Electronic Supplementary Material (ESI) for Nanoscale.


# Supramolecular Polymerization of [6]Helicene-Based Cyano-Luminogens. On the Overall Efficiency of Self-Assembled Circularly Polarized Emitters

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## 1. Experimental Procedures

**General methods.** All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh or Scharlau 60, 230–240 mesh). Analytical thin-layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 MHz ($^{1}$H: 300 MHz; $^{13}$C: 75 MHz) spectrometer at 25 ºC using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts ($\delta$) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, m = multiplet, br = broad. FTIR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. FTIR spectra in film were recorded on a Jasco FT-IR4600 spectrometer using a $CaF_2$ cell with a path length of 0.1 nm. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. All the cooling or heating or cooling cycles have been performed at 1 ºC·min$^{-1}$. The freshly prepared solutions were measured and, after that, the samples were heated up to 90 ºC. The samples at 90 ºC were registered and cooled to 20 ºC. Atomic force microscopy was performed on a SPM Nanoscope IIIa multimode microscope working on tapping mode with a TESPSS tip (Veeco) at a working frequency of ~235 kHz. High-resolution mass spectra (HRMS) were recorded on a MALDI Bruker daltonics Ultraflex TOF/TOF spectrometer. GPC purification was performed in a Japan Analitical Instrument eluting in $CHCl_3$ at 10 ml/min flow.

Circularly polarized luminescence (CPL) measurements were performed using an in-house-developed JASCO CPL spectrofluoropolarimeter. The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. -The following parameters were used: emission slit width ≈ 10 nm, integration time = 4 sec, scan speed = 50 nm/min, 3 accumulations.

Fluorescence spectra were recorded on a FL 920 Edinburgh fluorimeter. Fluorescence quantum yields Φ were measured on a FL 920 Edinburgh fluorimeter equipped with an integration sphere.:

Lifetime measurements were measured at ScanMat Platform (UMS 2001) in Rennes. The decays were calculated by using an Ocean optics QEPro CCD detector (Range: 350–1100 nm). The excitation source has been a picosecond laser diode (10 KHz to 100 MHz) at 375 nm capable of operating in Burst mode below 10 KHz. For the detection windows, signals in UV-Vis (350–950 nm) are recorded as a function of time over a range of 135 nm simultaneously using a Hamamatsu C10910-25 streak camera mounted with a slow single sweep drawer. The range of measurable lifetimes is 100–300 µs. In the molecularly dissolved state lifetimes were below the detection range (t < 10 ns)

Enantiopure helicene derivatives and *N*-(2-(4-(cyanomethyl)benzamido)ethyl)-3,4,5-tris(dodecyloxy)benzamide were prepared following previously reported methods, see references S1, S2 and S3, respectively.

**Solvent denaturation model.**
In the equilibrium model reported by ten Eikelder,[S4a] the equilibrium constants are defined by the following equations:

Nucleation: $K_n = e(\frac{-\left((\Delta H^0 - \Delta H^0_{NP}) - T\Delta S^0\right)}{RT})$ Eq. 1

Elongation: $K_e = e\frac{-(\Delta H^0 - T\Delta S^0)}{RT}$ Eq. 2

The cooperativity factor (σ): $\sigma = \frac{k_n}{k_e} = e(\frac{\Delta H_{NP}}{RT})$ Eq. 3

The denaturation model[S4b] is based on the concentration-dependent supramolecular polymerization equilibrium model by Goldstein,[S4c] where the polymerization is described as a sequence of monomer addition equilibria.

$[Pn]=Kn\ [Pn-1][X]$ Eq. 4
$[Pn+1] = K\text{e}\ [Pn][X]$ Eq. 5
$[Pi]=K\text{e}\ [Pi-1][X]$ Eq. 6

For the cooperative model $k_n < k_e$ and for isodesmic process $k_n = k_e$. The concentration for each species *Pi* is given by $[Pi] = K\ i-1n\ [X]i$ for $i \leq n$and$[Pi]=Ki-n$ e $Kn-1\ n\ [X]i$for$i>n$.
The dimensionless mass balance is obtained by inserting the dimensionless concentration $pi = ke[Pi]$, the monomer concentration x= $K_e$ [X] and the concentration of each species *Pi* (for i≤ n): $pi = \sigma i-1xi$ and for $i$ > n : $pi = \sigma n-1xi$ ):

$x_{tot} = \sigma^{-1}\sum_{1=n}^{n} i\,(\sigma x)^i + \sigma^{n-1}\sum_{1=n+1}^{\infty} ix^i$ Eq. 7

Both sums are evaluated by using standard expressions for converging series:

$x_{tot} = \left(\frac{(\sigma x)^{n+1}(n\sigma x-n-1)}{(\sigma x-1)^2} + \frac{\sigma x}{(\sigma x-1)^2}\right) - \sigma^{n-1}\,(\frac{x^{n+1}(nx-n-1)}{(x-1)^2})$ Eq. 8
With $x_{tot}$ = $C_{tot}Ke$ and $c_{tot}$ = total monomer concentration
The sum solved by standard numerical methods (Matlabfzerosolver) yields the dimensionless monomer concentration $x$. Considering that every species with is defined as aggregate, the degree of $i$ > 1 aggregation results in:

$\alpha_{agg} = (x_{tot} - x)/\ x_{tot}$ Eq. 9

Via $k_e$= e($-\Delta G^0/RT$), the denaturation curves can be obtained with *X* defined as volume fraction of good solvent:

$\Delta G^{0'} = \Delta G^0 + mX$ Eq. 10

It is assumed that the cooperativity factor *σ* is independent on the volume fraction and the *m* value for the elongation regime equals the *m* value for nucleation. The denaturation data needs to be transformed into the normalized degree of aggregation, α, if fitted to the supramolecular polymerization equilibrium model, being *A* = *absorbance*:

