

SUPPORTING INFORMATION

For the Manuscript Entitled

Crystal structures of lignocellulosic furfuryl biobased polydiacetylenes with hydrogen-bond networks: influencing the direction of solid-state polymerization through modification of the spacer length

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Table of Contents

1. Synthetic procedures and characterizations of alkyne 1 and FAM-DA-3CH2	S.2
2. Polymerization procedures (FAM-DA-3CH2 → FAM-PDA-3CH2).....	S.3
3. X-ray crystallographic details.....	S.4
4. Computational details	S.8
5. IR and NMR spectra.....	S.9
6. FT-RAMAN spectra.....	S.11
7. References.....	S.12

General information

Infrared spectra were recorded using an Agilent Cary 630 FT-IR spectrometer equipped with an Attenuated Total Reflectance (ATR) sample technology employing a 45° single reflection diamond crystal. IR data are reported in cm⁻¹.

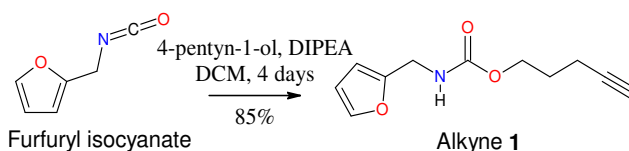
NMR spectra were recorded using a Bruker 300 MHz Advance III spectrometer. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra for all compounds were recorded at ambient temperature and were referenced to CDCl₃ (7.26 ppm (¹H NMR) or 77.2 ppm (¹³C NMR)). NMR resonance multiplicities were reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; coupling constants *J* were reported in Hz.

FT-Raman spectra were recorded at 2 cm⁻¹ resolution using a Bruker RFS 100/S spectrometer with Nd:YAG laser at 1064 nm excitation and a light power equal to 200 mW equipped with a photomultiplier Ge-diode, cooled at liquid nitrogen temperature (77K).

High-Resolution Mass Spectra (HRMS) were acquired on a maXis 3G (ESI-QqTOF) orthogonal mass spectrometer from Bruker Daltonik (Bremen, Germany) using electrospray ionization in positive ion mode.

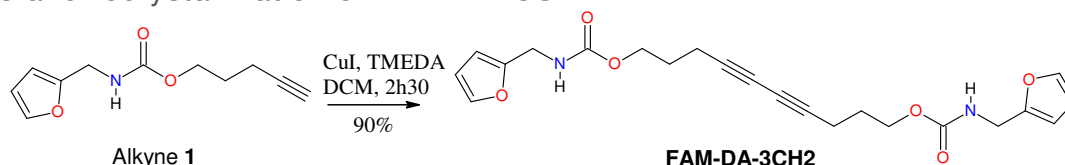
Synthetic procedures and characterizations

Synthesis of alkyne 1



To a solution of 4-pentyn-1-ol (1550 μL , 16.7 mmol) in DCM (50 ml) was added furfuryl isocyanate (1500 μL , 14.0 mmol) and DIPEA (2900 μL , 16.7 mmol) under argon. The reaction mixture was stirred under argon atmosphere for 4 days at room temperature. The resulting mixture was purified by a pad of silica gel (eluting with 10% DCM/hexane then 100% DCM) then by flash chromatography (2% acetone/DCM), yielding the **alkyne 1** as an orange oil (2466 mg, 85%). $R_f = 0.45$ (2% acetone/DCM). **FT-IR/ATR** (ν , cm^{-1}) = 3407, 3332, 3295, 2956, 2933, 2117, 1696, 1599, 1517, 1472, 1431, 1349, 1327, 1237, 1133, 1077, 1029, 1006, 913, 883, 813, 779, 734. **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ ppm: 7.36 (d, 1H, $J=1.9$ Hz), 6.32 (dd, 1H, $J=3.1, 1.9$ Hz), 6.23 (d, 1H, $J=3.1$ Hz), 5.00 (br, 1H), 4.36 (d, 2H, $J=5.7$ Hz), 4.20 (t, 2H, $J=6.2$ Hz), 2.28 (td, 2H, $J=7.0, 2.6$ Hz), 1.97 (t, 1H, $J=2.6$ Hz), 1.93-1.77 (m, 2H). **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ ppm: 156.34, 151.70, 142.36, 110.52, 107.38, 83.30, 69.05, 63.75, 38.18, 28.07, 15.28. **HRMS** (ESI/QqTOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_3\text{Na}$, 230.0788; Found: 230.0795.

Synthesis and recrystallization of FAM-DA-3CH2



To a solution of alkyne 1 (214 mg, 1.0 mmol) in DCM (1 ml) was added Hay catalyst [freshly prepared by stirring CuI (239 mg, 1.2 mmol) and TMEDA (250 μL , 2.4 mmol) in DCM (2 ml) under argon]. The reaction mixture was stirred under oxygen atmosphere (balloon) for 2h30 mainly in the absence of light. The resulting mixture was purified directly by flash chromatography (2% acetone/DCM). Slow evaporation (7 days in the absence of light) of the eluent in the chromatography test tubes provided the title compound **FAM-PDA-3CH2** as transparent crystals with a blue tint (186 mg, 90%, figure **S1**). This procedure afforded few plate-like single crystals, then X-ray diffraction data were collected during the next 24h. $R_f = 0.25$ (2%Acetone/DCM). **FT-IR/ATR** (ν , cm^{-1}) = 3295, 3120, 3068, 2974, 2952, 2900, 1677, 1543, 1506, 1469, 1454, 1424, 1357, 1256, 1237, 1200, 1137, 1081, 1044, 1006, 991, 928, 909, 883, 816, 783, 731. **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ ppm: 7.36 (d, 1H, $J=2.0$ Hz), 6.32 (dd, 1H, $J=3.3, 2.0$ Hz), 6.23 (d, 1H, $J=2.9$ Hz), 5.03 (br, 1H), 4.35 (d, 2H, $J=5.9$ Hz), 4.17 (t, 2H, $J=6.2$ Hz), 2.34 (t, 2H, $J=7.0$ Hz), 1.92-1.76 (m, 2H). **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ ppm: 156.29, 151.68, 142.34, 110.52, 107.36, 78.43, 65.93, 63.74, 38.17, 27.95, 16.13. **HRMS** (ESI/QqTOF) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_6\text{Na}$, 435.1527; Found: 435.1534.

