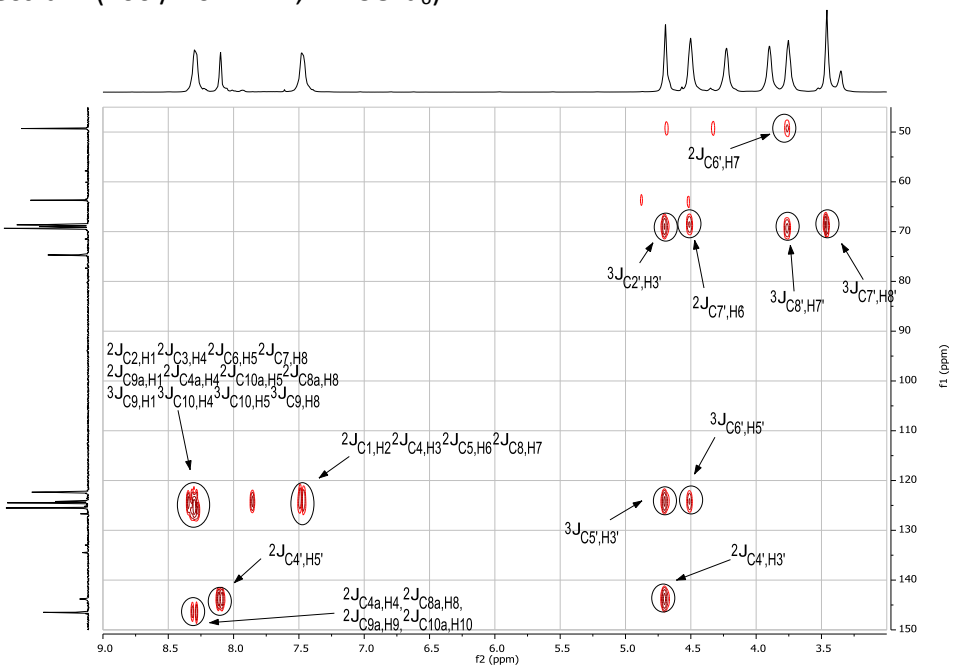

**Cosy spectrum** (400 MHz, DMSO-$d_6$)**:**



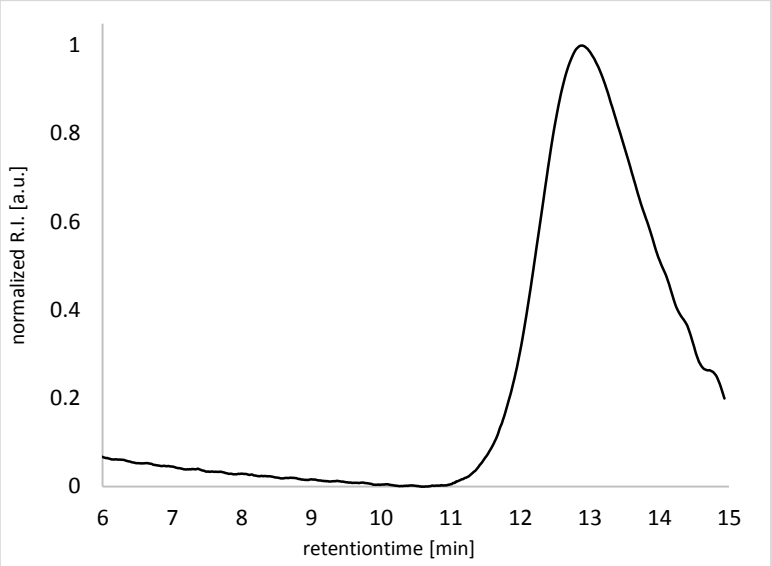

**edHSQC spectrum** (400 / 101 MHz, DMSO-$d_6$):




**HMBC spectrum** (400 / 101 MHz, DMSO-$d_6$):



GPC trace of PAPA in HFIP. $M_n$: 12700 g/mol, $M_w$: 220030 g/mol $M_z$: 35400 g/mol Đ: 1.74.