$\alpha = \frac{A(X)-A(X=0)}{A(X=1)-A(X=0)}$ Eq. 11

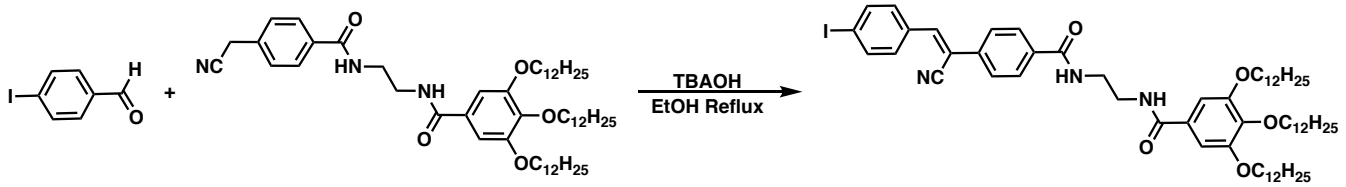
The optimization of the four needed parameters ($\Delta G^0$, *m*, σ and p) to fit the equilibrium model to the experimental data (normalized degree vs. f) is done by the non-linear least-squares analysis using Matlab (lsqnonlinsolver). The data is then fitted with the non-linear least squared regression (Levenberg Marquardt algorithm).

**Synthetic details and characterization**

**General Protocol for the Synthesis of Derivatives 1 and 2**

The corresponding bisethynyl-helicene and aryl iodide were dissolved in a mixture of dry THF and $Et_3N$ (1/1) which was degassed by bubbling Ar for 10 min. CuI and $Pd(PPh_3)_4$ were added and the reaction mixture was stirred overnight at 60ºC. The organic layer was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM/MeOH (97/3) for both derivatives **1** and **2**. The fractions containing the product were evaporated under reduced pressure and the residue was further purified by recycling GPC eluting with $CHCl_3$ (2 cycles), affording the corresponding the pure compounds.

**Synthesis of (*Z*)-*N*-(2-(4-(1-cyano-2-(4-iodophenyl)vinyl)benzamido)ethyl)-3,4,5-tris(dodecyloxy)benzamide**

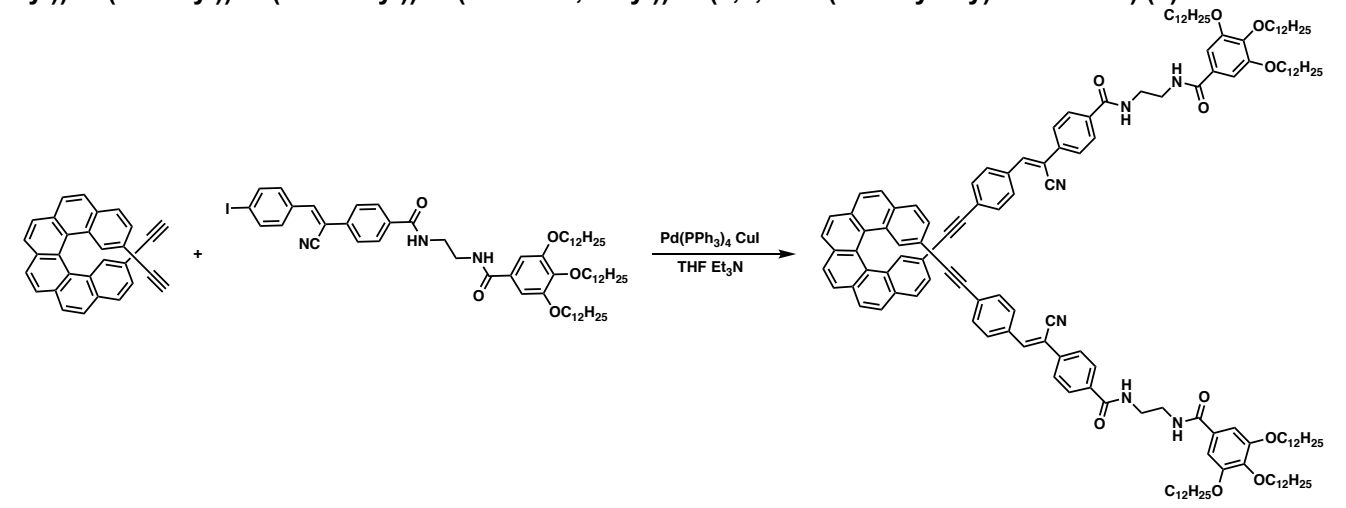



In a round bottom flask, 4-iodobenzaldehyde (0.14 g, 0.56 mmol, 1.1 equiv) and *N*-(2-(4-(cyanomethyl)benzamido)ethyl)-3,4,5-tris(dodecyloxy)benzamide (0.48 g, 0.61 mmol, 1.0 equiv) were dissolved in 30 mL of EtOH. The mixture was refluxed and a catalytic amount of TBAOH was added. After 10 min, the solution was cooled down and EtOH was evaporated at reduced pressure. The crude obtained was dissolved in the minimum amount of dichloromethane and poured into cold acetonitrile. The precipitates were centrifuged, and the mother liquor was eliminated. The obtained solid was dissolved and precipitated two additional times obtaining the desired compound as a yellow solid (0.47 g) in 78% yield. Due to large tendency of aggregation in $CDCl_3$ the carbon NMR was not registered.

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 (s, 1H), 7.38 (s, 1H), 6.92 (s, 1H), 3.99 (q, *J* = 6.8 Hz, 6H), 3.73 (s, 4H), 1.77 (dt, *J* = 22.7, 7.2 Hz, 6H), 1.25 (s, 46H), 0.87 (t, *J* = 6.4 Hz, 9H).

HRMS (MALDI-TOF) calcd. for $C_{61}H_{92}IN_3O_5$ $[M+H]^+$, 1074.615; found, 1074.554.

***N*,*N*'-(((4,4'-((1*Z*,1'*Z*)-((hexahelicene-2,15-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(1-cyanoethene-2,1-diyl))bis(benzoyl))bis(azanediyl))bis(ethane-2,1-diyl))bis(3,4,5-tris(dodecyloxy)benzamide) (1)**




Following the general protocol for Sonogashira, (*P*)- *or* (*M*)-Helicene (10 mg, 0.027 mmol, 1 eq.), 3,4,5-tris(dodecyloxy)-*N*-(2-(4-iodobenzamido)ethyl)benzamide (64 mg, 0.067 mmol, 2.5 eq.), $Pd(PPh_3)_4$ (4 mg, 0.0035mmol, 0.05 eq.) and CuI (1 mg, 0.0067 mmol, 0.1 eq.) were dissolved in 10 mL solution of THF/$Et_3N$ (1/1). After the purification following the general protocol depicted above, obtaining **1** as a bright-yellow solid ((*P*)-**1**: 41 mg, 68 %; (*M*)-**1**: 46 mg, 72%).