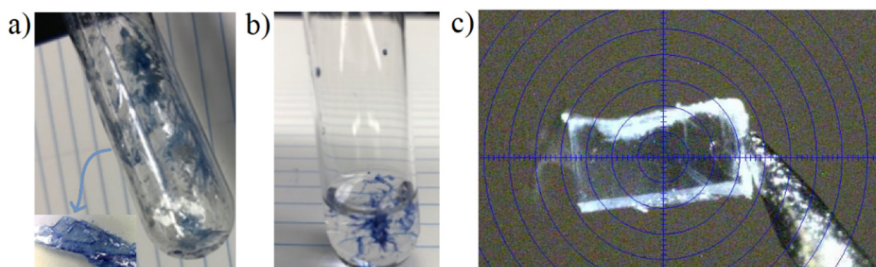


Figure S1. a) Pictures of the single crystals of **FAM-DA-3CH2** obtained after slow evaporation of the eluent in the chromatography test tubes. b) Formation of blue fiber after addition of DCM in the test tubes containing **FAM-DA-3CH2**. c) Crystal of **FAM-DA-3CH2** mounted on a goniometer head.

Polymerization procedures (FAM-DA-3CH2 → FAM-PDA-3CH2)

Heat polymerization

If a **FAM-DA-3CH2** single crystal is heated at 60 °C for six days, the quality of X-Ray Diffraction (XRD) data is greatly diminished, but this is still sufficient to demonstrate that the resulting unit cell matches that of the initial monomer, even if the single crystal becomes darker (figure S2). Higher temperatures or longer heating times result in the loss of most of the diffraction of the single crystal, making structural analysis by XRD impossible under these conditions.

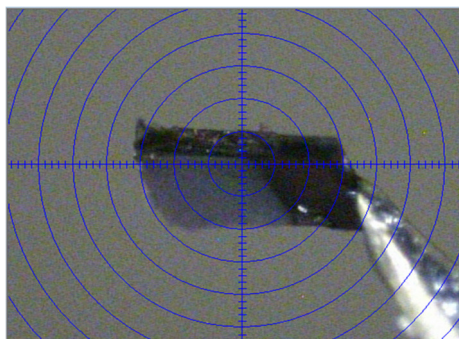
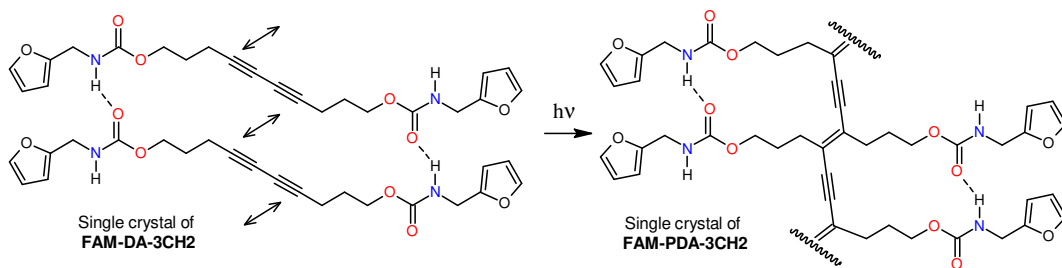


Figure S2. Picture of the single crystal of **FAM-DA-3CH2** obtained after heating the sample at 60°C for six days.

UV polymerization

A small selected single crystal of **FAM-DA-3CH2** was irradiated at 254 nm for four hours before analyzing it successfully by X-ray diffraction.



UV-Chamber Specifications

Manufacturer: Dinies Technologies GmbH

Model: ELG100S

Number of lamps: 2x11W

Operating temperature: approx. 50 °C

Irradiation time: 4 hrs

UV-C power lamp (254 nm): approx. 12 mW/cm² on the surface

X-ray crystallographic details

• *Single Crystal Structures Analysis of FAM-DA-1CH2 and FAM-PDA-1CH2*

See the following reference: Dory, Y.L.; Caron, M.; Duguay, V.O.; Chicoine-Ouellet, L.; Fortin, D.; Baillargeon, P. Preparation and Single Crystal Structure Determination of the First Biobased Furan-Polydiacetylene Using Topochemical Polymerization. *Crystals* **2019**, *9*, 448.

<https://doi.org/10.3390/cryst9090448>

• *Single Crystal Structure Analysis of FAM-DA-3CH2*

A Plate-like specimen of $C_{22}H_{24}N_2O_6$, approximate dimensions 0.080 mm x 0.350 mm x 0.665 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 1.54178 \text{ \AA}$).