## 3 - Backbone cleavage experiments

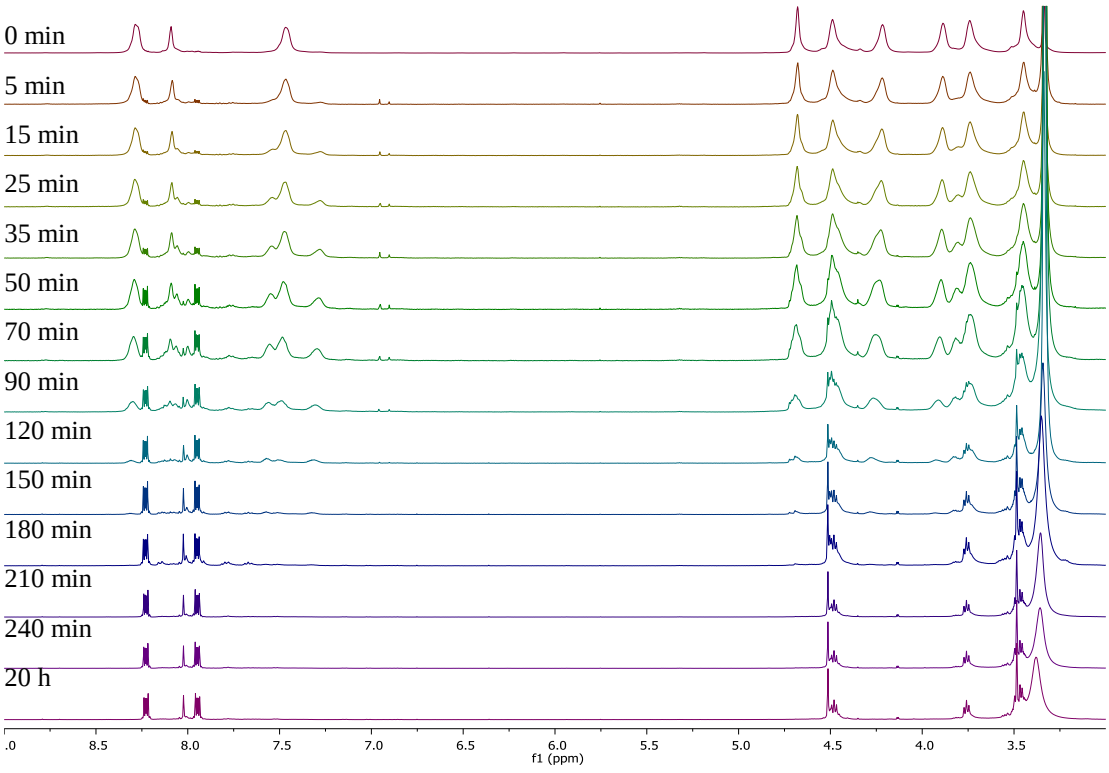
### General procedure for the backbone cleavage of PAPA

Polymer **PAPA** (50 mg) and Eosin Y (1.5 mg, 2.3 µmol, 3 wt.%) were added to a vial and dissolved in DMSO-$d_6$ (2 ml). The solution was illuminated by a 1 W green LED with 15° beam angle from a distance of 5 cm and air was bubbled through.

To monitor the reaction, aliquots of 0.1 ml were withdrawn by syringe at the given times, diluted to 0.5 ml with DMSO-$d_6$, and measured with the above given parameters for quantitative $^1$H-NMR. Signals of **PAPA** (7.47 and 8.30 ppm), EPO (7.30 and 7.56 ppm) and AQ (7.95 and 8.23 ppm) were integrated to determine their ratios and thus the backbone cleavage. Results were corrected for residual anthraquinone already present at the first recorded time point.