$^1$H NMR ($CD_2Cl_2$, 300 MHz, $\delta$ ppm ): 8.07 – 7.99 (m, 3H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.85 (m, 3H), 7.83 – 7.79 (m, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.51 – 7.47 (m, 1H), 7.42 – 7.36 (m, 2H), 7.08 (t, *J* = 4.7 Hz, 1H),

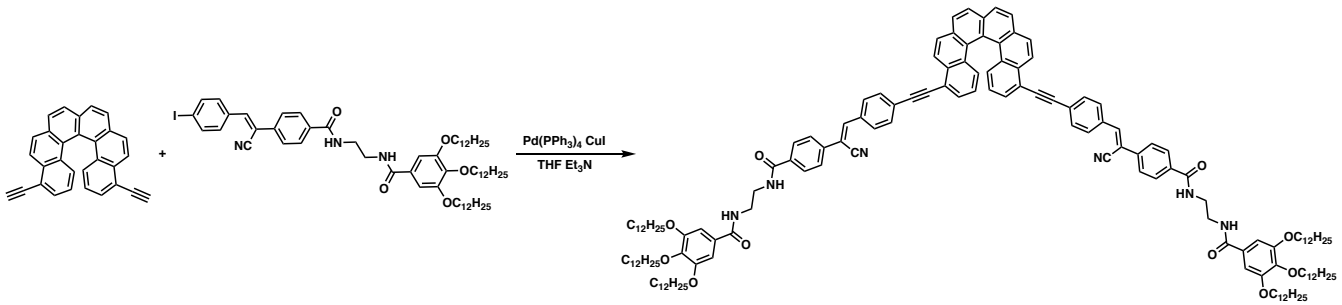
7.02 (s, 2H), 4.00 (dt, *J* = 10.5, 6.5 Hz, 6H), 3.72 (d, *J* = 4.0 Hz, 4H), 1.84 – 1.70 (m, 6H), 1.47 (p, *J* = 7.0 Hz, 6H), 1.38 – 1.20 (m, 53H), 0.87 (td, *J* = 6.9, 3.6 Hz, 8H).

$^{13}$C NMR ($CD_2Cl_2$, 75 MHz, $\delta$ ppm): 169.1, 167.8, 153.3, 142.6, 141.4, 137.5, 134.5, 133.5, 132.7, 132.3, 132.0, 131.9, 129.5, 129.3, 128.8, 128.1, 127.7, 127.6, 127.3, 126.5, 126.2, 124.1, 119.1, 117.7, 110.7, 105.8, 93.2, 88.4, 73.7, 69.5, 53.5, 41.4, 41.1, 32.1, 30.5, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 26.3, 26.2, 22.8, 14.2.

HRMS (MALDI-TOF) calcd. for $C_{152}H_{198}N_6O_{10}Na$ $[M+Na]^+$, 2014.4398; found, 2014.4374.

Experimental optical rotation values: *P*-(+)-**1**: $[\alpha]_D$ = +1773 ($CH_2Cl_2$, 2.5 mg·L$^{-1}$), *M*-(-)-**1**: $[\alpha]_D$ = -1754 ($CH_2Cl_2$, 2.5 mg·L$^{-1}$).

***N,N'*-(((4,4'-((1Z,1'Z)-((hexahelicene-3,14-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(1-cyanoethene-2,1-diyl))bis(benzoyl))bis(azanediyl))bis(ethane-2,1-diyl))bis(3,4,5-tris(dodecyloxy)benzamide) (2)**




Following the general protocol for Sonogashira, enantiopure (*P* or *M*) Helicene (15 mg, 0.04 mmol, 1 eq.), 3,4,5-tris(dodecyloxy)-*N*-(2-(4-iodobenzamido)ethyl)benzamide (113 mg, 0.12 mmol, 3 eq.), $Pd(PPh_3)_4$ (4 mg, 0.002 mmol, 0.05 eq.) and CuI (1 mg, 0.011 mmol, 0.18 eq.) were dissolved in 10 mL solution of THF/$Et_3N$ (1/1). After the purification following the general protocol depicted above, obtaining **2** as a bright-yellow solid ((*P*)-**1**: 44 mg, 70 %; (*M*)-**1**: 42 mg, 69%).
(26 mg, 33 %).

$^1$H NMR ($CDCl_3$, 300 MHz, $\delta$ ppm ): 8.59 (d, *J* = 8.8 Hz, 1H), 8.09 – 8.02 (m, 3H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.77 (t, *J* = 8.6 Hz, 4H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.54 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.42 (d, *J* = 4.8 Hz, 1H), 7.02 (s, 3H), 6.72 (dd, *J* = 8.6, 7.2 Hz, 1H), 4.03 – 3.98 (m, 7H), 3.73 (d, *J* = 4.1 Hz, 4H), 1.81 (p, *J* = 6.7 Hz, 5H), 1.75 – 1.71 (m, 2H), 1.50 – 1.44 (m, 7H), 1.37 – 1.22 (m, 60H), 0.88 (td, *J* = 7.0, 1.7 Hz, 9H).

$^{13}$C NMR ($CDCl_3$, 75 MHz, $\delta$ ppm): 169.1, 167.8, 153.3, 142.5, 141.4, 137.4, 134.6, 133.6, 133.1, 132.2, 132.0, 131.5, 130.6, 129.8, 129.7, 129.1, 128.8, 128.1, 128.0, 127.6, 126.4, 126.2, 125.8, 124.4, 124.1, 120.0, 117.7, 110.9, 105.8, 93.8, 91.5, 73.7, 69.4, 41.3, 41.1, 35.6, 32.8, 32.1, 30.5, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.5, 26.6, 26.5, 26.3, 26.2, 23.0, 22.8, 14.2.