The total exposure time was 10.75 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 8429 reflections to a maximum θ angle of 72.54° (0.81 \AA resolution), of which 1953 were independent (average redundancy 4.316, completeness = 96.0%, $R_{int} = 5.25\%$, $R_{sig} = 4.52\%$) and 1781 (91.19%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 5.1702(3) \text{ \AA}$, $b = 44.831(3) \text{ \AA}$, $c = 4.8093(3) \text{ \AA}$, $\beta = 111.856(2)^\circ$, volume = $1034.60(11) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 8749 reflections above $20 \sigma(I)$ with $5.914^\circ < 2\theta < 145.1^\circ$. Data were corrected for absorption effects using the Numerical Mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.623. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4695 and 0.7536.

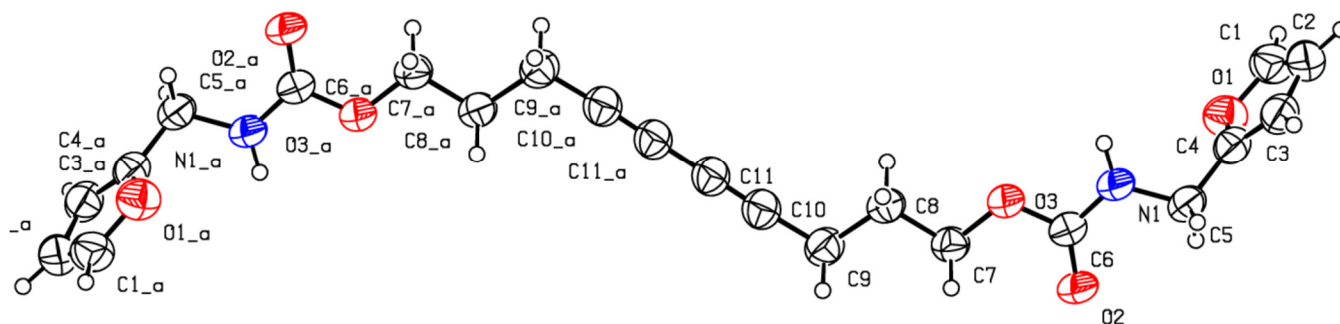
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with $Z = 2$ for the formula unit, $C_{22}H_{24}N_2O_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 137 variables converged at $R1 = 7.56\%$, for the observed data and $wR2 = 21.07\%$ for all data. The goodness-of-fit was 1.116. The largest peak in the final difference electron density synthesis was 0.212 e/\AA^3 and the largest hole was -0.270 e/\AA^3 with an RMS deviation of 0.058 e/\AA^3 . On the basis of the final model, the calculated density was 1.324 g/cm^3 and $F(000)$, 436 e⁻.

Table 1. Sample and crystal data for FAM-DA-3CH2

CCDC Deposition Number	2151367	
Chemical formula	$C_{22}H_{24}N_2O_6$	
Formula weight	412.43 g/mol	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal size	0.080 x 0.350 x 0.665 mm	
Crystal habit	Plate-like specimen	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	$a = 5.1702(3) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 44.831(3) \text{ \AA}$	$\beta = 111.856(2)^\circ$
	$c = 4.8093(3) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1034.60(11) \text{ \AA}^3$	
Z	2	
Density (calculated)	1.324 g/cm^3	
Absorption coefficient	0.805 mm^{-1}	
F(000)	436	

Table 2. Data collection and structure refinement for FAM-DA-3CH2.

Theta range for data collection	1.97 to 72.54°
Index ranges	-6<=h<=6, -54<=k<=55, -5<=l<=5
Reflections collected	8429
Independent reflections	1953 [R(int) = 0.0525]
Coverage of independent reflections	96.0%
Absorption correction	Numerical Mu Calculated
Max. and min. transmission	0.7536 and 0.4695
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1953 / 0 / 137
Goodness-of-fit on F ²	1.116
Final R indices	1781 data; >2σ(I) R1 = 0.0756, wR2 = 0.2066 all data R1 = 0.0799, wR2 = 0.2107
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0654P)^2+1.1835P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0078(16)
Largest diff. peak and hole	0.212 and -0.270 eÅ ⁻³
R.M.S. deviation from mean	0.058 eÅ ⁻³



- **Single Crystal Structure Analysis of FAM-PDA-3CH2**

A gold Plate-like specimen of $C_{22}H_{24}N_2O_6$, approximate dimensions 0.100 mm x 0.375 mm x 0.550 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 1.54178$ Å).

The total exposure time was 6.06 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 6609 reflections to a maximum θ angle of 70.95° (0.82 Å resolution), of which 1834 were independent (average redundancy 3.604, completeness = 97.7%, $R_{int} = 8.05\%$, $R_{sig} = 7.42\%$) and 1342 (73.17%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 4.9791(5)$ Å, $b = 43.236(5)$ Å, $c = 4.8848(5)$ Å, $\beta = 110.041(8)^\circ$, volume = $987.91(18)$ Å³, are based upon the refinement of the XYZ-centroids of 4715 reflections above $20 \sigma(I)$ with $6.139^\circ < 2\theta < 141.7^\circ$. Data were corrected for absorption effects using the Numerical Mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.718. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6540 and 0.9200.