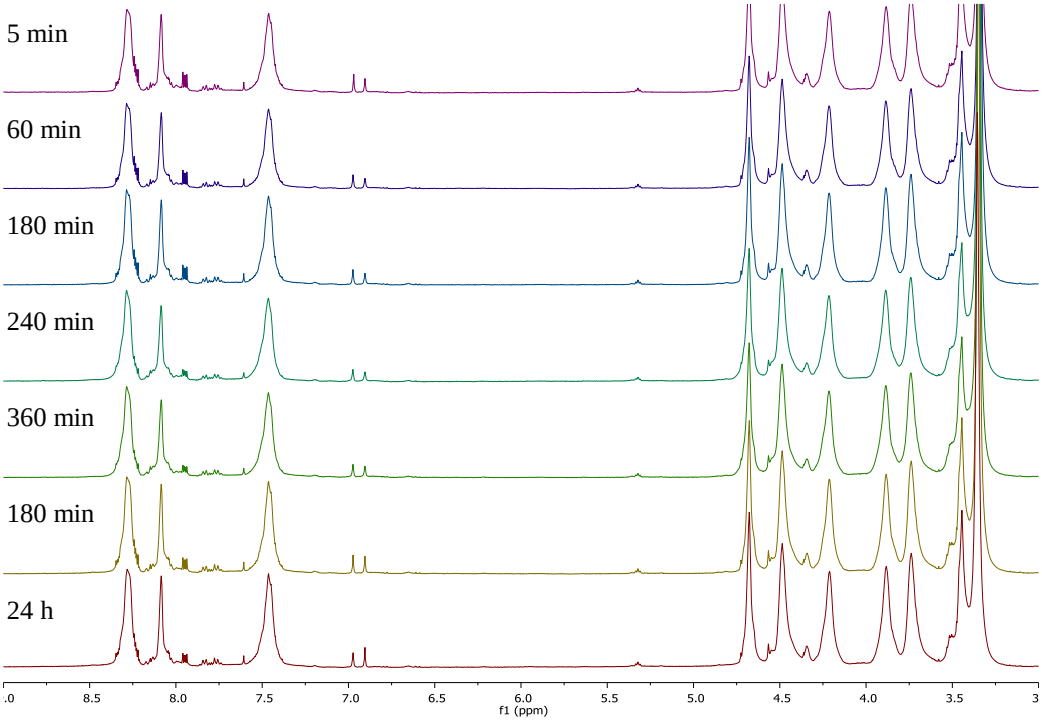
### $^1$H-NMR traces of backbone cleavage of PAPA

Conditions: Concentration of **PAPA** = 25 mg/ml in DMSO-$d_6$, 3 wt.% Eosin Y, illumination from a distance of 5 cm, 15° beam angle. Air was bubbled through a syringe needle connected to an aquarium pump.



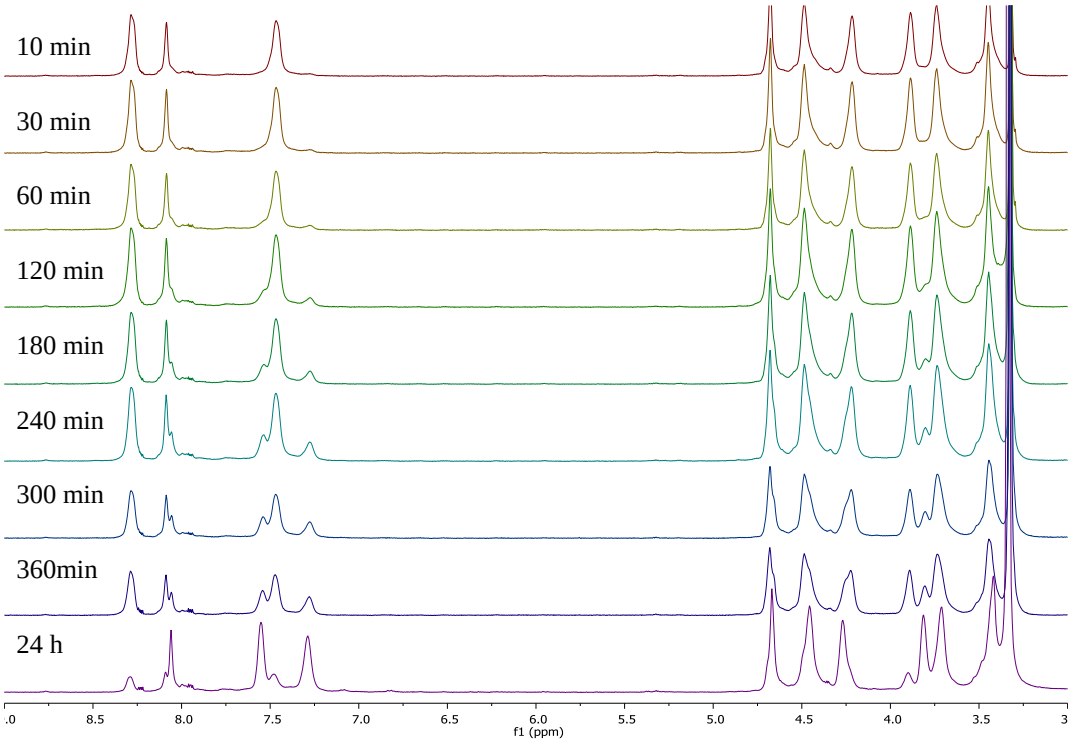
**$^1$H-NMR traces of blindtest for the backbone cleavage of PAPA – no oxygen**

Conditions: Concentration of **PAPA** = 25 mg/ml in degassed DMSO-$d_6$, 3 wt.% Eosin Y, illumination from a distance of 5 cm, 15° beam angle.