HRMS (MALDI-TOF) calcd. for $C_{152}H_{198}N_6O_{10}Na$ $[M+Na]^+$, 2014.4398; found, 2014.4377.

Experimental optical rotation values: *P*-(+)-**2**: $[\alpha]_D$ = +1303 ($CH_2Cl_2$, 2.5 mg·mL$^{-1}$), *M*-(-)-**2**: $[\alpha]_D$ = -1297 ($CH_2Cl_2$, 2.3 mg·mL$^{-1}$)

## 3. Supplementary Figures

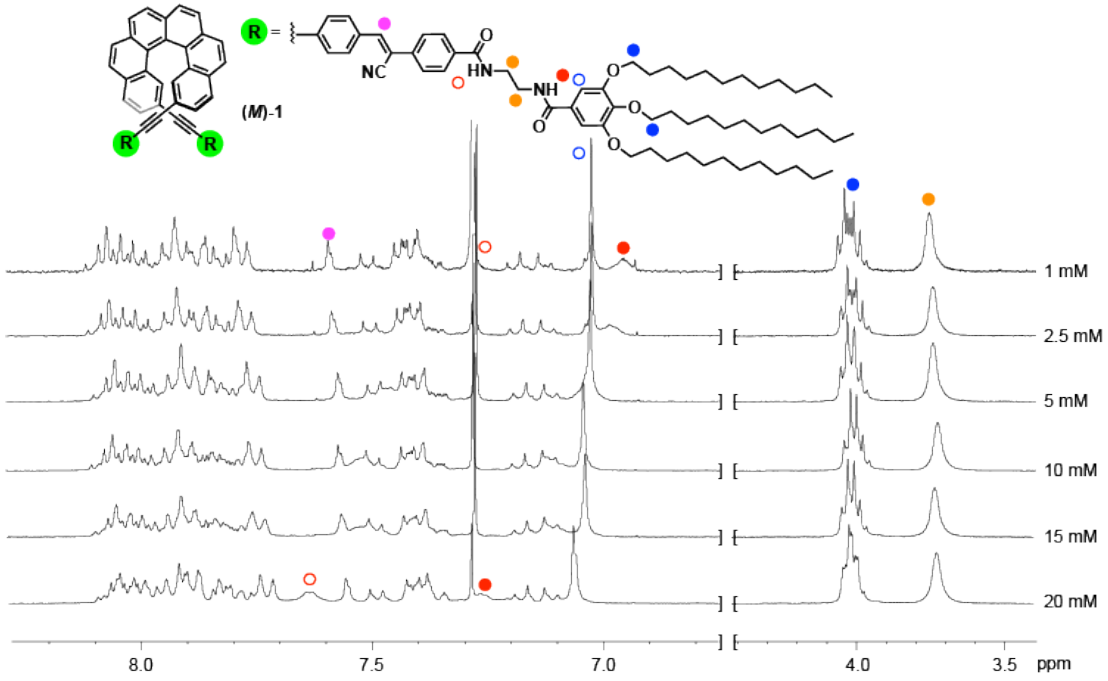



**Figure S1.** Concentration-dependent $^{1}$H NMR spectra of **(*M*)-1** in $CDCl_3$ (300 MHz, 25 ºC) showing the signals associated to the aromatic and some of the aliphatic protons.

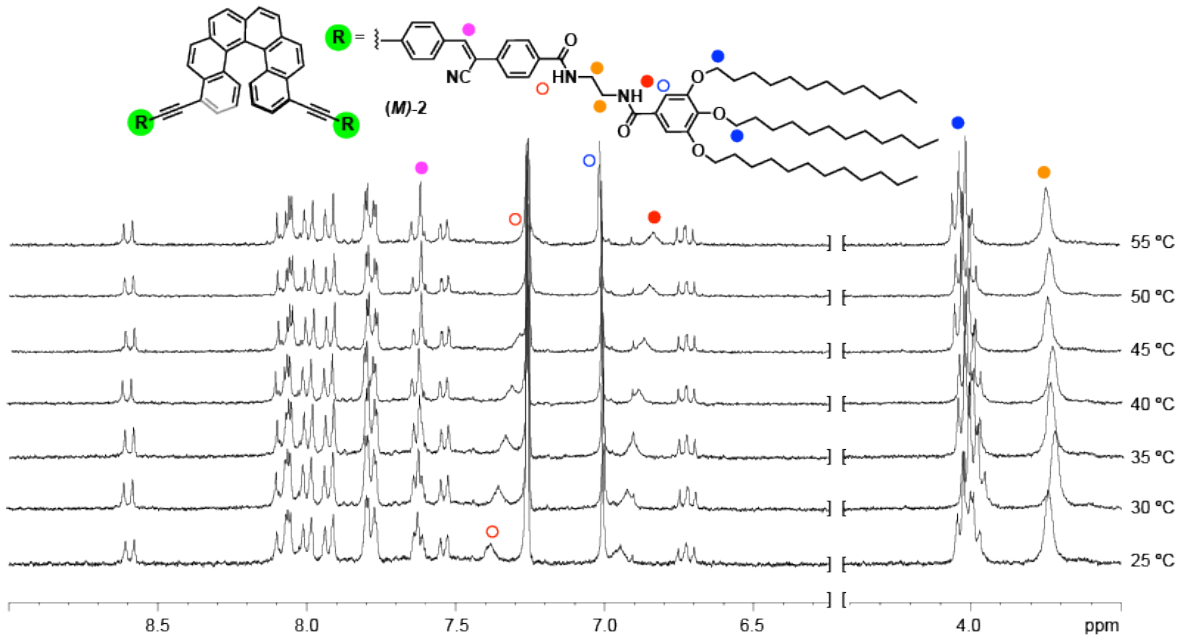



**Figure S2.** Concentration-dependent $^{1}$H NMR spectra of **(*M*)-2** in $CDCl_3$ (300 MHz, 25 ºC) showing the signals associated to the aromatic and some of the aliphatic protons.