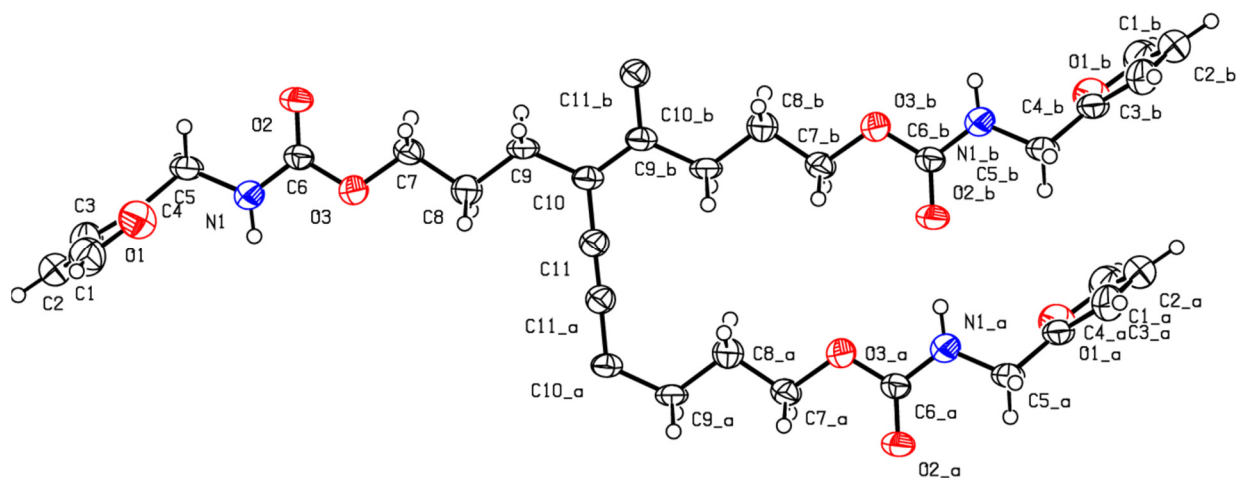
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 2 for the formula unit, $C_{22}H_{24}N_2O_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 137 variables converged at $R1 = 15.31\%$, for the observed data and $wR2 = 38.01\%$ for all data. The goodness-of-fit was 1.178. The largest peak in the final difference electron density synthesis was $0.369 e^-/\text{Å}^3$ and the largest hole was $-0.374 e^-/\text{Å}^3$ with an RMS deviation of $0.103 e^-/\text{Å}^3$. On the basis of the final model, the calculated density was 1.386 g/cm^3 and $F(000)$, 436 e^- .

Table 3. Sample and crystal data for FAM-PDA-3CH2.

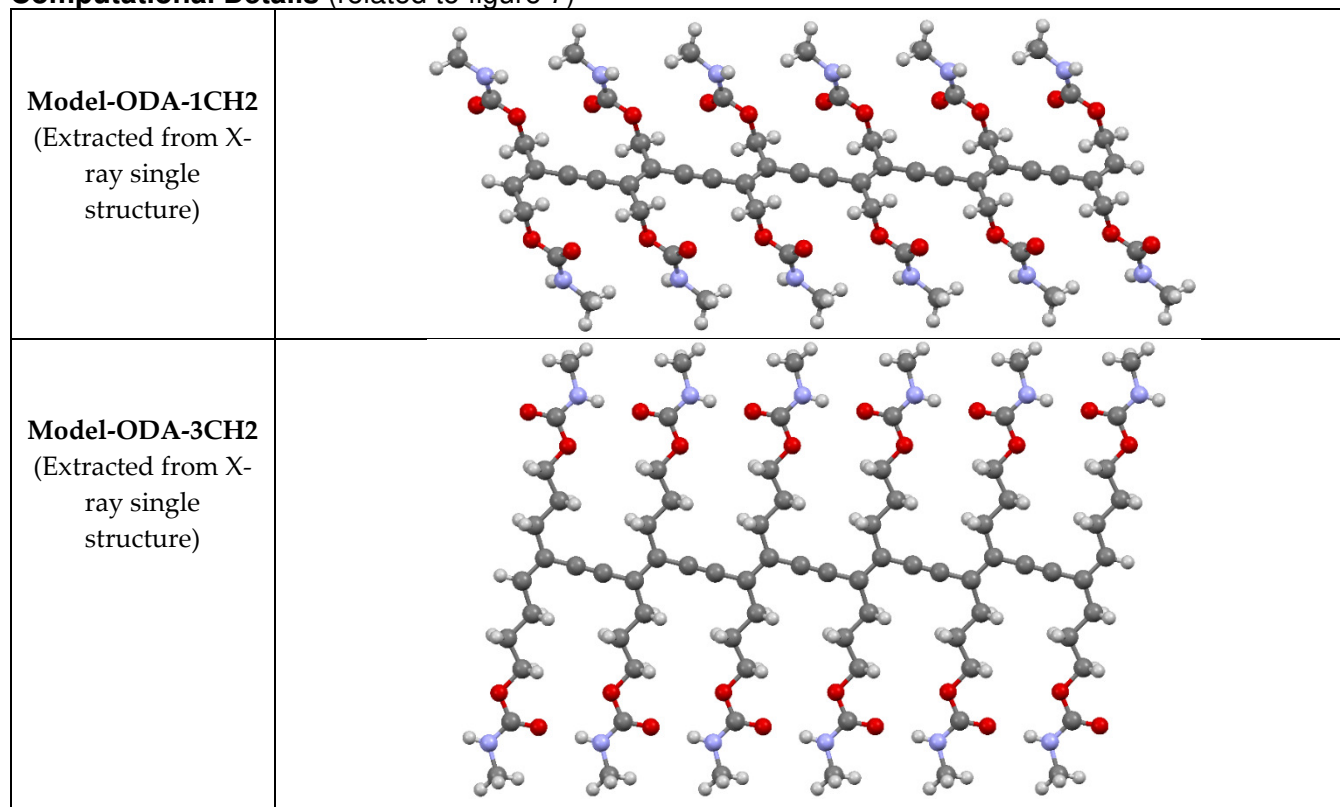
CCDC Deposition Number	2151365	
Chemical formula	$C_{22}H_{24}N_2O_6$	
Formula weight	412.43 g/mol	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal size	0.100 x 0.375 x 0.550 mm	
Crystal habit	A gold Plate-like specimen	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	$a = 4.9791(5)$ Å	$\alpha = 90^\circ$
	$b = 43.236(5)$ Å	$\beta = 110.041(8)^\circ$
	$c = 4.8848(5)$ Å	$\gamma = 90^\circ$
Volume	$987.91(18)$ Å ³	
Z	2	
Density (calculated)	1.386 g/cm^3	
Absorption coefficient	0.843 mm^{-1}	
F(000)	436	