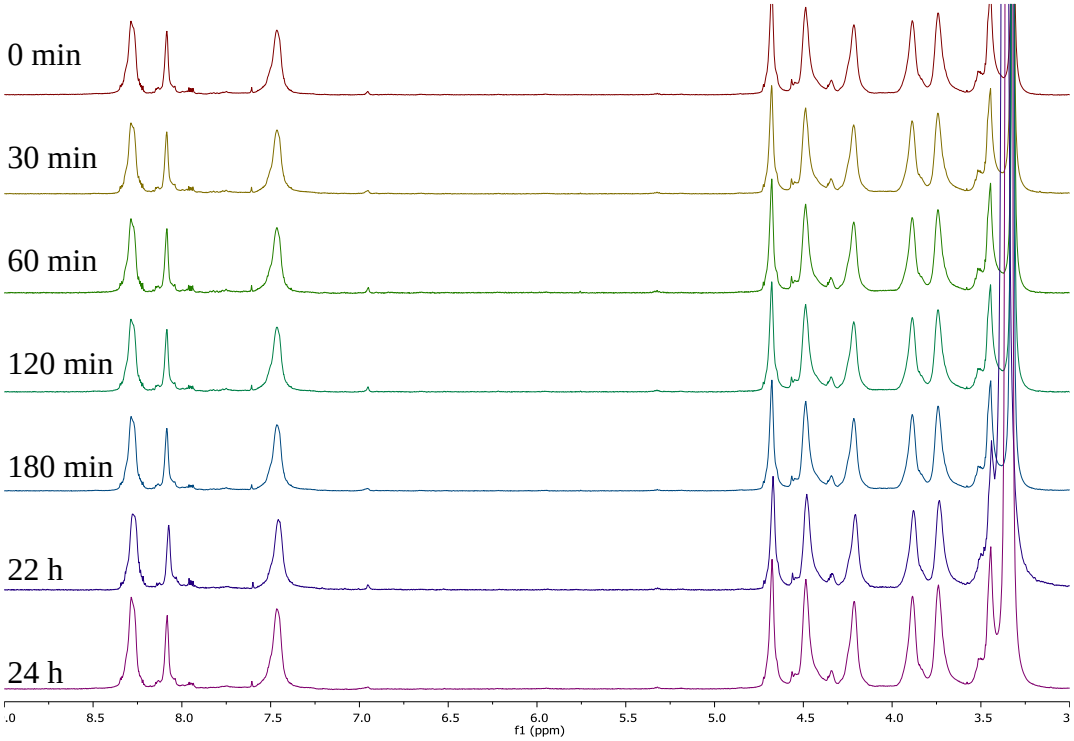

**$^1$H-NMR traces of blindtest for the backbone cleavage of PAPA – no photosensitizer**

Conditions: Concentration of **PAPA** = 25 mg/ml in DMSO-$d_6$, illumination from a distance of 5 cm, 15° beam angle. Air was bubbled through a syringe needle connected to an aquarium pump.



**$^{1}$H-NMR traces of blindtest for the backbone cleavage of PAPA – no light**

Conditions: Concentration of **PAPA** = 25 mg/ml in DMSO-$d_6$, 3 wt.% Eosin Y. Air was bubbled through a syringe needle connected to an aquarium pump. This experiment was conducted in the dark.



**$^1$H-NMR traces for the delayed backbone cleavage of PAPA**

Conditions: Concentration of **PAPA** = 25 mg/ml in DMSO-$d_6$, 12 wt.% Eosin-Na, illumination from a distance of 5 cm, 15° beam angle. Air was bubbled through a syringe needle connected to an aquarium pump.