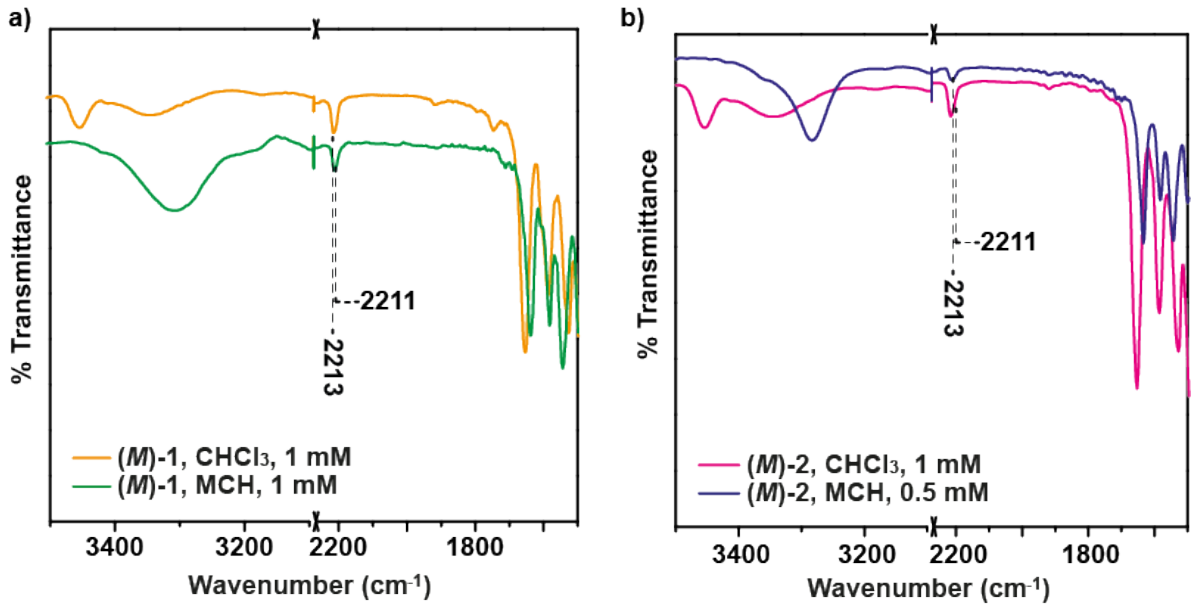



**Figure S3.** FTIR spectra of ***(M)*-1** (a) and ***(M)*-2** (a) in $CHCl_3$ and MCH. The dotted lines show the wavenumber values for the stretching cyano band.

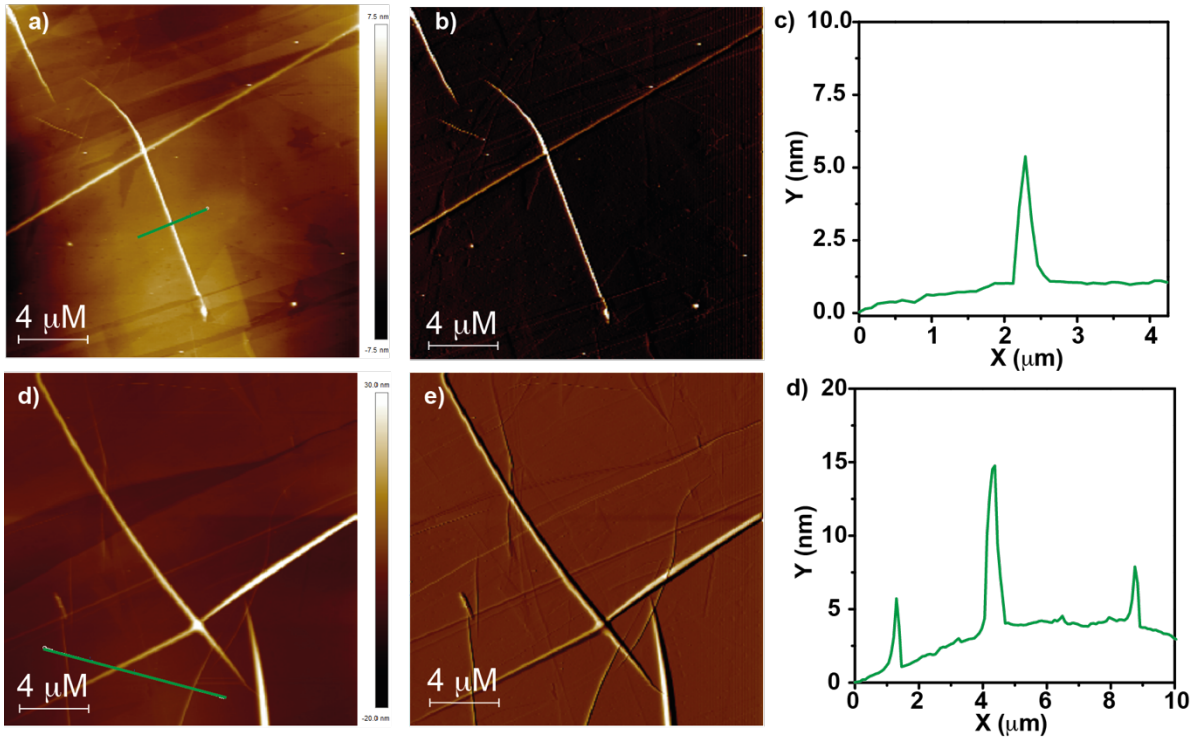



**Figure S4.** Height (a, d) and phase (b, e) AFM images of the fibrillar aggregated of ***(M)*-1**; c) height profiles along the green line in panels (a) and (d). Experimental conditions: HOPG as surface; $c_T$ = 10 μM; MCH as solvent.