Table 4. Data collection and structure refinement for FAM-PDA-3CH2.

Theta range for data collection	2.04 to 70.95°	
Index ranges	-6<=h<=5, -52<=k<=52, -5<=l<=5	
Reflections collected	6609	
Independent reflections	1834 [R(int) = 0.0805]	
Coverage of independent reflections	97.7%	
Absorption correction	Numerical Mu Calculated	
Max. and min. transmission	0.9200 and 0.6540	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1834 / 0 / 137	
Goodness-of-fit on F ²	1.178	
Final R indices	1342 data; >2σ(I)	R1 = 0.1531, wR2 = 0.3694
	all data	R1 = 0.1742, wR2 = 0.3801
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0663P)^2+9.6999P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0055(18)	
Largest diff. peak and hole	0.369 and -0.374 eÅ ⁻³	
R.M.S. deviation from mean	0.103 eÅ ⁻³	



Computational Details (related to figure 7)



Starting from the experimental x-ray structures of **FAM-PDA-1CH2** and **FAM-PDA-3CH2**, we extracted isolated hexamer (see structure above), in addition to supramolecular stacks of 2 to 8 of these hexamer structures. In order to reduce the size of the systems and keep them computationally tractable, we removed the furfuryl groups on the PDA side chains. We then performed DFT single-point calculations on these model systems (B97D3/Def2SVP with density fitting using W06 as basis set).

All DFT calculations were performed with the Gaussian 16 package.¹ All the structures reported were calculated in the gas phase with the B97D3 density functional² in combination with the Def2SVP basis set³ and the W06 auxiliary basis set.⁴ A fine grid density was used for numerical integration in the calculations.

Computational Details (related to figure 8)

We investigated, using a similar computational approach as the one recently reported by Brédas *et al.* in 2010 and in 2014,^{5,6} the torsional potential of the above model oligodiacetylene (ODA). Six units were used as this model gives torsion potentials close to the polymer limit. The odd number of alkynes enables the rotation of two symmetric groups along the central alkyne.

GFN2-xTB (gas phase) calculations were performed using the xtb 6.4.1 package⁷ using the default convergence parameters ($5 \times 10^{-6} Eh$ for the energy and $1 \times 10^{-3} Eh \times \alpha^{-1}$ for the gradient). Starting from the x-ray structures, the dihedral angles between the alkenes on each side of the alkynes were constrained with a harmonic potential (force constant of $10 Eh/a_0^2$) as implemented in xtb, starting at 180° . Relaxed scans were performed with increments of 1.6° for all dihedral angles (one to form the right-handed helix and one to form the left-handed helix.) The dihedral angles reported are the average of the three central dihedral angles.