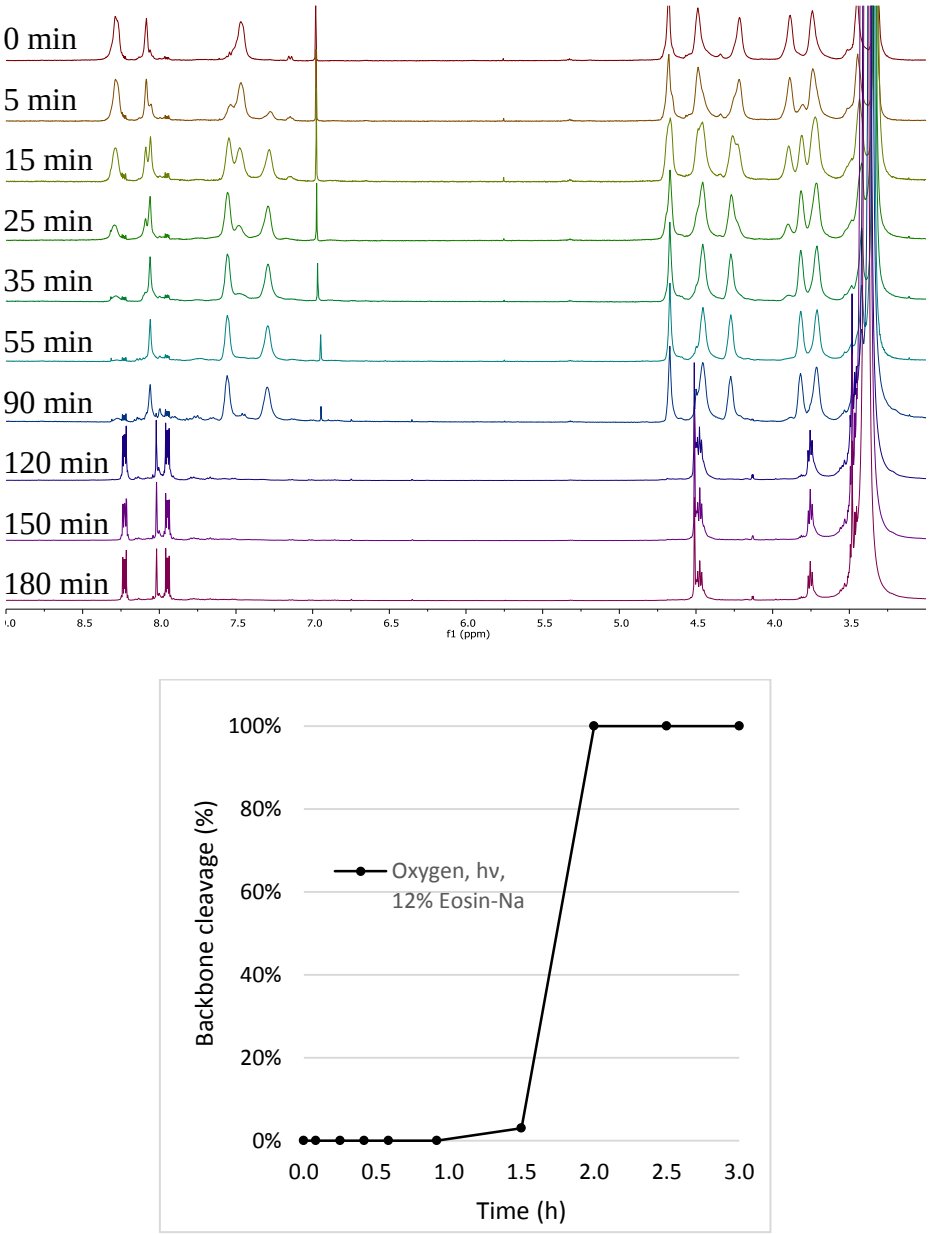



**Figure 1:** Delayed cleavage of **PAPA** in DMSO-$d_6$ over time. Cleavage starts after 1.5 h (3 %) and is complete after 2 h.

**Analysis of degradation products:**

Polymer **PAPA** (103 mg) was dissolved in a 20 mL vial in DMSO-$d_6$ (5.0 mL). A solution of Eosin Y (300 µl, 10 mg/mL in DMSO-$d_6$, 3 wt.%) were added. The solution was illuminated by a 1 W green LED with 15° beam angle from a distance of 5 cm and air was bubbled through. After full degradation, 0.2 ml were removed for a $^1$H-NMR comparison to anthraquinone **4** (see Figure 2). The remaining solution was diluted with $H_2O$ (5.0 mL) to precipitate anthraquinone **4**. The resulting suspension was centrifuged (5 min, 4000 rpm), decanted and the solvent was removed under reduced pressure. The residue was taken up in DMSO-$d_6$ (2.0 mL) and remaining anthraquinone **4** was again precipitated by addition of $H_2O$ (5.0 mL). The resulting suspension was centrifuged (5 min, 4000 rpm), decanted and the solvent was removed under reduced pressure. The obtained residue was analyzed by $^1$H- and $^{13}$C-NMR (spectra "watersoluble reside") as well as by mass spectrometry (HRMS- spectrum "MS (APCI) watersoluble reside").

**APCI**: m/z = 401.2121 $[M + H]^+$; corresponds to the molecular formula ($C_{16}H_{28}N_6O_6$ + H) = $C_{16}H_{29}N_6O_6$ (m/z = 401.2149).