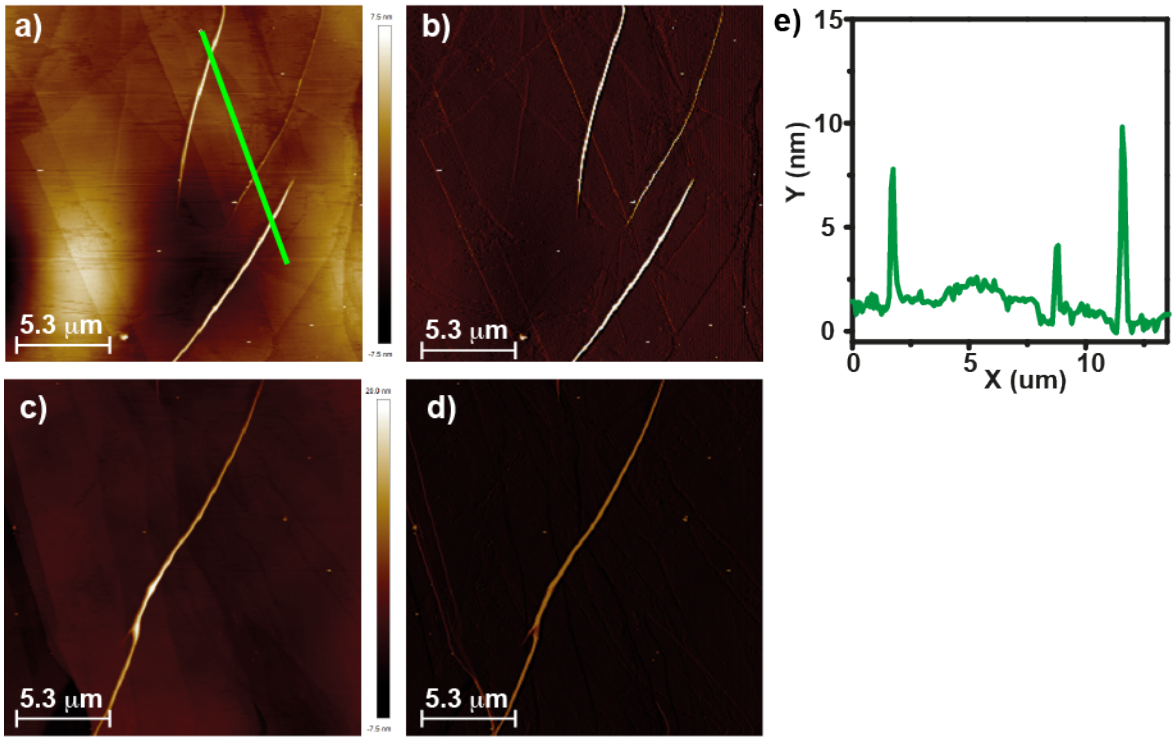



**Figure S5.** Height (a, c) and phase (b, d) AFM images of the fibrillar aggregated of **(*M*)-2**; c) height profile along the green line in panel (a). Experimental conditions: HOPG as surface; $c_T$ = 10 μM; MCH as solvent.

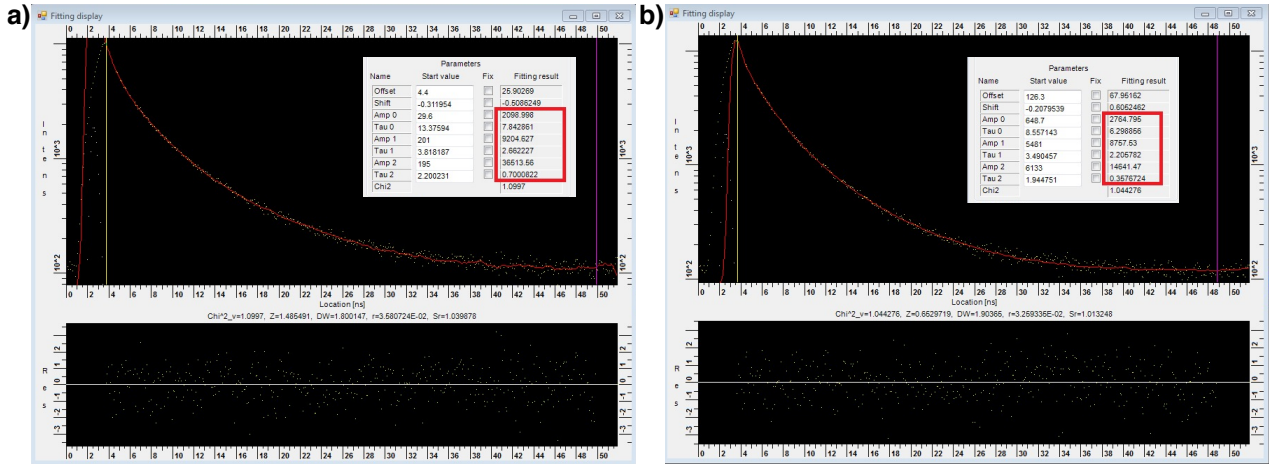



**Figure S6.** Lifetime measurements of a) (*P*)-**1** and b) (*P*)-**2** in MCH ($c_T$ = 10 μM, $\lambda_{exc}$= 365 nm)