IR and NMR spectra

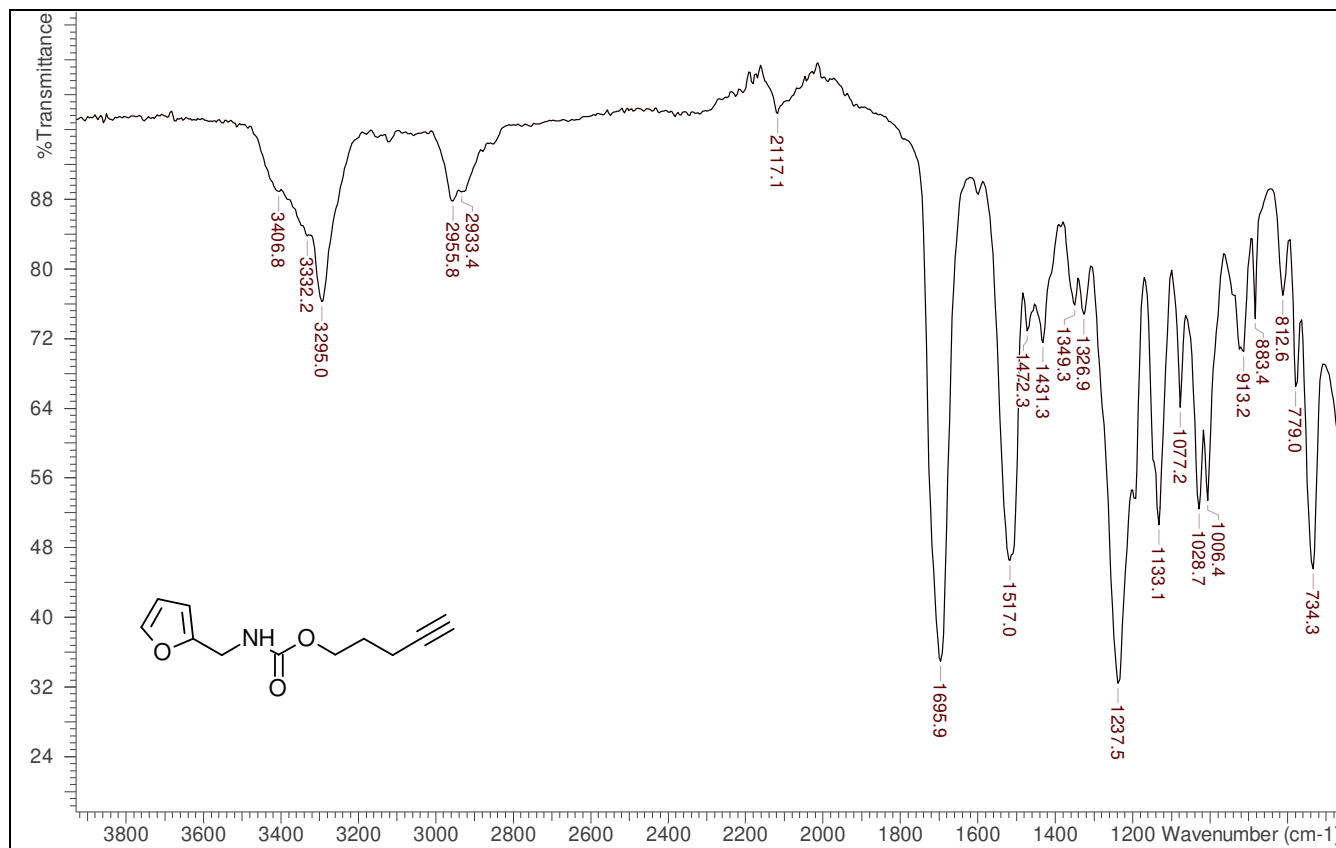


Figure S3 FT-IR (diamond ATR) spectrum of alkyne 1

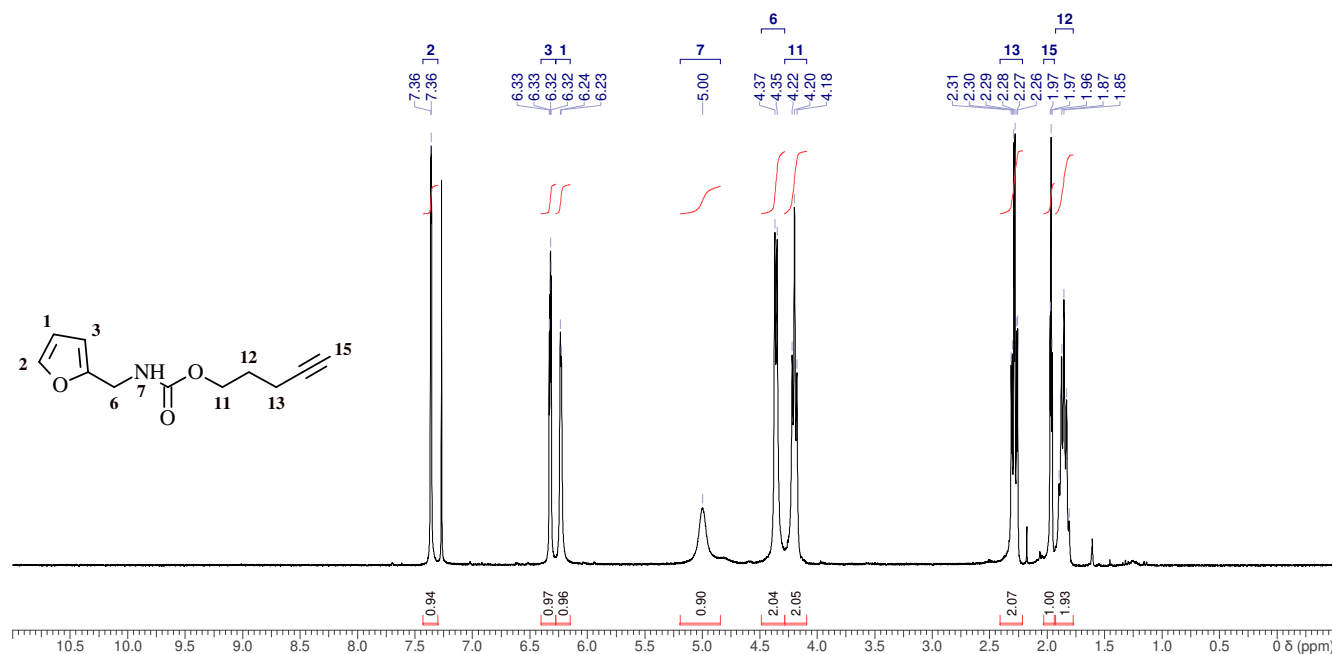


Figure S4 ¹H NMR spectrum of alkyne 1 in CDCl₃

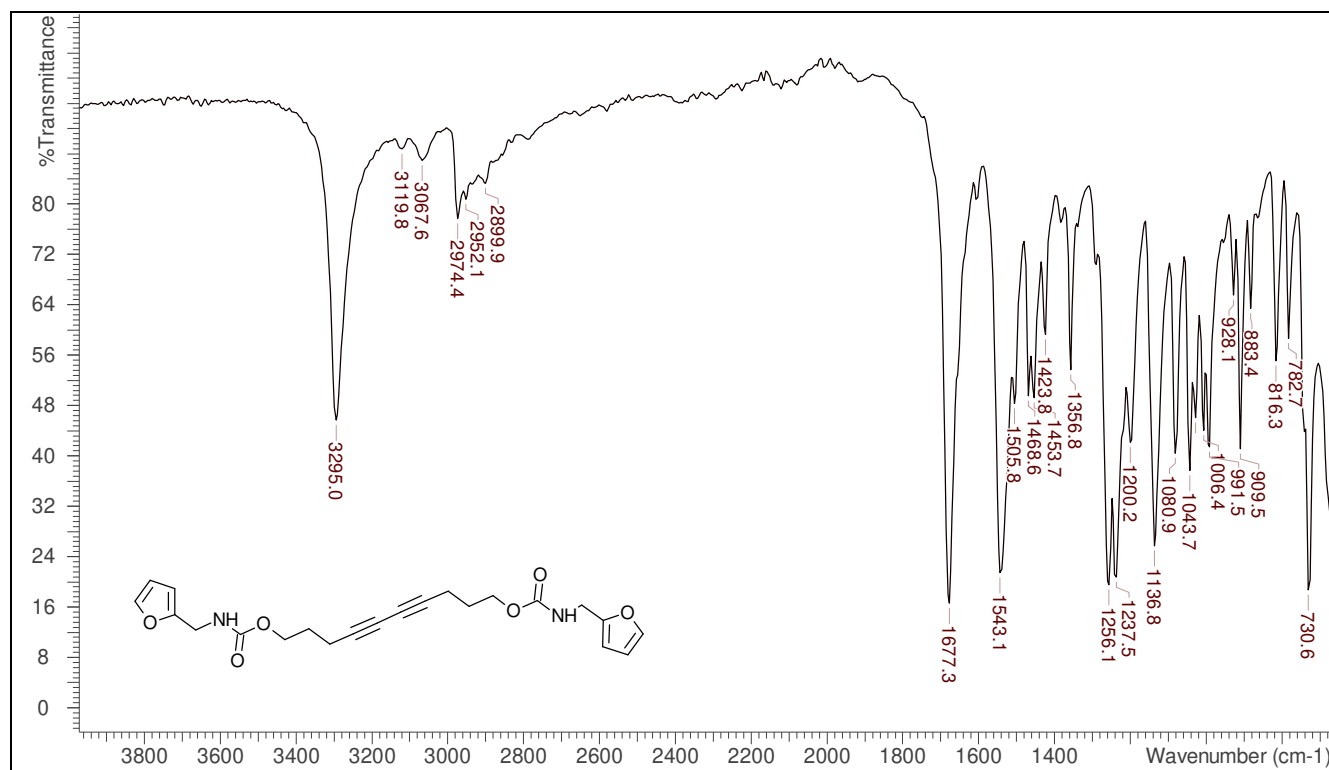


Figure S5 FT-IR (diamond ATR) spectrum of **FAM-DA-3CH2**