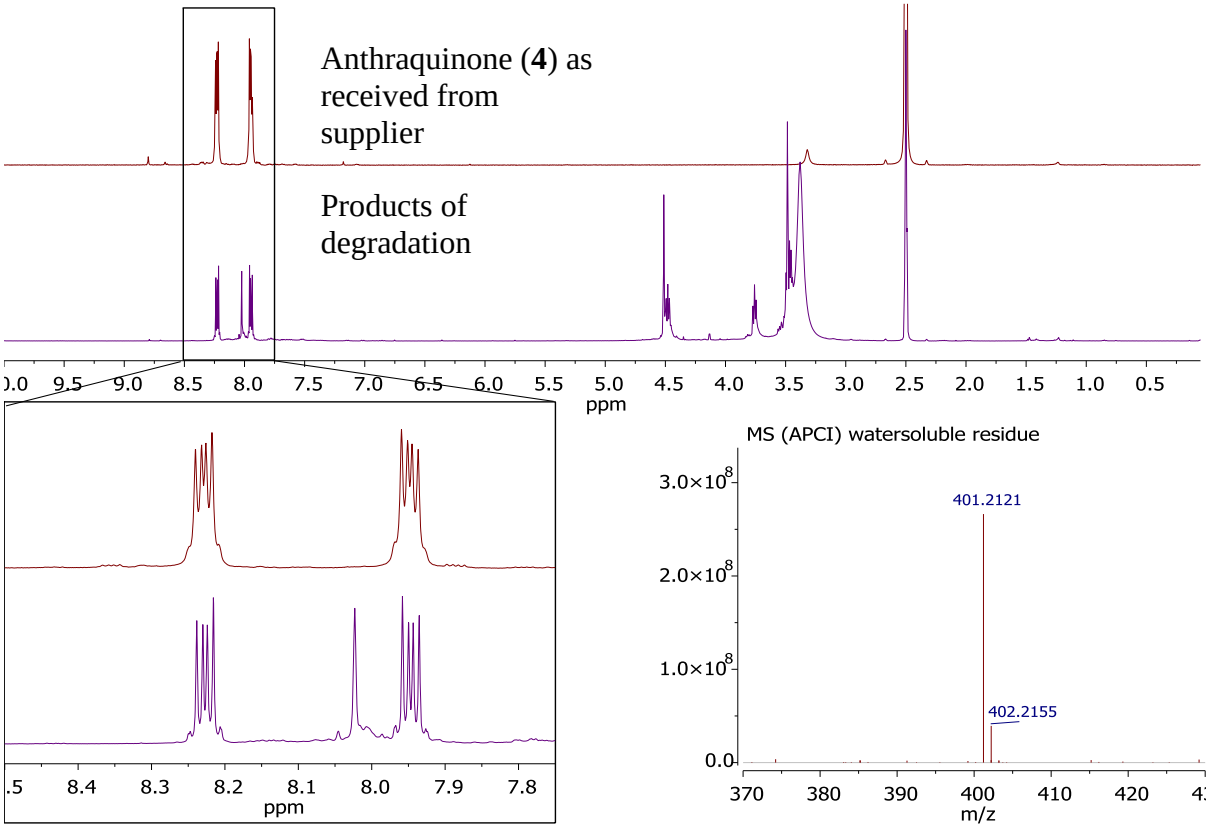
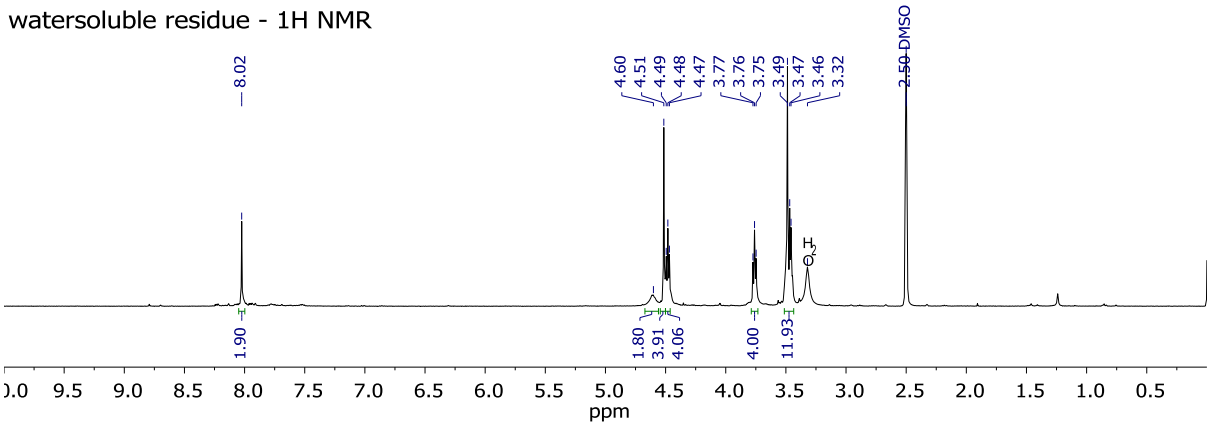
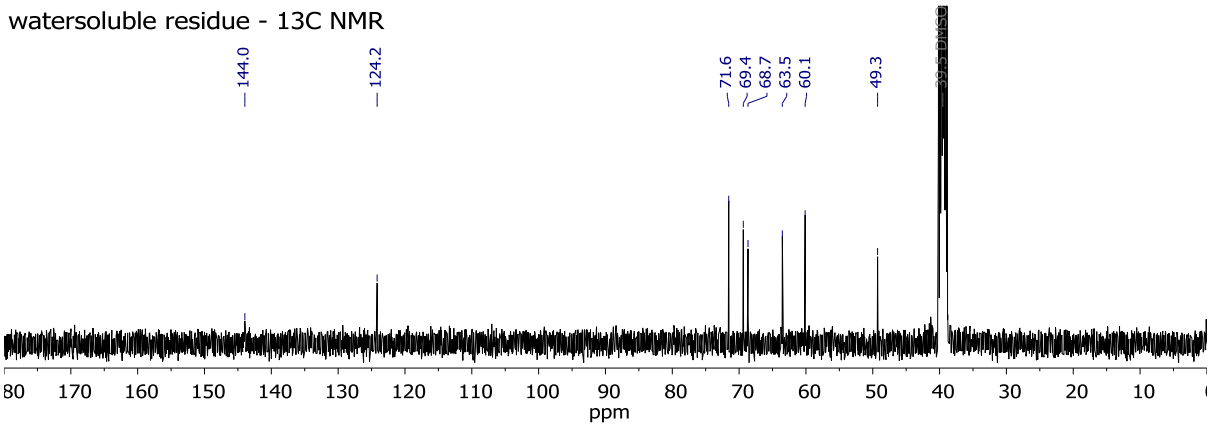