## 4. Collection of NMR spectra

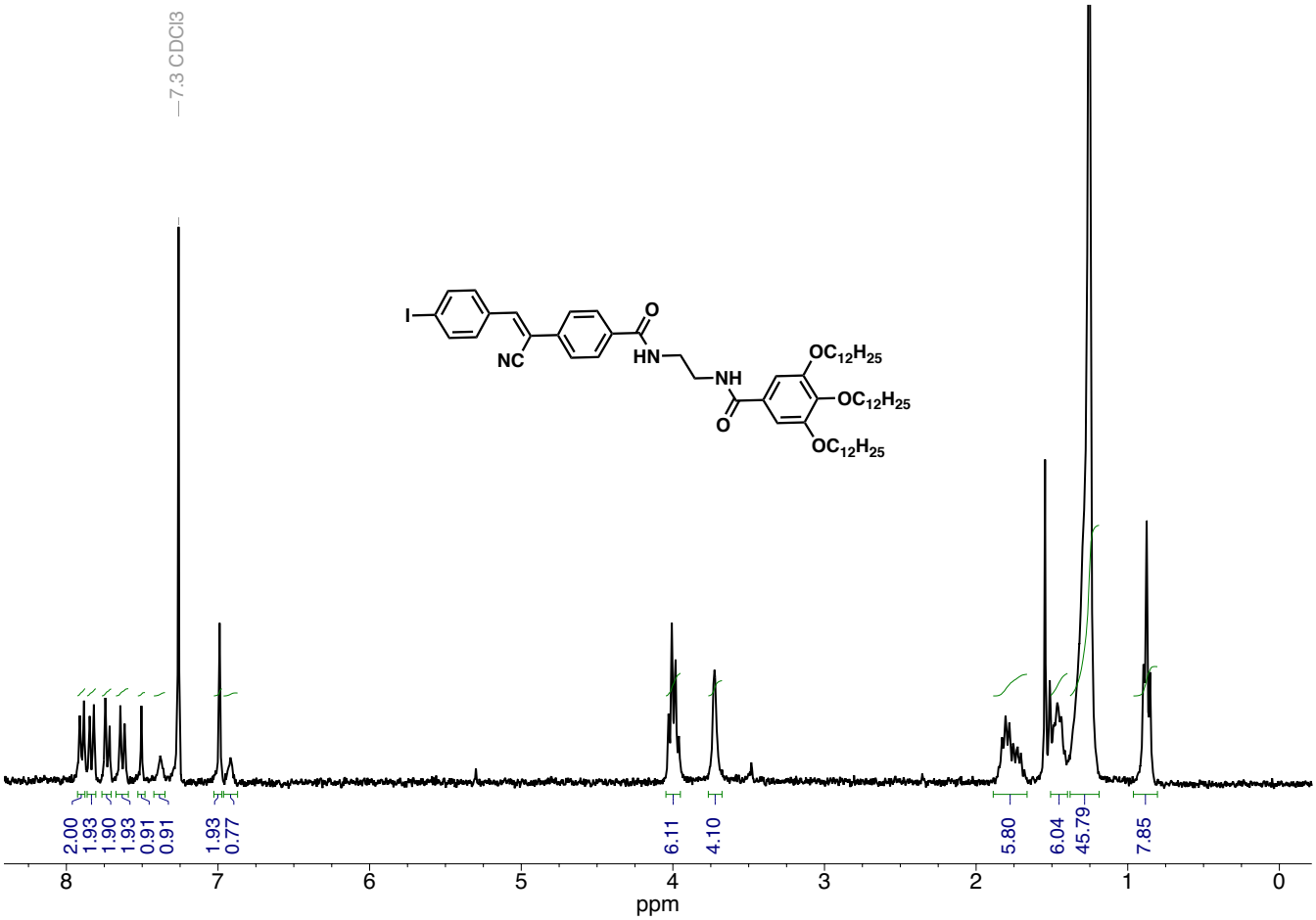



**Figure S7.** $^{1}H$ NMR spectra of (*Z*)-*N*-(2-(4-(1-cyano-2-(4-iodophenyl)vinyl)benzamido)ethyl)-3,4,5-tris(dodecyloxy)benzamide (300 MHZ, $CDCl_3$, 298K).