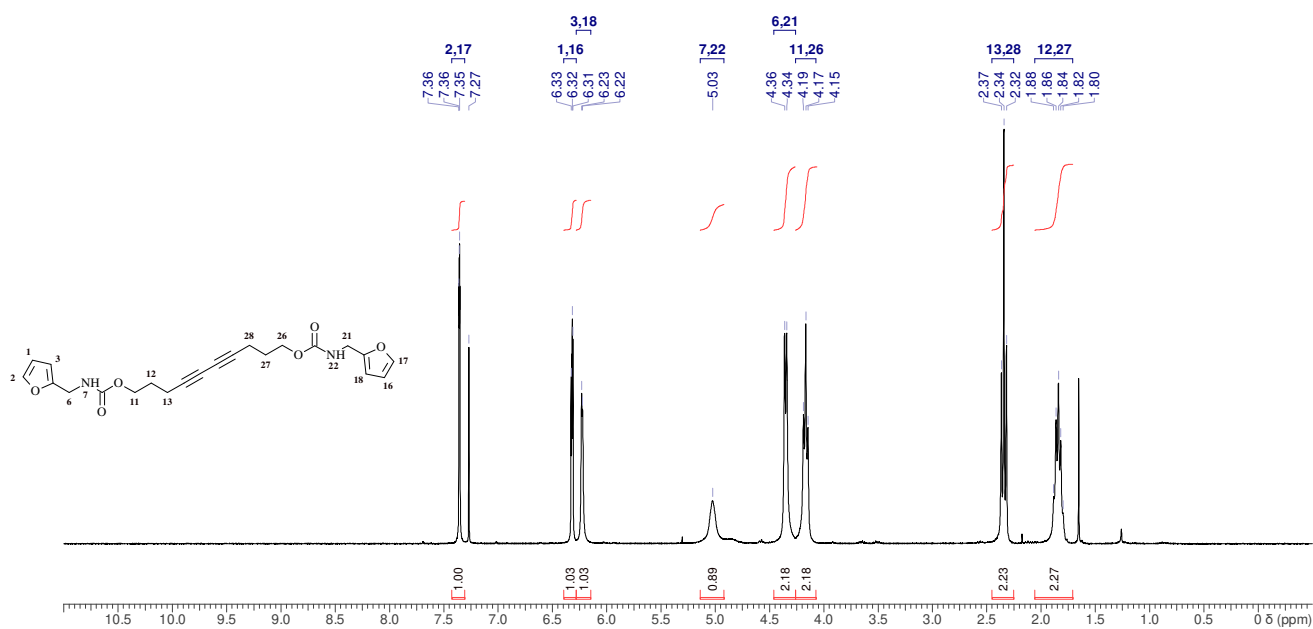


Figure S6 ¹H NMR spectrum of **FAM-DA-3CH2** in CDCl₃

FT-Raman spectra

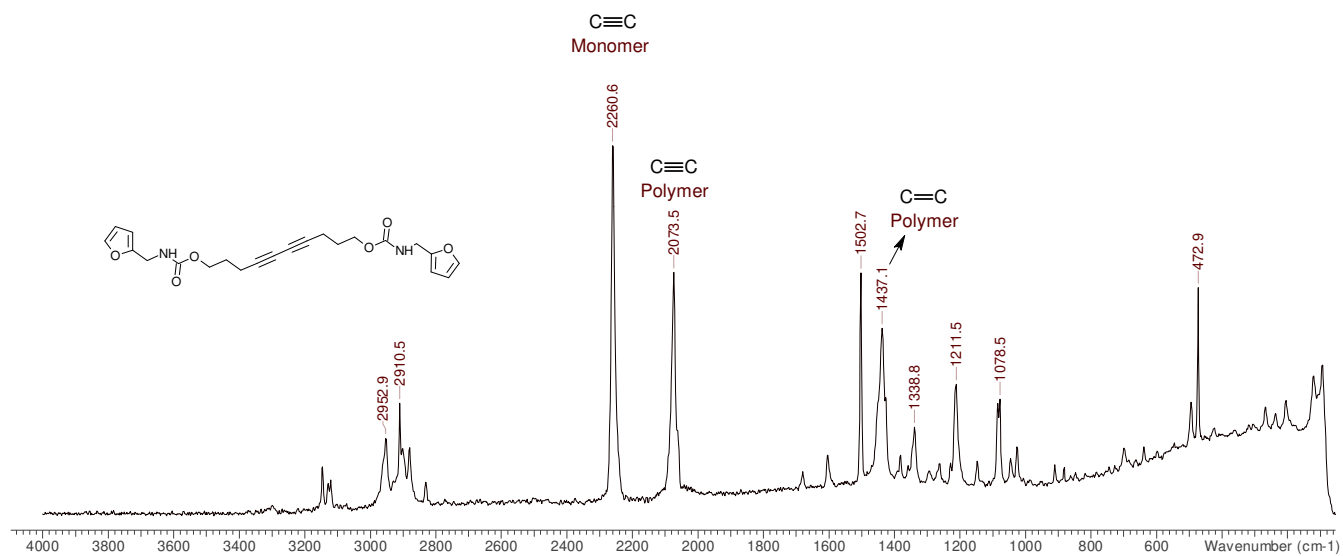


Figure S7. FT-Raman spectrum of non-UV irradiated **FAM-DA-3CH2** (the signal of the polymer already