**Figure 2:** NMR comparisson and HRMS data of the degradation products.



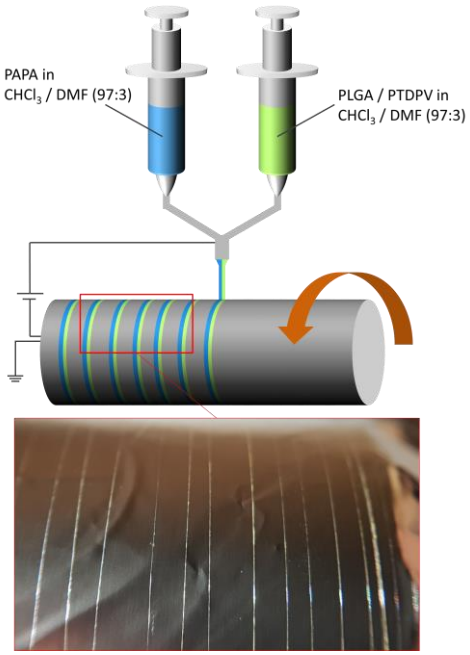

**$^{1}$H-NMR** (400 MHz, DMSO-$d_6$) δ = 8.02 (s, 2 H, 2 × 5-H), 4.60 (br. s, 2 H, 2 × OH), 4.51 (s, 4 H, 2 × 3-$H_2$), 4.48 (t, *J* = 5.3 Hz, 4 H, 2 × 6-$H_2$), 3.76 (t, *J* = 5.2 Hz, 4 H, 2 × 7-$H_2$), 3.52 – 3.43 (m, 12 H, 2 × 1-$H_2$, 2 × 2-$H_2$, 2 × 8-$H_2$) ppm.




**$^{13}$C-NMR** (101 MHz, DMSO-$d_6$) δ = 144.0 (C-4), 124.2 (C-5), 71.6 (C-2), 69.4 (C-8), 68.7 (C-7), 63.5 (C-3), 60.1 (C-1), 49.3 (C-6) ppm.