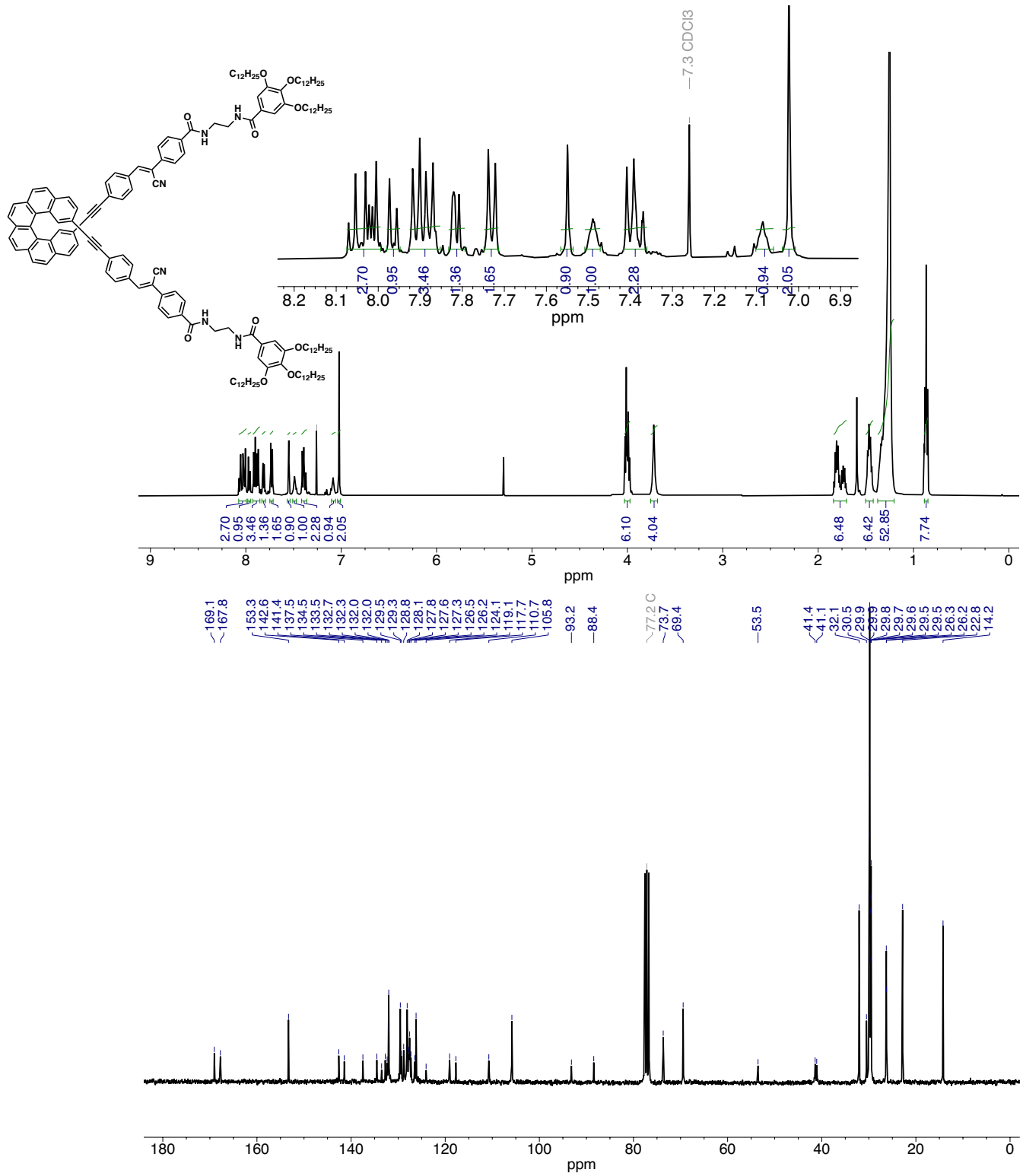



**Figure S8.** $^{1}H$ and $^{13}C$ NMR spectra of (*P*)-**1** ($CDCl_3$, 300 and 75 MHz, respectively, 298K)

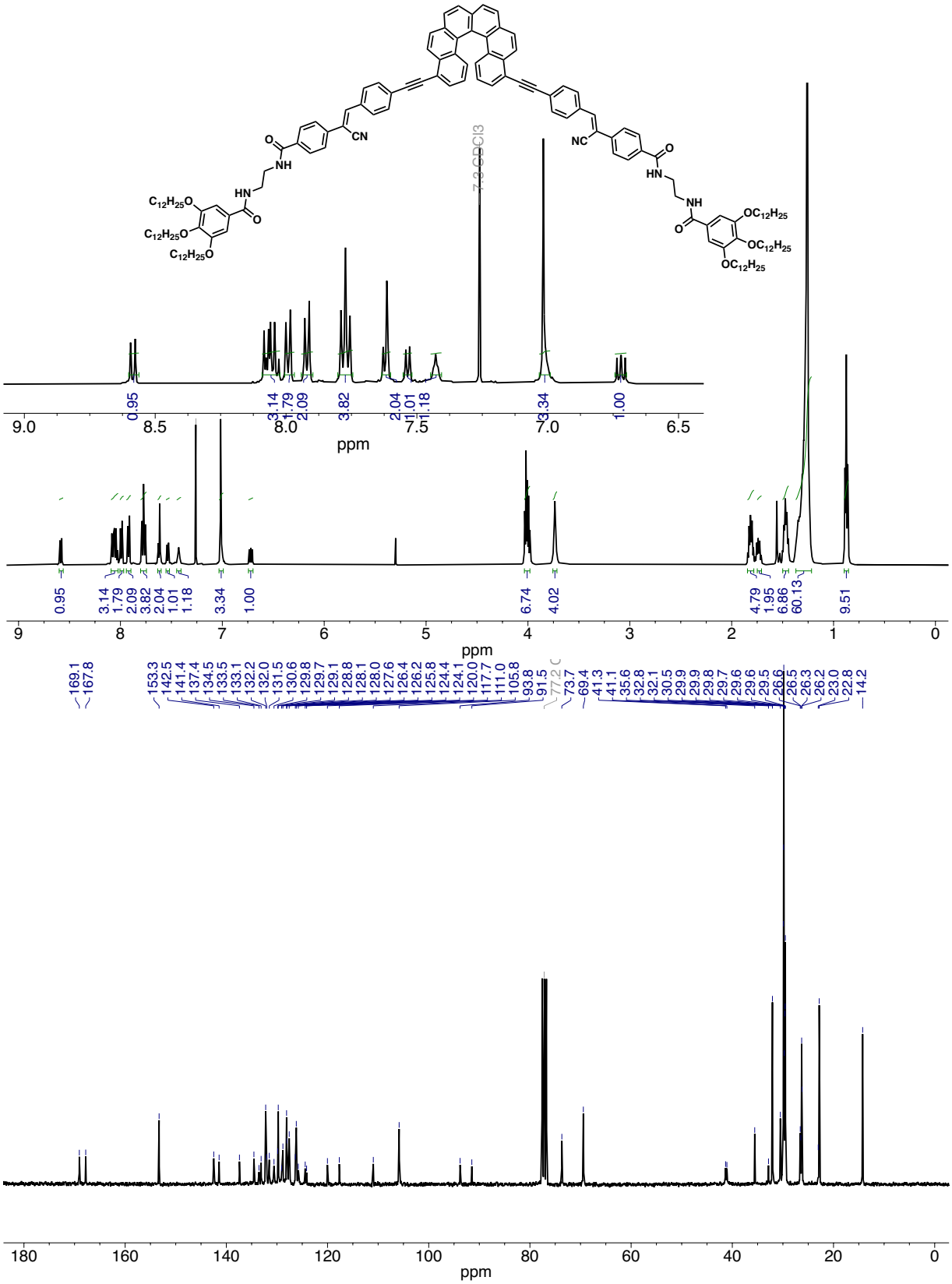



**Figure S9.** $^{1}H$ and $^{13}C$ NMR spectra of (*P*)-**2** ($CDCl_3$, 300 and 75 MHz, respectively, 298K).

## 5. References


S1.- A. U. Malik, F. Gan, C. Shen, N. Yu, R. Wang, J. Crassous, M. Shu and H. Qiu, *J. Am. Chem. Soc.*, 2018, **140**, 2769.

S2.- E. Anger; M. Srebro; N. Vanthuyne; L. Toupet; S. Rigaut; C. Roussel; J. Autschbach; J. Crassous and R. Réau. *J. Am. Chem. Soc*. 2012, ***134***, 15628.

S3.- F. Aparicio, S. Cheremukki, A. Ajayaghosh and L. Sanchez, *Langmuir*, 2016, **32**, 284.

S4.- a) H. M. M. ten Eikelder, A. J. Markvoort, T. F. A. de Greef and P. A. J. Hilbers*, J. Phys. Chem. B*, 2012, **116**, 5291; b) P. A. Korevaar, C. Schaefer, T. F. A. de Greef and E. W. Meijer, *J. Am. Chem. Soc*., **2012**, *134*, 13482; c) R. F. Goldstein and L. Stryer, L. *Biophys. J.* 1986, **50**, 583