starts to be perceptible at this stage since a blue color appears on the surface of the crystal)

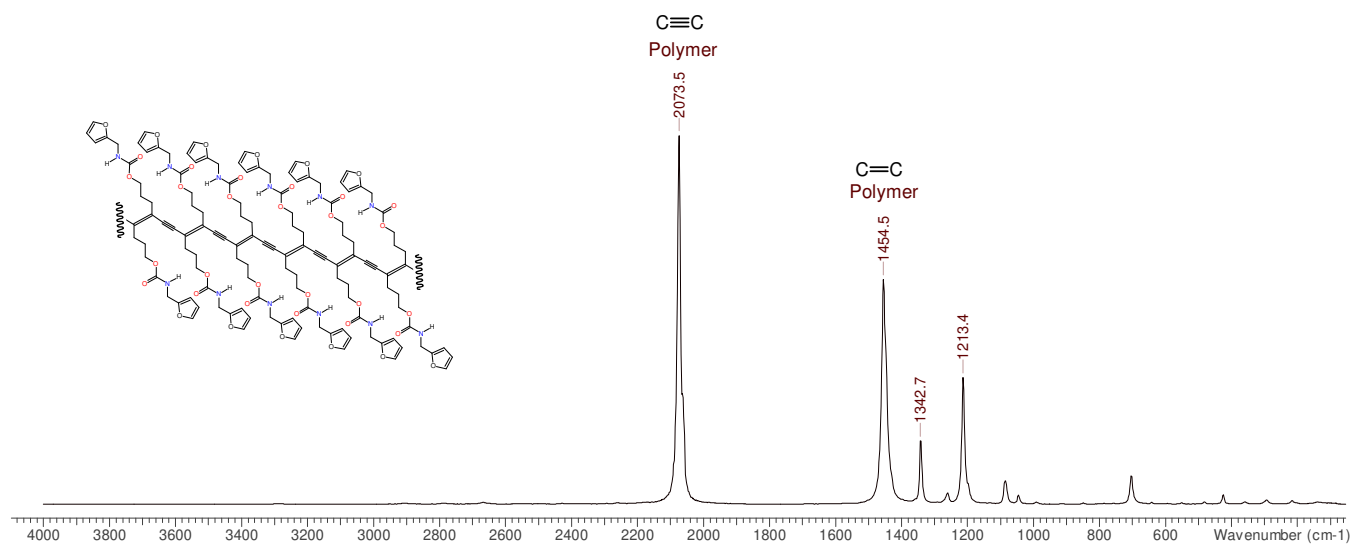


Figure S8. FT-Raman spectrum of **FAM-PDA-3CH2** after 20 minutes under UV irradiation

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