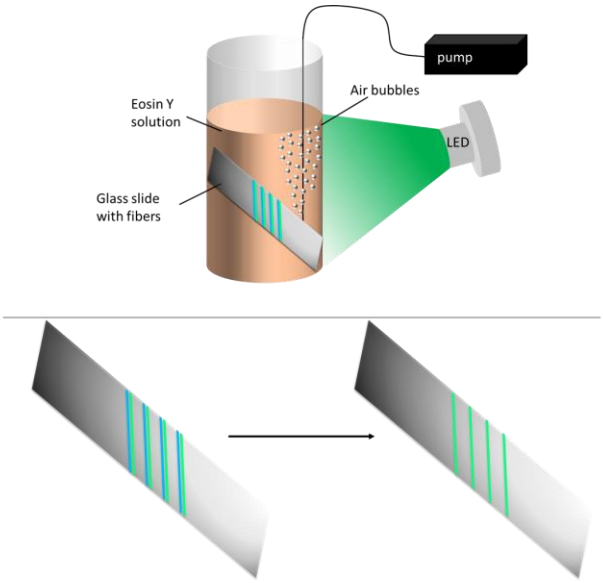
## 4 – Bicompartmental Fibers

### EHD Co-Jetting



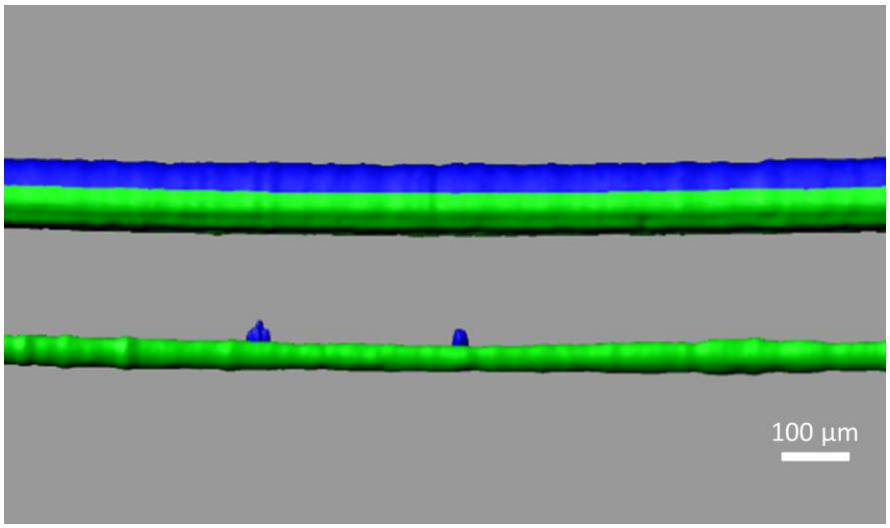

Polymer **PAPA** (241 mg) was dissolved at 45 wt.% in $CHCl_3$/DMF (536 µL, 97:3, v:v). PTDPV (4 mg) was dissolved in $CHCl_3$ (20 mL) and this solution was filtered with a 0.2 µm syringe filter. PLGA (50-75 kDa, 199 mg) was dissolved at 30 wt.% in the PTDPV solution/DMF (663 µL, 97:3, v:v). The **PAPA** solution and the PLGA solution were filled in separate 1 mL syringes and pumped with a syringe pump (pump rate 100 µL/h) through two parallel 25 G needles, attached to a working electrode. The resulting fibers were collected on a turning counter electrode made of aluminum (distance between electrodes 1 cm, voltage 4.7 kV). For CLSM imaging the fibers were transferred on glass slides.

**Fiber degradation**




A 0.06 M solution of Eosin Y in $H_2O$ was prepared (19.7 mg / 500 mL). The **PAPA**-PLGA fibers were placed in the Eosin Y solution (90 mL) and illuminated by a 1 W green LED (beam angle 15°) from a distance of 5 cm for 24 h and air was bubbled through with a needle connected to an aquarium pump. The Eosin Y solution was replaced after 90 min and 16 h. The fibers were imaged with a CLSM after the degradation.

**3D reconstruction of a fiber, before and after degradation**




A bicompartmental **PAPA**-PLGA fiber was used in a 3.5 h long degradation experiment and imaged with confocal laser scanning microscopy before and after the degradation. The 3D reconstruction is based on the confocal laser scanning microscopy and shows the bicompartmental fiber in the upper part of the 3D reconstruction. The **PAPA** compartment is shown in blue, the PLGA with PTDPV in green. After degradation the **PAPA** compartment is only left in traces, while the PLGA remained stable.